DOCTORAL THESIS

Shelf-Life Assessment and Applicability of Accelerated Shelf-Life Testing Models for Long Shelf-Life Foods

Kärt Saarniit

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

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Author's Contribution to the Publications

Contribution to the papers in this thesis are:

I The author conducted literature overview, participated in the original draft preparation and in the review and editing of the publication.

II The author conceptualized the study, designed the experimental plan, conducted data analysis, drafted the original manuscript, and handled the review and editing process for the publication.

III The author developed the experiment concept, performed formal analysis, wrote the initial manuscript draft, and managed the review and editing stages of the publication.

Introduction

Food shelf-life and quality are essential concepts in the food industry, impacting not only the safety and acceptability of food products but also the economy and environmental impact of food systems. Shelf-life refers to the date of minimum durability until which a food product retains its quality and safety when stored and handled according to prescribed conditions (European Union, 2011). This means that the product remains safe to consume, retains its desired sensory, chemical, physical, and microbiological properties, and complies with any label declarations when stored under recommended conditions. Quality, on the other hand, encompasses a broader range of attributes, including appearance, texture, flavour, nutritional value, and safety, that collectively determine the overall acceptability of a food product by consumers.

In an era marked by growing global population, climate change, and heightened consumer awareness, ensuring food quality and extending shelf-life have emerged as crucial challenges. The global food supply chain is complex and involves multiple stakeholders, including producers, manufacturers, distributors, retailers, and consumers, all of whom rely on accurate assessment and management of shelf-life and quality to minimize food waste, ensure consumer satisfaction, and comply with stringent regulatory requirements. The United Nations estimates that approximately one-third of all food produced globally is wasted each year, much of it due to inadequate understanding or mismanagement of shelf-life (UNEP, 2024).This underscores the critical need for robust methods to assess and predict shelf-life while maintaining quality.

The importance of shelf-life assessment extends beyond mere compliance with regulations as it is also essential for ensuring public health. In more detail, low food quality can lead to the growth of pathogenic microorganisms, posing risks to consumers. Therefore, the evaluation of shelf-life and food safety are inherently connected, as both are focused on ensuring that food products remain safe for consumption throughout their intended storage period.

From a commercial perspective, accurate determination of shelf-life enables manufacturers to optimize product development, packaging, and storage conditions, ensuring cost-effectiveness while minimizing spoilage and waste. Moreover, it supports sustainable practices by reducing the environmental impact associated with the disposal of expired products.

Despite advancements in food science and technology, accurately assessing food shelf-life and quality remains a complex challenge due to the diversity of food matrices, storage conditions, and environmental factors. Therefore, it is essential to approach food shelf-life and quality evaluation innovatively, increasing the potential of enhancing the precision and efficiency of shelf-life prediction and quality assessment.

In summary, this research seeks to advance the understanding and practical application of accelerated shelf-life testing for a range of long shelf-life foods. By systematically investigating preservation and packaging strategies, monitoring nutritional and colour-related changes, and comparing chemical and sensory indicators, this study aims to provide reliable, product-specific guidelines for selecting appropriate quality markers and acceleration factors. The outcomes are expected to enhance the reliability of shelf-life predictions, support informed product development, and contribute to improved quality management strategies for cereal products, savoury snacks, and berry-rich formulations.

Abbreviations

AL	aluminium
ANC	anthocyanins
ASLT	accelerated shelf-life test
a_w	water activity
CFU/g	colony-forming units per gram
CFU/ml	colony-forming units per milliliter
EVA	ethylene vinyl acetate
EVOH	ethylene vinyl alcohol
FAME	fatty acid methyl ester
FGBB	four-grain puree with banana and blueberry
GAE	gallic acid equivalent
SPME-GC-MS	solid phase microextraction/gas chromatography-mass spectrometry
HACCP	hazard analysis critical control points
HDPE	high-density polyethylene
HS-SPME/GC-O	headspace solid phase microextraction/gas chromatography-olfactometry
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MAP	modified atmosphere packaging
MCB	mango-carrot-sea buckthorn puree
OPP	oriented polypropylene
PA	polyamide
PET	polyethylene terephthalate
PVC	polyvinyl chloride
PVdC	polyvinylidene chloride
PP	polypropylene
TPA	texture-profile analysis
TPC	total phenolic content
PV	peroxide value

1 Literature review

1.1 Shelf-life of food products

1.1.1 Shelf-life definition and determination

The shelf-life or storage time of food refers to the duration over which a product retains its quality and safety when stored and handled according to prescribed conditions. One of the main definitions of food shelf-life is determined by the European Union (EU) Regulation 1169/2011, stating that the shelf-life of food products is indicated by either a "best before" date, referring to the minimum durability period, or a "use by" date, which specifies the safety limit for consumption (Table 1).

Table 1. Differences between "Best before" and "Use by" dates.

<table>
<tr><th></th><th colspan="2">"Best before"</th><th>"Use by"</th></tr>
<tr><td>Approach</td><td colspan="2">Quality-related changes</td><td>Food safety related changes</td></tr>
<tr><td>Explanation</td><td colspan="2">Period during which the food is expected to retain its specific properties, like organoleptic or nutritional attributes, when properly stored</td><td>Safety-related indicator which is set for highly perishable products</td></tr>
<tr><td>Consumption after expiry</td><td colspan="2">Typically safe if sensory properties are intact</td><td>The food is unsafe to eat after expiry</td></tr>
<tr><td>Storage time</td><td colspan="2">Months to years</td><td>Days to weeks</td></tr>
<tr><td>Examples of products</td><td colspan="2">Dry goods (pasta, chips, flours, cereals, grains, powdered milk, bakery products, confectionary), pasteurized and canned foods</td><td>Fresh meat, dairy, ready-to-eat products, fresh vegetables, fruits and berries, fresh bakery products</td></tr>
<tr><td rowspan="9">Main degradation processes</td><td>Chemical deterioration (Kong & Singh, 2016)</td><td>Physical deterioration (Kong & Singh, 2016)</td><td>Microbiological spoilage (Lianou et al., 2016)</td></tr>
<tr><td>Lipid oxidation</td><td>Mechanical damage</td><td>Growth of molds (e.g. Aspergillus, Mucor, Penicillium, Rhizopus)</td></tr>
<tr><td>Enzymatic degradation (lipolysis, proteolysis)</td><td>Moisture change</td><td>Growth of yeasts (e.g. Candida, Lachancea, Saccharomyces, Torulaspora, Zygosaccharomyces)</td></tr>
<tr><td>Nonenzymatic browning</td><td>Glass transition</td><td rowspan="5">Growth of bacteria (e.g. Pseudomonas spp., Clostridium spp., Bacillus spp., Lactobacillus spp.)</td></tr>
<tr><td>Light-induced chemical changes</td><td>Starch gelatinization and retrogradation</td></tr>
<tr><td>Hydrolysis</td><td>Chill injury</td></tr>
<tr><td rowspan="2">Enzymatic browning and degradation of polyphenols</td><td>Crystal growth</td></tr>
<tr><td>Emulsion breakdown</td></tr>
</table>

The “best before” date refers to the period during which the food is expected to retain its optimal quality and specific properties, like organoleptic or nutritional attributes, when properly stored (European Union, 2011; Table 1). These are mostly low-risk foods with intermediate or long shelf-lives from months to years, for example chips, flours, cereals, grains, powdered milk, pasteurized and canned foods. Typically, such products have low microbiological risk if the packaging is intact, and the food shows no signs of spoilage. However, these products can lose quality over time because of chemical and physical processes (Table 1; Figure 1). Moreover, the nutritional content of such products often declines due to the breakdown of vitamins and bioactive substances, leading to contents lower than those stated on the label (Corradini, 2018). On the other hand, the phrase “use by” is a strict safety-related indicator, set for highly perishable products (fresh meat, dairy and ready-to-eat meals) that usually have short shelf-lives (days to weeks) due to being prone to microbial spoilage (European Union, 2011; Table 1). While the quality of these products may also degrade as the “use by” date approaches, the emphasis is on microbial safety as the spoilage caused by molds, yeasts, and bacteria (Lianou et al., 2016) may cause pathogens to grow to unsafe levels before it can be organoleptically detected on the food (Table 1; Figure 1).

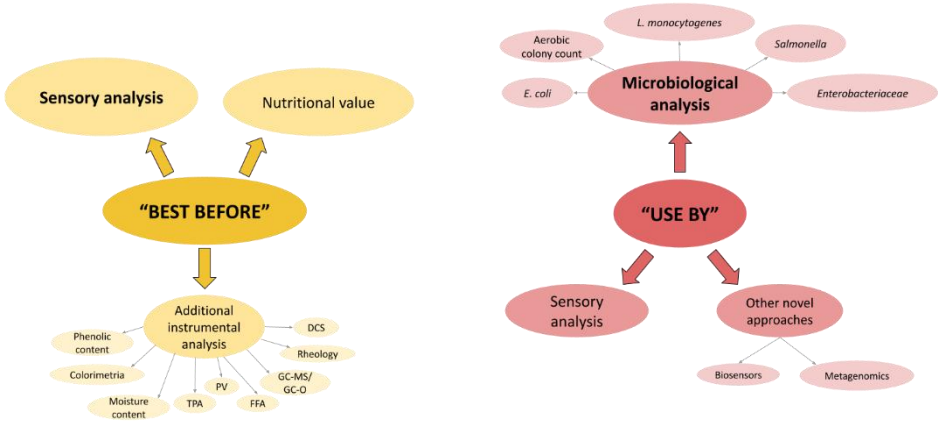

Figure 1. Examples of methods to analyze food degradation processes (TPA = Texture Profile Analysis, PV = Peroxide Value; FFA = Free Fatty Acids; GC-MS/GC-O = Gas Chromatography-Mass Spectrometry/Gas Chromatography–Olfactometry; DCS = Differential Scanning Calorimetry), (Figure created by the author).

During storage, food must stay safe to consume, maintain its intended sensory qualities, chemical composition, physical properties, microbiological stability, and functional attributes. Additionally, it should meet any declared nutritional information on the label, provided it is stored as recommended (Kilcast & Subramanian, 2000). Also, it is clearly stated that food must not be released on the market if it is unsafe to consume. The definition “unsafe” is used if the food ready to be launched on the market would be injurious to human health or be unfit for human consumption (Man, 2016).

In addition, there is a noticeable contrast with how the retailer must handle food products, either they are marked with “best before” or “use by” dates. With the first one, the food consumed after the designated date is still edible, but its quality has degraded below the manufacturer’s standards. With the latter, it is forbidden to sell food after reaching its “use by” date (Robertson, 2013).

Food shelf-life testing is critical in ensuring the safety, quality, and consumer acceptance of food products. This process involves evaluating how long a product can maintain its desired characteristics and safety under specific storage conditions before it becomes unacceptable for consumption. To determine the acceptable storage time for a food product, different approaches may be used. The most straightforward method for establishing shelf-life involves conducting experimental storage trials under conditions that mirror those encountered throughout its life cycle from manufacturing until consuming. This is mostly used for short shelf-life products which safe storage time is defined by the "use by" date. The safe shelf-life of food must be conducted with HACCP (Hazard Analysis Critical Control Points) principles in mind, where the required food safety management procedure is a priority (European Union, 2004). The regulation, including principles of HACCP, establishes a food safety criterion which sets the standard for determining the acceptability of a product or batch of food, ensuring its suitability for market placement.

Also, other applicable food safety criteria should be used when determining the safe shelf-life of foods. The EU Regulation nr 2073/2005 helps to secure a microbiological shelf-life during product development and to evaluate the microbiological safety of a food item or batch, all within the scope of a robust HACCP-based food safety management system (European Union, 2005). Therefore, there are many aspects to align with when conducting shelf-life tests to establish the safe shelf-life of food. Firstly, the specific physico-chemical characteristics of the product must be determined. This includes the pH, a_w (water activity value), and the concentration of salt and preservatives. Also, possible packaging solutions and storage conditions must be defined, followed by the scientific literature overview of possible microbial growth. Finally, tests to evaluate the growth of microorganisms must be conducted (Man, 2016). In addition, it is also possible to predict the growth of microbes concerned with using mathematical models. Predictive microbiology is used when one wants to quantify the impact of different controlling factors on shelf-life, providing insight into their relative significance. Also, they explain the interplay among these factors, giving a more complex understanding of impact on food and bacterial systems (O'Mahony & Seman, 2016).

Another method for food shelf-life determination includes storage trials which enable to identify the end of storage time for "best before" food products with relatively long shelf-life faster than it usually would take. This essential tool is the accelerated shelf-life testing (ASLT) methodology which is mainly applicable to chemical, physical or biochemical processes. The principle of ASLT is to accelerate the reactions occurring in the product by changing the storage conditions (Kilcast & Subramanian, 2000), mainly temperature, oxygen, light, and relative humidity. The most used factor is changing the storage temperature since it affects the kinetics of the reactions the most (Calligaris et al., 2019). In more detail, the impact of raising temperature on the chemical reaction rates is set by an understanding that typically, a 10°C increase in temperature accelerates the reaction rates by a factor of 2 or 3 in food systems. This relationship between the reaction rate and temperature is assessed according to the Arrhenius model (Equation 1):

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

where k represents the reaction rate, k_0 is the exponential factor representing the collision frequency of the reacting molecules, E_a is the activation energy (J), R is the universal gas constant (8.3144 J/mol·K), and T is the absolute temperature (K) (Calligaris et al., 2019; Taoukis & Giannakourou, 2004).

Knowing the kinetics of quality degradation processes in the product during shelf-life, it is possible to determine the acceleration factor Q_{10} (Equation 2):

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\frac{10}{T_2 - T_1}} \quad (2)$$

where k_1 and k_2 represent the reaction rate at temperatures T_1 and T_2 (Fu & Labuza, 1997). This factor represents how many times a reaction rate alters with a 10°C shift in temperature (Toledo, 2007) and it is distinctive to the main quality process of the food during shelf-life (Bravi et al., 2020). Knowing the Q_{10}-factors of a product in interest and its shelf-life defining processes is necessary when planning the acceleration time period that reflects changes in ambient conditions. For example, it is possible to calculate the ASLT time points, corresponding to the changes at room temperature, by knowing the relevant Q_{10}-factor and the time period during which the product is stored in real-life conditions (Equation 3):

$$Accelerated\ aging\ time\ (AAT) = \frac{Desired\ real\ time\ (RT)}{Q_{10}^{\left(\frac{T_{AA} - T_{RT}}{10}\right)}} \quad (3)$$

where AAT is the accelerated aging time at accelerated aging temperature (T_{AA}) and RT is the real storage time at real storage time temperature (T_{RT}) (ASTM International, 2021). The calculation model shows that the smaller the Q_{10} value, the longer the storage time under ASLT conditions. Similarly, when high acceleration coefficients are used, the ASLT time period becomes shorter.

When applying ASLT methods, both their potential and limitations must be taken into account. For instance, ASLT can only be applied reliably when the principal quality-degrading process observed under accelerated conditions is the same as that occurring during normal storage (Man, 2016). However, degradation mechanisms may shift under accelerated conditions, resulting in reaction pathways that are absent during typical storage (Elmlund, 2014). Another critical consideration is the selection of quality indicators. Reliance on a single or poorly chosen indicator risks overlooking significant quality losses. On the other hand, while multivariate indicators generally provide broader and more representative insights, they require larger datasets and are more complex to implement (Lima et al., 2023). Furthermore, ASLT models are not universally applicable across different product matrices. The degradation of a given quality parameter may follow distinct kinetic patterns depending on the processing method, even when the same indicator is used (Choi et al., 2017). Consequently, ASLT predictions must always be validated against real-time storage data for each specific product and process (Haouet et al., 2019; Man, 2016). Nonetheless, if these restrictions are considered, the application of ASLTs can provide significant advantages for both research and industry. In particular, ASLTs offer a time- and cost-efficient approach for producers when introducing new products with extended shelf-lives to the market (Calligaris et al., 2019). They are equally valuable in evaluating the consequences of modifications to product formulations, processing technologies, or packaging materials, thereby supporting rapid decision-making and product development (Mizrahi, 2004). Beyond its role in providing an estimate of shelf-life, ASLT also serves as a diagnostic tool. It can facilitate the identification of dominant degradation mechanisms and the selection of the most sensitive quality indicators, which in turn allows for the targeted optimization of formulation strategies and packaging solutions (Bilbie, 2022). Moreover, recent advances highlight the growing potential of combining ASLT with multivariate statistical approaches. While traditional

ASLT studies often rely on the monitoring of a single marker, multivariate modelling enables the simultaneous consideration of multiple, interdependent quality attributes. This integration not only improves the predictive capacity of shelf-life models but also yields a more comprehensive understanding of product deterioration dynamics (Lima et al., 2023). In this way, ASLT, when properly designed and combined with modern analytical and modelling tools, can extend its utility beyond prediction to become a powerful framework for product optimization and innovation.

1.1.2 Food quality deterioration and spoilage processes

As foods are complex systems, various processes affect their deterioration and spoilage during storage. The changes that set the period for the food's shelf-life are mainly categorized as microbiological, physical, biochemical or chemical. These processes can take place individually or in parallel, invoking different, complex processes leading to the loss of quality. However, usually one specific process is likely to dominate the quality degradation and will set the end of the expiration date (Man, 2016).

1.1.2.1 Microbiological changes

The microbiological changes during storage cause the spoilage of food to the extent where it becomes unacceptable and unsafe for the consumer, determining the end of its shelf-life. Microbial spoilage occurs when the growth of microorganisms, such as yeasts, molds, and bacteria, exceeds an acceptable level. The microorganisms causing problems during storage of food may be either spoilage or pathogenic. In the first case, the growth of organisms is recognizable sensorially, by changes in visual appearance, odor or flavor. With the latter, the growth of microbes may not emerge in appearance but can cause the production of toxins dangerous to human health (Man, 2016). The level of acceptable number of microorganisms in food is often correlated with sensorial perception. More generally, the counts between 10^6 and 10^8 CFU/g or CFU/ml have been associated with the end of shelf-life for perishable foods (Corradini, 2018).

The growth of microbes during a product's lifespan depends on multiple factors. For example, the intrinsic properties, such as the a_w, pH, nutrients, total acidity, and presence of natural preservatives or antimicrobials play an important role (Man, 2016). Also, the structure of the food is relevant (Petruzzi et al., 2017). In addition, external factors like the temperature and the relative humidity of the storage environment, as well as the atmosphere surrounding the product influence the growth rate of microorganisms. Next to that, the processing of a food prone to microbial spoilage can delay or avoid the deterioration as the product has been heat processed, frozen, or packaged properly (Man, 2016).

Many types of microbes contribute to food deterioration. Bacteria, for instance, are responsible for quickly spoiling various foods like meat and dairy. In contrast, molds and yeasts tend to grow more slowly and are often seen on the outer layers of foods like bread. Despite their slower growth, molds and yeasts can break down a range of substances and survive in harsher environments than bacteria (Petruzzi et al., 2017).

1.1.2.2 Physical changes

In addition to microbiological changes, physical deterioration also plays a crucial role in the quality of food. As a fundamental aspect of food science, physical deterioration encompasses a wide array of mechanisms that result in changes to the appearance, texture, and structural integrity of foods over time. The common physical deterioration mechanisms include moisture loss or gain, mechanical damage, freezing and thawing or

other texture changes caused by complex processes like glass transition and starch retrogradation, but also physical collapse of emulsions due to their unstable nature (Kong & Singh, 2016).

In more detail, foods can lose moisture through evaporation or gain moisture from the surrounding environment, whether they be packed or un-packed, leading to changes in softening, toughening, swelling or shrinkage (Roudaut & Debeaufort, 2010). The mechanical stresses during processing, handling, or storage can also cause physical damage to food, resulting in changes in texture such as softening, crumbling, or loss of structural integrity. In addition, the formation of ice crystals during freezing and subsequent thawing can disrupt the cellular structure of foods, causing texture deterioration, water loss, and changes in flavour. Other issues caused by crystal growth are sugar and fat bloom. Both are mainly causing problems in chocolate products. Sugar bloom takes place when the sugar shifts from a glassy to a rubbery state, resulting in the formation of grey sugar crystals on the surface of the product. Conversely, fat bloom involves the migration and recrystallization of fats onto the chocolate's surface, creating a haze. This defect often arises from improper tempering during manufacturing, leading to less stable forms of fat crystals. In addition to these complex processes, emulsion-based products are prone to collapsing as the phases in this thermodynamically unstable system separate due to physical pressure or temperature changes. Finally, starch retrogradation is the main cause of staling in bakery products. In more detail, it is a process wherein gelatinized starch, composed of amylose and amylopectin polysaccharides, undergoes reassociation or recrystallization, resulting in firming of the crumb, losing overall crispness or changing the flavour of the product (Kong & Singh, 2016).

1.1.2.3 Biochemical changes

The quality and safety of food during shelf-life may also be affected by biochemical reactions. For example, these complex processes include fat oxidation caused by enzyme lipoxygenase, resulting in the off-flavors of the product, mainly due to the formation of aldehydes and ketones. In addition, lipolysis and proteolysis take place as the enzymes lipase and protease work actively, forming free fatty acids and rancid taste in the first case, and free amino acids and peptides, but also bitter taste and changes in the texture, in the latter case. Finally, the enzymatic browning of polyphenols is also known as a biochemical reaction, causing the unwanted browning of many plant-based products rich in phenolic compounds (Kong & Singh, 2016).

1.1.2.4 Chemical changes

Chemical processes lead to overall quality degradation after which the food is still edible but may not be acceptable for the consumer. The occurrence of these processes changes the appearance and flavor of the food and can cause loss of nutrients. In more detail, some of the chemical changes in food include the degradation of bioactive compounds lipid oxidation, enzymatic and nonenzymatic browning (Kong & Singh, 2016).

1.1.2.4.1 Degradation of polyphenols

An important process affecting the shelf-life and quality of many foods available on market is the degradation of bioactive compounds. Phenolics, a broad category of secondary metabolites synthesized by plants, encompass a diverse range of molecules united by the shared feature of at least one hydroxyl group attached to an aromatic ring within their structure. In more detail, polyphenols are categorized mainly by structure, including simple molecules as phenolic acids, to more complex structures like cinnamic acids, flavonoids, stilbenes, etc (Figure 2).

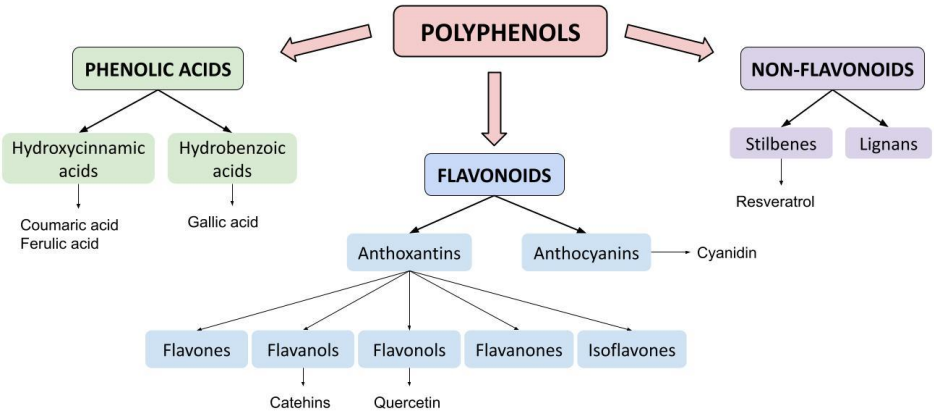

Figure 2. Classification of polyphenols with examples of compounds (Figure created by the author).

Among these, phenolic acids and flavonoids are particularly abundant in plant-derived foods and beverages, and they play a central role in determining both the functional properties of foods and their potential health benefits (Kumar & Goel, 2019). Phenolic acids are relatively simple phenolic compounds that can be categorized into two major subclasses of hydroxybenzoic acids and hydroxycinnamic acids. The first ones are commonly found in berries, tea, and certain nuts. They are well known for their strong antioxidant capacity and have been associated with protective effects against oxidative stress-related cellular damage (Cizmarova et al., 2021). Hydroxycinnamic acids, including coumaric acid and ferulic acid, are more widespread in cereals, fruits, and vegetables. In addition to their role as antioxidants, they contribute to sensory properties such as flavor and color, and they have been studied for their potential anti-inflammatory and antimicrobial activities (Xie et al., 2024). Flavonoids, on the other hand, constitute one of the largest and most structurally diverse groups of polyphenols. They share a common structure but differ in the degree of hydroxylation, glycosylation, and other substitutions, which give rise to several subclasses. These include anthoxanthins (pale yellow pigments), anthocyanins (responsible for red, blue, and purple coloration in many fruits and vegetables, e.g., cyanidin), flavones (e.g., apigenin in parsley and celery), flavanols (e.g., catechins abundant in tea, cocoa, and apples), flavonols (e.g., quercetin found in onions, kale, and berries), flavanones (e.g., hesperidin in citrus fruits), and isoflavones (e.g., genistein in soy products). Beyond their contribution to plant pigmentation and defense, flavonoids exert a wide range of bioactivities relevant to human health, including antioxidant and anti-inflammatory effects (Ullah et al., 2020).

Polyphenols have a wide physiological and morphological importance for plants, protecting them against UV-radiation, mechanical damage, and microbial infection (Siracusa & Ruberto, 2014). In food, for example in cereals, coffee beans, fruits, olives, vegetables and tea leaves (Friedman, 2004), phenolic compounds play a crucial role in determining the colour, sensory attributes and nutritional value, but even more importantly, they act as natural preservatives (Siracusa & Ruberto, 2014). Polyphenols are also known for their health-beneficial properties. For example, phenolic compounds exhibit diverse biological effects, such as inhibiting the oxidation of LDL-cholesterol,

safeguarding DNA from oxidative harm and possessing properties like antithrombotic, anti-inflammatory, antimicrobial, anticarcinogenic, and antimutagenic activities (López-Nicolás & García-Carmona, 2009).

While the occurrence of phenols in food is beneficial in many ways, the amount of these compounds can decrease either during processing or storage. Overall, the degradation of polyphenols during shelf-life is often a complex process influenced by multiple factors, including the specific type of polyphenol, food matrix, storage conditions, and processing methods (Friedman, 2004; Salazar-Orbea et al., 2023; Zhang et al., 2021). For example, it has been stated that polyphenols are sensitive to thermal treatments, which may inactivate the enzymes responsible for polyphenol breakdown (Polak et al., 2024) and that polyphenol degradation is generally faster in products with higher water activity than in dry matrices (Rocha-Parra et al., 2016). In addition, if a particular phenolic compound proves to be unstable during food processing, its efficacy as an antioxidant, anticarcinogen, or antibiotic in heated or high-pH food environments may be compromised (Friedman, 2004).

Polyphenols can undergo degradation during shelf-life due to various factors. Among others, these include either enzymatic or non-enzymatic oxidation, temperature-related degradation and pH-dependent reactions. In more detail, polyphenols can be susceptible either to enzymatic or non-enzymatic oxidation reactions. For example, the enzymatic degradation of polyphenols by the involvement of oxidative enzymes has been reported to be effective due to the enzymes' high redox potential which allows them to interact with initially stable compounds. As a result, oxidases and peroxidases engage with oxygen, initiating the formation of reactive oxygen intermediates. Subsequently, these intermediates undergo further reactions with reducing substrates (López-Nicolás & García-Carmona, 2009). The non-enzymatic oxidation of polyphenols takes place as they are susceptible to oxidation reactions, particularly when exposed to oxygen in the air. This process can lead to the formation of reactive oxygen species and result in the degradation of polyphenols into simpler compounds (Chen et al., 2023; Tanaka et al., 2009). In addition, high temperatures, such as those encountered during food processing, storage, or cooking, can accelerate the degradation of polyphenols. Heat can promote chemical reactions that break down polyphenol molecules or accelerate enzymatic degradation (Antony & Farid, 2022). Next to these mechanisms, changes in pH can also influence the stability of polyphenols. In acidic or basic environments, polyphenols may undergo hydrolysis or other chemical transformations that lead to degradation (Friedman & Jürgens, 2000).

1.1.2.4.2 Lipid oxidation

Lipids are high-energy nutrients and the least stable macronutrients in food (Kong & Singh, 2016). Beyond being a dense energy source, they supply essential fatty acids and fat-soluble vitamins, and significantly affect taste, odor, and texture (Olsen, 2009). Thus, lipid content and composition are key quality factors in fatty foods.

Food lipids include triacylglycerols (TAGs), diacylglycerols, monoacylglycerols, glycolipids, phospholipids, sphingolipids, fatty acids, long-chain alcohols, waxes, sterols, and vitamins A, D, E, and K (Shahidi & Zhong, 2010). TAGs, composed of glycerol and three fatty acids, are the dominant form—over 95% of total lipids in vegetable oils (Jacobsen, 2019). Fatty acids are their building blocks and determine lipid properties (Shahidi & Zhong, 2010). These can be saturated (no double bonds) or unsaturated (with one or more C=C bonds) (Moghadasian & Shahidi, 2017). Common unsaturated fatty

acids like oleic (C18:0), linoleic (C18:2), and linolenic (C18:3) are found in plant and marine oils, rich in omega-6 and omega-3 polyunsaturated fatty acids—essential nutrients that must be obtained from the diet (Shahidi & Zhong, 2010).

Saturated fatty acids are more stable, while unsaturated ones are prone to oxidation. The oxidation begins when unsaturated fatty acids react with activated oxygen or radicals, as atmospheric oxygen ($^3O_2$) doesn't react directly with double bonds (Mozuraityte et al., 2016). Instead, it reacts with lipid radicals (Choe & Min, 2006), or oxidation occurs via reactive oxygen species like hydroxyl or superoxide radicals (Mozuraityte et al., 2016). Singlet oxygen ($^1O_2$) can also react directly with double bonds (Choe & Min, 2006).

Lipid oxidation is catalyzed by light, heat, enzymes, metals, and microorganisms, resulting in autooxidation, photooxidation, or enzymatic oxidation (Shahidi & Zhong, 2010). Autooxidation (Figure 3) is the primary pathway and proceeds through initiation, propagation, and termination stages (Jacobsen, 2019).

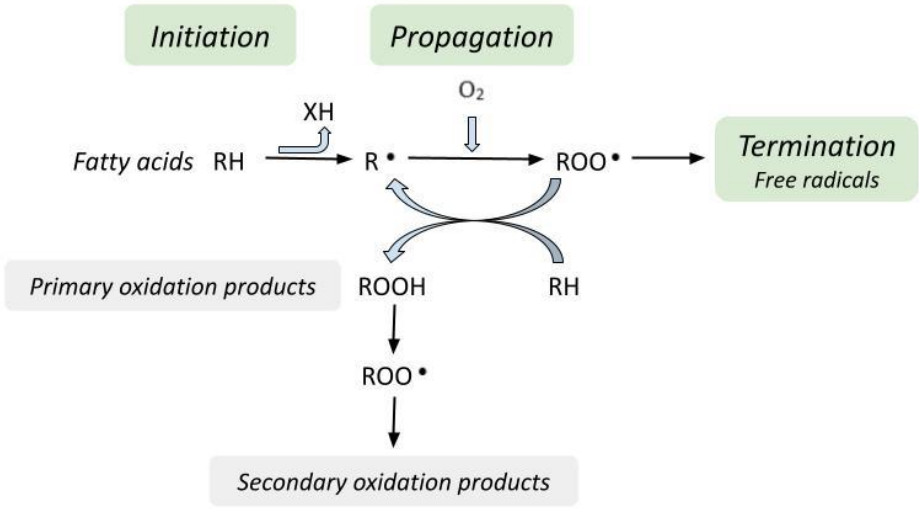

Figure 3. Lipid autooxidation process (RH = fatty acid; XH = hydrogen abstraction; R• = lipid radical; ROO• = peroxyl radical; ROOH = lipid hydroperoxide), (Figure created by the author).

In the initiation step, unsaturated lipids lose a hydrogen atom, forming free radicals. This process requires catalysts such as heat, light, ionizing radiation, or metal ions/metalloproteins (Shahidi & Zhong, 2010). During propagation, these radicals interact with oxygen, generating peroxyl radicals (Mozuraityte et al., 2016). The latter oxidise other unsaturated fatty acids, producing primary oxidation products, hydroperoxides. Additionally, more lipid radicals are generated, and this ongoing cycle drives the process forward. The first products of oxidation are tasteless and odorless due to their low volatility (Jacobsen, 2019). Different fatty acids yield distinct hydroperoxides—for example, oleic acid forms mainly 9- and 10-hydroperoxides, linoleic acid produces 9- and 13-hydroperoxides, and linolenic acid forms 9- and 16-hydroperoxides (Choe & Min, 2006). In the presence of catalysts, hydroperoxides decompose into volatile and non-volatile secondary products (Mozuraityte et al., 2016), including aldehydes, ketones, alcohols, hydrocarbons, and organic acids—many with strong, undesirable odors. Rancidity is largely associated with these secondary oxidation

products (Shahidi & Zhong, 2010). The chain reaction ends when two radicals combine to form a stable, non-radical product (Jacobsen, 2019).

The oxidation of lipids is affected by many factors, such as the fatty acid composition of the matrix, applying heat or light, concentration of oxygen and presence of minor components (Choe & Min, 2006). First and foremost, lipid oxidation is mainly determined by the types of fatty acids they contain, particularly on the number and positions of double bonds in the fatty acids. Since lipid oxidation occurs when the double bonds of a fatty acid are attacked by oxygen, hydrogen or enzymes (Kong & Singh, 2016), it is concluded that the fatty acids containing two or more double bonds are most susceptible to oxidation (Shahidi & Zhong, 2010). In simpler terms, it is easier to take the hydrogen atom away from a methyl carbon, especially if that carbon is between double bonds (Amaral et al., 2018). While the characteristics of the lipid play a crucial role in determining how oxidation processes unfold, the changes in the environment during processing and storage can also impact how quickly lipids oxidise. These environmental factors include temperature, light, the presence of atmospheric oxygen and moisture (Shahidi & Zhong, 2010). Temperature is considered as one of the crucial factors as the rate of autooxidation of lipids increases with the rise of temperature. Overall, it is known that for every rise of 10°C in temperature, the rate of autooxidation doubles (Mozuraityte et al., 2016). However, it needs to be acknowledged that lipid oxidation process includes an induction period—characterized by a low oxidation rate at first, and then followed by a rapid deterioration, perceived also in organoleptic perception (Calligaris et al., 2019). Moreover, at lower temperatures, the generation of autooxidation compounds during the induction phase proceeds at a reduced rate but starts rising with higher temperatures. In addition to temperature, the exposure to light and free atmospheric oxygen is affecting the oxidation rate of lipids. The photooxidation pathway is related to the light source, intensity, wavelength and exposure time. Next to that, the amount of dissolved oxygen in the matrix plays an important role (Mozuraityte et al., 2016), as both the concentration and type of oxygen affects the oxidation of lipids (Choe & Min, 2006). Fats and oils also include minor components which impact the rate of possible oxidation. Some of these elements, like transition metals, are regarded as prooxidants, which either enhance the hydroperoxide formation, free radical formation or hydroperoxide decomposition. On the other hand, compounds that inhibit lipid oxidation are known as antioxidants, including phospholipids, tocols, carotenoids and phenolic compounds (Cui & Decker, 2016).

1.1.2.4.3 Nonenzymatic browning

Finally, the complex chemical processes in food also involve nonenzymatic browning mechanisms, also known as a Maillard reactions which occur between amino acids and reducing sugars. Usually, these processes are taking place when applying heat treatment on various foods, creating desirable brown colour and complementary flavour. However, these reactions are not preferred when storing long shelf-life foods since in addition to causing unwanted darkening in colour, it also creates undesirable off-odour and off-flavours (Kong & Singh, 2016; Xiang et al., 2021). Depending on the composition of the food and the technological processing, the Maillard reaction can produce a variety of end-products. The volatile compounds formed during the reactions influence the aroma and taste characteristics of the product. In addition, brown polymers, melanoidins, are also formed during the reaction, which give the food product the characteristic brown colour associated with the Maillard reaction (Arnoldi, 2004). In general, Maillard reaction includes multiple stages. Firstly, the early stage of the Maillard mechanism begins with

the condensation of sugar and amine, after which the unstable Schiff's base is formed. Then, the Amadori rearrangement takes place, leading to the formation of the Amadori compound. The reactions progress onward via Strecker degradation and polymerization processes, yielding volatile compounds and deep-coloured pigments (Kong & Singh, 2016; Nursten, 2002). Various factors influence the occurrence and rate of Maillard reaction in food. Firstly, the composition of the food plays a crucial role. For example, low molecular weight sugars, like fructose and glucose react more rapidly in this process. In addition, the properties of the involved amino acid are to keep in mind. In more detail, in addition to the structure of the amino acids involved, the pK_a value influences the reactivity of the amino acids (O'Brien, 2009). Next to attributes already brought out, the pH and water activity value of the food also play an important role. For example, at high pH-values, more pyrazines are formed, whereas at lower pH-s, furans are formed (Arnoldi, 2004).

1.2 Various factors affecting food shelf-life

Understanding the factors affecting the shelf-life of food is crucial for maintaining its quality and safety. Various elements, ranging from intrinsic properties of the food itself to external environmental conditions (Figure 4), play a significant role in determining how long food products remain fresh and palatable. By identifying and managing these factors effectively, food producers and consumers alike can extend shelf-life, reduce waste, and ensure the delivery of high-quality food to consumers (Robertson, 2009; Singh & Anderson, 2004).

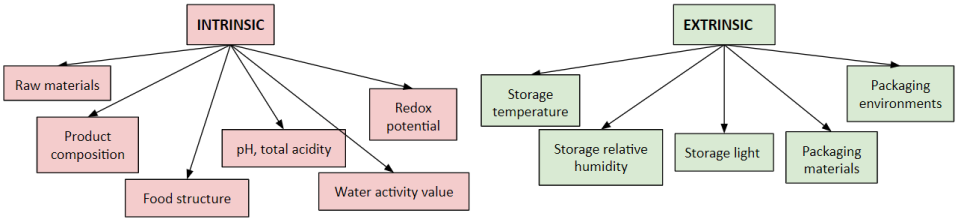

Figure 4. Intrinsic and extrinsic factors affecting food shelf-life (Figure created by the author).

1.2.1 Product properties

In more detail, the factors affecting food shelf-life may be either internal or external. The internal factors influencing product's stability over time primarily stem from the properties of the food. For example, these are the origin of raw ingredients, the products formulation, structure or chemical parameters such as pH, total acidity, water activity value or redox potential (Figure 4). With internal factors, it is also observed if the product contains any preservatives that may impact the spoilage mechanisms (Man, 2016). In addition, the presence of enzymes in food can affect the quality as they catalyze biochemical reactions leading to spoilage (Robertson, 2009). Additionally, the physical form of food significantly influences how microbes grow. For example, fruits and nuts have protective outer layers that prevent microbes from reaching the interior. As a result, microbial activity stays on the outer layers of these foods. In contrast, in liquid matrixes, microbes can move freely throughout the entire product, leading to faster deterioration (Petruzzi et al., 2017). Also, the pH level, water activity value and moisture content play an important role as they affect the occurrence and speed of various reactions in food (Man, 2016). To begin with, the acidity level of food plays a major role in determining

which microbes thrive within it. Many microbes prefer a neutral pH around 7.0 for optimal growth. However, some organisms can survive outside this typical extent. For instance, in highly acidic foods with pH values below 3.7, bacteria such as *Lactobacillus* and *Acetobacter* are commonly found. Meanwhile, yeasts have an optimal growth in mildly acidic to neutral conditions, between pH 4.5 and 7.0, whereas molds have a broader tolerance, thriving from pH 3.5 up to 8.0 (Singh & Anderson, 2004; Petruzzi et al., 2017).

Furthermore, moisture content and water state critically affect chemical, biochemical, and microbial stability during storage. Water exists as bound (associated with food components) or free (available for microbial growth and reactions). Water activity (a_w), measuring free water, often differs from total moisture content. Fresh foods typically have $a_w > 0.95$, allowing microbial growth, while growth is inhibited below a_w 0.6, except for some salt- or sugar-tolerant microbes (Singh & Anderson, 2004). Water activity also influences lipid oxidation, enzymatic activity, and browning. Lipid oxidation is high at $a_w < 0.2$, suppressed between 0.2-0.5, and increases up to a_w 0.75. Higher a_w accelerates browning and vitamin loss, while enzyme activity decreases at a_w lower than 0.7 (Robertson, 2013). Water further affects physical stability through moisture migration, causing texture changes such as sogginess or brittleness (Singh & Anderson, 2004).

Finally, another intrinsic factor affecting food shelf-life is redox potential which shows the tendency of food components to either donate or accept electrons during reactions. The food's oxidative-reductive capacity plays an important role in chemical processes where it shows whether the component is either oxidized or reduced. In addition, it is widely used in the microbiological area, for example when tracking the progression of fermentation processes or predicting the growth of aerobic or anaerobic microorganisms (Nicoli et al., 2004).

1.2.2 Food packaging materials

The external factors influencing food quality during shelf-life are the storage temperature, relative humidity, exposure to light, but also the choice of packaging materials and environments (Figure 4). Food packaging, for example, is a crucial extrinsic factor as it protects food from processing to retail, ensuring containment, protection, convenience, and communication. Beyond containment, packaging acts as an interface between producers and consumers, preserving safety and quality while providing essential information like nutrition and handling. It also helps reduce food waste by extending shelf life and supporting efficient distribution. Thus, packaging is very important in maintaining food integrity throughout the supply chain, safeguarding public health and economic sustainability (Robertson, 2013).

Packaging in the supply chain includes multiple levels. Primary packaging contacts the food directly and is usually the consumer's retail package, providing essential protection. Secondary packaging, like boxes or cases, holds multiple primary packages and aids transport and retail display. Tertiary and quaternary packaging group multiple lower-level packages for bulk transport and distribution (Robertson, 2013).

The selection of materials is critical for maintaining food quality and safety during shelf-life. Key factors here include incorporating barrier layers to control oxygen, carbon dioxide, and moisture transfer, protecting against light, flavor loss, and nutrient degradation (Morris, 2017). Also, packaging must have sufficient physical strength to prevent damage during transport. Furthermore, chemical migration from packaging to food, influenced by material type, temperature, and storage time, poses safety concerns

(P. Singh et al., 2017). Additionally, packaging must prevent microbial contamination to ensure the biological safety of food (Barone et al., 2015).

Packaging materials must provide effective barriers to protect food quality and safety. Polyolefins, such as LDPE (low-density polyethylene), LLDPE (linear low-density polyethylene), HDPE (high-density polyethylene), and PP (polypropylene), are common thermoplastics with varying barrier properties. LDPE offers good water vapor barrier and flexibility but poor gas and light barriers, while LLDPE has higher strength. HDPE is more rigid with moderate gas barrier properties, used mainly for bottles and jars. PP has the best barrier properties among polyolefins, including higher temperature resistance. Polyesters like PET (polyethylene terephthalate) provide strong oxygen and water vapor barriers and protect against oil contamination, though they offer limited light protection due to transparency. Glass, on the other hand, offers absolute barriers to oxygen and moisture, with colored glass needed for light-sensitive products. Metals also provide complete barriers against oxygen, moisture, and light, with high temperature tolerance. However, paper is mainly used where gas or moisture barriers are not required but provides good light protection (P. Singh et al., 2017). To enhance barrier performance, materials such as AL (aluminum), PVC (polyvinyl chloride), EVA (ethylene vinyl acetate), EVOH (ethylene vinyl alcohol), and PAs (polyamides) are often combined, offering robust protection against gases, moisture, fats, oils, and odors (Robertson, 2013).

1.2.3 Packaging atmosphere and storage conditions

The quality and safety of food during shelf-life are influenced by many external factors, including how the product is packaged and stored. In more detail, the packaging environment (Figure 4) plays an important role in inhibiting spoilage and quality degradation processes. For example, applying vacuum packaging, modified atmosphere packaging (MAP) or other active packaging solutions such as using absorbers or emitters can prolong the shelf-life of food significantly (Robertson, 2013).

Since oxygen affects many chemical and microbiological processes during storage, controlling its level in packaging is crucial for some products. Vacuum packaging removes air to keep oxygen below 1%, depending on product texture, requiring hermetic sealing and proper flushing to maintain package integrity (Degirmencioglu et al., 2011; Emblem, 2013). This method also reduces package volume by tightly fitting the material to the product, aiding large-scale transport. If simply removing air from the packaging is not preferred, other techniques can be applied, for example by changing the gas composition inside the packaging. Alternatively, MAP adjusts gas composition inside the package to extend shelf-life. For example, nitrogen acts as a filler gas, while carbon dioxide inhibits microbial growth by forming carbonic acid in food (Fernandez et al., 2006; Fik et al., 2012). Oxygen is minimized but retained, when necessary, to preserve red meat color or for respiring fruits and vegetables to prevent fermentation (Degirmencioglu et al., 2011; Emblem, 2013). Finally, the desired environment within the package can be achieved by using either absorbers or emitters as the primary examples of active packaging (Ahvenainen, 2003; Conte et al., 2013). While absorbers remove unwanted gases like oxygen, moisture, ethylene, or odors, emitters release beneficial compounds such as gases, antioxidants, antimicrobials, or ethanol (Lee et al., 2015; Yildirim et al., 2018).

Finally, one of the key extrinsic factors affecting food quality and safety during shelf-life is the storage environment, including temperature, relative humidity, and light (Robertson, 2009; Figure 4). Temperature greatly influences spoilage. While high temperatures speed up chemical reactions, microbial growth, and enzymatic activity,

causing faster deterioration, low temperatures slow these processes and extend shelf-life (Taoukis & Giannakourou, 2004). Excessive heat can also destabilize emulsions, melt fats, or cause crystallization, while freezing can damage fresh foods and cereals by forming ice crystals that alter structure (Kong & Singh, 2016; Singh & Anderson, 2004). Also, different microbes grow at various temperature ranges: psychrotrophs thrive around 20–30°C but can also grow below 7°C, mesophiles prefer 30–40°C but overall grow between 10–45°C and thermophiles favour 45–65°C (Singh & Anderson, 2004). In addition, relative humidity affects food's physical and chemical properties by causing moisture gain or loss until equilibrium is reached, often leading to quality loss. For example, moisture absorption causes caking in powders, while moisture loss makes foods brittle or wilted. Even foods kept deeply frozen can encounter issues with moisture loss since moisture can evaporate from the surface to a dry external environment even at -20°C and lower temperatures, causing drying or freezer burn of the product (Singh & Anderson, 2004). Finally, products prone to oxidation are also sensitive to light as it accelerates the photo-oxidation process and eventually starts developing rancidity (Kong & Singh, 2016). In addition, the presence of UV-light, can cause the degradation of color pigments, such as carotenoids and anthocyanins, resulting in the product losing color (Solymosi et al., 2015).

In conclusion, to minimize the influence of both internal and external factors on the quality and safety of the product during its shelf-life, one must know the properties of the product but also package it in suitable materials and environments and store the product consistently in the correct environment.

2 Aims of the study

The main objective of this doctoral thesis was to evaluate the applicability of accelerated shelf-life testing (ASLT) models for long shelf-life foods and to provide product-specific guidelines for selecting quality indicators and Q_{10} values to enable reliable shelf-life predictions. The specific aims of this study were:

- To investigate possible food preservation methods and potential packaging strategies for prolonging the shelf-life of cereal products and savoury snacks.
- To assess the suitability of ASLT methodology for evaluating nutritional and colour-related changes in pasteurized purees, based on total phenolic and anthocyanin contents.
- To investigate the applicability of ASLT for evaluating the degradation kinetics of colour-giving anthocyanins in long shelf-life berry rich mueslis.
- To evaluate the use of chemical versus sensory markers in ASLT based on lipid oxidation indicators of sunflower oil-based potato chips.

3 Materials and methods

3.1 Sample products and packaging

The samples of packaged purees were supplied by a local producer (Salvest AS, Tartu, Estonia). Three different organic purees were used in this study: four-grain puree with banana and blueberry (FGBB), mango-carrot-sea buckthorn puree (MCB), and fruit and yogurt puree with biscuit (FYB). The FGBB contained water, 30% of banana puree, 8% of blueberry puree, 7% of four-grain cereals (rye, oat, wheat, barley) and rapeseed oil. FYB included banana puree (37%), mango puree (36%), yogurt (15), raspberry puree (10%) and 2% of biscuit, containing wheat flour, butter and water. MCB contained 53% of mango puree, 40% of carrot puree and 8% of sea buckthorn puree. All concentrations and percentages in the purees are expressed as mass fractions (w/w). The purees were packaged in two types of doypack pouches where the original product version included an AL-layer and in the case of the second package, an AL-free material was tested (Gualapack S.p.A, Castellazzo Bormida, Italy). In addition, the doypacks included materials like PET, OPA (oriented PA), and PP. In more detail, the doypack composition with AL-layer consisted of 12 µm PET/9 µm AL/15 µm OPA/75 µm PP. The doypack without the AL-layer consisted of 12 µm PET/15 µm OPA/70 µm PP. The spout material of both packages was PP. The oxygen and water vapor transmission rates for both doypacks were < 1 cm^3/m^2/24h and < 1 g/m^2/24h, respectively. The packaged purees were heat treated with the internal temperature being 108°C for 31 min for FGBB, 103°C for 43 min for MCB, and 103°C for 17 min for FYB.

The muesli samples were produced using rolled oats (Balti Veski AS, Estonia), freeze-dried strawberry (Fragaria spp., SB), blueberry (Vaccinium spp., BB) and blackcurrant (Ribes spp., BC) slices (Freezedry OÜ, Estonia), sugar syrup (Nordic Sugar A/S, Denmark), whole milk powder (Valio OY, Finland), strawberry concentrate (Bayernwald KG, Germany), and vanilla sugar (Santa Maria AS, Estonia). To produce the basis of the muesli, rolled oats, sugar syrup, strawberry concentrate and vanilla sugar were mixed and baked at 130°C for 45 min. After that, the baked basis was cooled at room temperature for 4 h. Then, the dry and cooled basis was mixed with whole milk powder and berry slices. The muesli samples were packaged in stand-up pouches, containing 20 µm Matt-BOPP/12 µm PET/7 µm aluminum/110 µm LDPE (DaklaPack Europe, Netherlands). The oxygen transmission rate was < 0.5 m^3/m^2/24 h. The water vapor permeability was < 0.5 g/m^2/24 h. In addition, 50 mm × 57 mm of iron-based oxygen absorber (Tianhua Tech Co., Ltd, China) was added into each package.

Potato chips were sourced from a local retailer (Coop, Estonia) and manufactured by Pata S.p.A in Italy. According to the packaging, every 100 g of these chips contained 33 g of fat, including 3.7 g of saturated fatty acids, along with 50 gof carbohydrates, 6.2 gof protein, and 1 g of salt. For the study, 42 g of chips were placed into plastic bags, made from a multilayer film consisting of 12 µm PET and 40 µm LLDPE (provided by AS Estiko-Plastar, Estonia). The packaging's oxygen permeability was 130 cm^3/m^2/24h, while the moisture vapor transmission rate was < 3 g/m^2/24h.

3.2 Reagents and standards

Folin–Ciocalteu reagent (Sigma-Aldrich, Taufkirchen, Germany), gallic acid monohydrate (Sigma-Aldrich, Germany), sodium bicarbonate (Sigma-Aldrich, Germany), sodium acetate (Sigma-Aldrich, Germany), potassium chloride (Sigma-Aldrich, Germany), poly(vinyl-polypyrrolidone) (PVPP) (Sigma-Aldrich, Germany), acetone (Sigma-Aldrich, Germany).

Reference standards of delphinidin, cyanidin, peonidin, petunidin, malvidin, pelargonidin 3-*O*-glucoside, quercetin, ellagic acid, *p*-coumaric acid, (+)-catechin and *trans*-cinnamic acid were obtained from Sigma-Aldrich (United States). The solvents of LC and MS grade, such as acetonitrile, formic acid, hydrochloric acid, ethyl acetate, and methanol, were purchased from Honeywell (Finland).

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

3.3 Design of shelf-life tests

Purees packaged in doypacks were stored in a carton board box at room temperature (23°C) and in a climate chamber at 40°C, set up at 50% of relative humidity (Memmert UN750, Büchenbach, Germany). The samples were stored in the dark to simulate the most likely condition applied in the warehouse. As the expected shelf-lives of the samples at room temperature were 12 months, the testing time points were chosen based on this to describe possible changes taking place before and after the expected end of storage. Therefore, the testing points for room temperature storage were 0-point (immediately after production), 182 days (6 months), 274 days (9 months), 365 days (12 months), and 427 days (14 months). For the ASLT at 40°C, the storage time for each corresponding analysis point was calculated using Equation 3. As the literature states, the Q_{10} for almost all food products is approximately 3 (Choi et al., 2017). Therefore, the time points of the ASLT which corresponded to 6, 9, 12, and 14 months in room temperature storage were calculated to be 28, 42, 56, and 66 days at 40°C. At each time point, 2 sample replicates from both storage conditions were taken for analysis.

The packaged mueslis were stored at room temperature (23°C) and in a climate chamber at 40°C (Memmert UF110, Germany), respectively. In the test at 23°C, the testing points of storage time were 6 and 12 months. For the ASLT at 40°C, the testing time points were calculated with Q_{10} factor, using Equation 3. The Q_{10} value was set as 3. The time points of the ASLT were calculated to be 28, 56, 89, 120, 169, 197 and 365 days at 40°C, to simulate the storage at room temperature for 0.5, 1, 1.5, 2, 3, 3.5 and 6.5 years, respectively.

Packaged chips were placed 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) without humidity. Over a 90-day storage period, samples were collected at 10-day intervals. For every time point and storage condition, triplicate analyses were conducted.

3.4 Analysis of total phenolic content

The content of total phenolic compounds was determined using the F–C (Folin–Ciocalteu) method as described by Yap et al., 2019. The extraction of total phenolic compounds from different food matrices was performed as described by Sulaiman et al., 2011with some modifications, and the polyvinylpolypyrrolidone (PVPP) treatment was performed as described by Bridi et al., 2014 with some modifications. Briefly, 1 g of sample was weighed into 15 mL high-speed centrifuge tubes, 5 mL of 70% (v/v) acetone was added, and mixed thoroughly. Sample extracts were rotated for 60 min using rotator Stuart SB3 (TEquipment, Long Branch, NJ, USA). Sample extracts were centrifuged (21,000 × g at 18°C for 10 min), filtered with a microfilter (CHROMAFIL Xtra PET-20/13, 0.2 µm), and diluted with acetone up to 5 times, if necessary. To separate polyphenols and non-polyphenolic derivatives (sugars, ascorbic acid, and sulphite) from the samples and, therefore, to see the amount of interfering compounds, a pretreatment with polyvinylpolypyrrolidone (PVPP) was used. The PVPP was suspended in milliQ water and was well shaken before being added to the filtered sample. PVPP treatment was applied as follows: 0.5 mL of PVPP suspension (40 g/L) was added to 0.5 mL of filtered sample and the mixture was rotated for 10 min using rotator Stuart SB3 (TEquipment, USA). After PVPP treatment, the samples were centrifuged (21,000 × g at 18°C for 10 min), filtered with a microfilter (CHROMAFIL Xtra PET-20/13, 0.2 µm), and diluted with acetone up to 5 times, if necessary. The content of TPC was determined using the F–C method. For this, 20 µL of filtered and diluted sample extracts (PVPP treated or untreated) were mixed with 100 µL of 0.2N F–C reagent. After 5 min, the reaction was stopped by adding 80 µL of 7.5% (w/v) sodium carbonate solution. After stopping the reaction, the samples were incubated for 30 min at 37°C. The absorbance was determined after the incubation period with a BioTek Synergy H1 multi-mode microplate reader (Agilent Technologies, Inc., Santa Clara, CA, USA) at a wavelength of 765 nm. A 70% acetone solution was used as an absorbance blank. The values were given as gallic acid equivalent (GAE). TPC of the sample was calculated as a difference between before and after PVPP pretreatment in mg/g of the gallic acid equivalent (mg GAE/g).

3.5 Analysis of specific phenolic compounds

Anthocyanin contents of purees were quantified using the pH differential method. Buffer A (pH 1.1) was prepared by dissolving 1.86 g KCl in 1 L Milli-Q water (pH adjusted with HCl), and buffer B (pH 4.5) by dissolving 32.8 g sodium acetate in 1 L water (pH adjusted with HCl). 2 g of sample was homogenized and extracted with 4 mL of either buffer, vortexed, allowed to stand for 10 min, re-vortexed, centrifuged at 14 000 rpm for 10 min, and filtered through 0.2 µm syringe filters. Extracts were diluted with the corresponding buffer to ensure absorbance at 520 nm fell within the linear range (0.10–2.00). Measurements of absorbance were recorded at 520 nm and 700 nm using a BioTek Synergy H1 microplate reader (Agilent Technologies, Inc., USA) with pathlength correction (Gen5 software). The values were given as mg C3GE/100 g (mg cyanidin-3-glucoside equivalents per 100 g of product).

The dried berries at different time points (2-4 replicates at each time point during both storage tests) were first picked from muesli samples and then crushed into fine powders with mortar and pestle. Anthocyanins and other phenolic compounds of dried berries were extracted from the berries using two different methods described in (Tian et al., 2017), with a slight modification. For anthocyanins, approximately 1.0 g of berry

powders were mixed with acidified methanol (methanol/hydrochloric acid, 99:1, *v*/*v*) at a solid and solvent ratio of 1:3 (*w*/*v*). Extraction was assisted with ultra-sonication (for 10 min) and centrifuge (10 min, at 1500 × *g*). The supernatants from three-time extraction were combined and diluted to a final volume of 10 mL with acidic methanol. For other phenolic compounds, the berry powders (3.8 g) were mixed with 20 mL of aqueous ethyl acetate (water/ethyl acetate, 1:1, *v*/*v*), followed by 3 min of vortex and 15 min of centrifuge (1500 × *g*). The supernatants after centrifugation were collected and completely dried by using a rotary evaporator (at 35°C, Heidolph, Germany). The residues were re-dissolved in 3 mL of methanol. The extracts of anthocyanins and other phenolic compounds were filtered with 0.2 mm syringe filters and preserved at –20°C until further testing. The identification of phenolic compounds was conducted by using a Shimadzu Ultra performance liquid chromatography (UPLC) system equipped with SPD-M40 photo diode array detector (PDA), a LCMS-8045 mass spectrometer (MS; Shimadzu Corp., Kyoto, Japan). LC chromatographic separation was performed with a Phenomenex Aeris peptide XB-C18 column (150 × 4.60 mm, 3.6 µm, Torrance, CA, United States). The reject volume was 10 µL. The total flow rate was set to 1 mL/min, and approximately 0.3 mL/min of samples were eluted into mass spectrometers. MS full scan and MS^2 product ion scan were operated in both ESI^+ and ESI^- mode. A Shimadzu LC-30AD liquid chromatograph system coupled with an SPD-M20A diode array detectors (Shimadzu Corp., Kyoto, Japan) were used for quantitative analysis of phenolic compounds. All chromatograms were monitored at the wavelength of 520 nm (for anthocyanins), 360 nm (flavonols and ellagic acid derivatives), 320 nm (hydroxycinnamic acids), and 280 nm (flavan-3-ols). The identified compounds were quantified by external reference standards. Approximately 1 mg of reference compounds were dissolved in 10 mL ethanol and diluted into four different concentrations. The calibration curves were established between peak areas in the HPLC-DAD chromatogram and corresponding concentrations.

3.6 pH analysis

The pH of purees was measured using a pH-meter (Mettler-Toledo International Inc., Columbus, OH, USA). The analysis was done by inserting a pH-electrode into a previously homogenized sample. Two measurements were performed for both sample replicates.

3.7 Degradation kinetics of anthocyanins

The degradation of anthocyanins during ASLT was analyzed following the first-order kinetics (Equation 4).

$$C_t = C_0 * e^{(-kt)} \qquad (4)$$

where C_t and C_0 are the anthocyanin concentrations at day t and day 0. The kinetic constant is represented by k and storage time (day) by t. The half-life value ($t_{1/2}$) of total anthocyanin content was calculated with Equation 5.

$$t_{1/2} = \frac{(ln\frac{1}{2})}{k} \qquad (5)$$

3.8 Analysis of Fatty Acid Methyl Esters (FAMEs) using GC-MS

To assess the changes in fatty acid composition, potato chip samples were analysed at the start of the study and following 70 and 90 days of storage under various temperatures. After collection, all samples were preserved at –20°C prior to analysis. Fatty acids were extracted from the samples using a Velp Scientifica 158 series Soxhlet apparatus (Velp Scientifica, Series 158, Italy). 3 grams of chips were first ground with a mortar. The oil was then extracted using petroleum ether as the solvent. The extraction cycle included the following steps: 20 minutes of immersion, 8 minutes of solvent removal, 20 minutes of washing, 10 minutes of recovery, and a 5-minute cooling period. After extraction, the petroleum ether was evaporated, and the recovered oil was stored at –20°C until further analysis. To prepare the oil for fatty acid composition analysis, derivatization was carried out. For this, 100 mg of extracted oil was combined with 1450 µL of hexane to form a stock solution. From this, 200 µL of the stock was mixed with 200 µL of a chloroform:methanol solution (2:1 ratio) and 300 µL of 0.6 M HCl in methanol. The mixture was then incubated at 100°C for one hour. After heating, 200 µL of hexane was added, and the mixture was vortexed for 5 minutes. The final samples were stored overnight at –20°C for subsequent analysis. Prior to gas chromatographic analysis, 5 µL of the upper phase from each processed sample was collected and diluted with 450 µL of hexane. Each sample underwent derivatization in triplicate to ensure analytical consistency. Separation of the resulting fatty acid methyl esters (FAMEs) was carried out using a gas chromatography system (GC 7890A, Agilent Technologies, USA) equipped with an ultra-inert splitless liner (type 5190-2293, Agilent Technologies). This GC system was interfaced with a 5975C mass spectrometer (Agilent Technologies, USA), employing electron impact ionization and a quadrupole analyzer for detection. Chromatographic separation was achieved using a ZB-5MSi capillary column (30 meters in length, 0.25 mm internal diameter, 0.25 µm film thickness, Agilent Technologies, USA). High-purity helium (grade 6.0) served as the carrier gas, maintained at a constant flow of 1 mL/min. A 2.5 µL volume of each prepared sample was injected in splitless mode at an injector temperature of 275°C. The GC oven temperature was programmed as follows: held at 32°C for 4 minutes, then incline to 225°C at 10°C/min and maintained for 6 minutes, followed by a second incline to 300°C at the same rate and held for an additional 5 minutes. The complete run time for each analysis was 41 minutes. Mass spectrometry was conducted in scan mode over an m/z range of 35–600 using 70 eV electron ionization. Operational temperatures were set at 250°C for the transfer line, 230°C for the ion source, and 150°C for the quadrupole. Data acquisition and processing were performed using Agilent MassHunter Qualitative Analysis software. Identification of individual fatty acids was confirmed by comparing retention times with those of a known standard mix and by referencing the NIST17 mass spectral library. Quantitative analysis was performed using five-point calibration curves.

3.9 Analysis of volatile profile using SPME-GC-MS

Volatile compound analysis using solid-phase microextraction (SPME) followed by gas chromatography–mass spectrometry (GC-MS) was conducted on potato chip samples collected at day 0 and after storage at different temperatures for 10, 30, 50, 70, and 90 days. Samples from each time point were stored at –20°C until processed. To extract volatiles, chips were first homogenized using a mortar, and 0.5 grams of the ground material was placed into a 10 mL headspace vial. These vials were pre-incubated at 50°C

for 5 minutes before extraction. A SPME fiber (30/50µm DVB/Car/PDMS Stableflex, 2 cm length) was inserted into the headspace of each vial to collect volatile compounds over a 20-minute adsorption period. The fiber was then thermally desorbed in the GC injector for 5 minutes to release the trapped analytes. Analysis was carried out on a Shimadzu GC-MS system (GC-2030 coupled with the 8050NX Triple Quadrupole mass spectrometer, Kyoto, Japan), using a ZB5-MS column (30 m × 0.25 mm i.d. × 1.0 µm film thickness; Phenomenex, USA). Helium served as the carrier gas at a linear velocity of 35 cm/sec. The oven temperature was programmed to start at 40°C, then increased at a rate of 7.5°C/min until reaching 280°C, with a final hold of 4 minutes, resulting in a total run time of 36 minutes. Mass spectrometry was operated in scan mode with electron impact ionization at 70 eV, covering a mass-to-charge (m/z) range from 35 to 250. Each sample was analyzed in triplicate for data reliability. Volatile compound identification was untargeted and performed using Shimadzu's GC-MS Solution software in combination with retention indices. Experimental RIs were determined by comparing the retention times of analytes with those of adjacent n-alkanes. Compound identification was confirmed by matching both mass spectra and RIs with entries in the NIST17 and FFNSC databases. For semi-quantitative analysis, 4-methyl-2-pentanol (200 ppb) was used as an internal standard.

3.10 GC-Olfactometry experimental procedure

Volatile compounds from potato chips stored for 90 days at 40°C were analyzed using headspace solid-phase microextraction combined with gas chromatography-olfactometry (HS-SPME/GC-O). For this analysis, 1.0 g of finely ground chips was transferred into an SPME vial and allowed to equilibrate at 50°C for 5 minutes. Volatiles were collected from the vial headspace using a 2 cm DVB/Car/PDMS fiber (Stableflex, Supelco) over a 20-minute extraction period, with continuous stirring at 50°C to enhance compound release. The GC-O analysis was performed using an Agilent 7890A gas chromatograph (Agilent Technologies, Palo Alto, CA) equipped with an olfactory detection port (ODP; Gerstel Inc.). Separation was achieved on a ZB5-MS capillary column (30 m length × 0.25 mm i.d. × 1.0 µm film thickness). The oven temperature was programmed as follows: an initial ramp from 35°C to 85°C at 45°C/min, followed by an increase to 200°C at 9°C/min, and a final ramp to 280°C at 45°C/min, held for 1 minute. The entire run lasted 16.67 minutes. A panel of four trained evaluators conducted the GC-olfactometry assessments. Each panelist described the odors corresponding to eluting compounds and rated their perceived intensity on a scale from 1 (very weak) to 5 (very strong). Each sample was evaluated in duplicate by every assessor.

3.11 Sensory analysis

The sensory evaluation of potato chips was performed by a panel of experienced assessors familiar with shelf-life testing. Throughout the study, eight individuals participated, with an average age of 31 ± 7 years. The sensory assessments utilized Quantitative Descriptive Analysis (QDA) and were carried out in a controlled sensory laboratory designed according to ISO 8589:2007 standards. Data collection was facilitated using RedJade software (RedJade Sensory Solutions LLC, Martinez, CA, USA). The panelists specifically rated the intensity of rancid odor in the samples. A 10-point scale with verbal descriptors was used, where 0 represented "none," 1 indicated "very weak," 5 was "moderate," and 9 signified "very strong" rancidity. At the outset, freshly prepared chips were evaluated to serve as a baseline reference, then stored at 4°C.

Subsequent sensory sessions involved testing chips stored at elevated temperatures of 20°C, 30°C, and 40°C across various time points. For each temperature and time combination, three replicate samples were presented, totaling nine samples per session. The 4°C-stored chips were included as the reference to help panelists assess the development and severity of rancid odors in the heat-stored samples. Each evaluation session lasted approximately 15 minutes.

3.12 Statistical analyses

Statistical significance testing of total polyphenolic content of purees was performed in R 4.2.2 (The R Foundation for Statistical Computing, Vienna, Austria) using package "emmeans" 1.8.3. The TPC response variable was modelled by a cubic B-spline of time data plus packaging. The model fit was evaluated visually and using the adjusted coefficient of determination. The significances were calculated across time points and packaging for each different product and each different storage temperature by using pairwise t-test comparisons between the estimated marginal means. The confidence level was set to 0.95 and adjusted using the Bonferroni method. p-values were adjusted according to the Benjamini–Hochberg method(Benjamini Yoav & Hochberg, 1995). The significance level for compact letter displays was set to 0.05.

The concentration of each identified phenolic compound of berry mueslis was calculated based on dry weight of berries and the values are expressed as mean ± standard deviation (SD). The *k* value used in anthocyanin degradation kinetics and correlations between individual phenolic compounds in berry slices were calculated using Origin Pro 2018 (Origin Lab, Northampton, MA, United States). Heatmap was performed using MetaboAnalyst 5.0 (www.metaboanalyst.ca). Statistical differences among data were calculated based on one way-ANOVA and Tukey's post hoc test ($p < 0.05$) by IBM SPSS Statistics 28 for Windows (SPSS Inc., NY, United states).

Statistically significant difference of fatty acids and volatile compound results were 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 ($\alpha = 0.05$).

4 Results

4.1 Food shelf-life processes and possible packaging solutions to extend shelf-life

A review article (**Publication I**) was conducted analysing the recent practices in food quality and shelf-life management, exploring packaging solutions to extend shelf-life with special focus on cereals and snacks. It examined key packaging functions, product traits, and deterioration mechanisms of these ready-to-eat long shelf-life products. The study also reviewed historical and modern packaging strategies, including traditional and advanced technologies for shelf-life extension.

Building upon this foundation, the study further identified the primary quality degradation processes specific to the products in focus by examining intrinsic factors such as water activity (a_w) and moisture content. The review established that cereal and snack products are mostly low-moisture foods, which deteriorate mainly through moisture absorption, causing loss of crispness, aroma changes, and structural damage like softening or clumping. For example, ready-to-eat savories and snacks with high-fat content often face oxidation, leading to off-flavors and odors. Despite these issues, their low water activity value makes them stable for dry storage. Microbial growth is minimal in these product categories but can be significant in convenience foods, where improper packaging can cause moisture desorption. Fresh bakery products, on the other hand, with higher a_w, have shorter shelf-lives, mainly due to microbial spoilage (molds, yeasts, and spore-forming bacteria) and water exchange, which leads to crust softening or crumb drying. Once the a_w drops below 0.5–0.7, sensory quality declines rapidly.

Understanding these deterioration mechanisms provides a basis for selecting appropriate packaging solutions tailored to each product's specific vulnerability, ensuring quality preservation throughout storage and distribution. Cereals and cereal products vary in packaging depending on their barrier requirements. Low-barrier items, such as breakfast cereals, are commonly packaged in paper, cardboard, or PE. In contrast, high-barrier cereals require materials like HDPE combined with barrier layers such as EVOH, often supplemented by secondary packaging like fiberboard for added protection. Snacks, particularly high-fat varieties, demand multilayer packaging materials—such as PET/aluminum/LDPE—to provide effective moisture and oxygen barriers. Puffed snacks, on the other hand, require packaging with strong water vapor barriers and secondary protection, typically cardboard boxes, to maintain product quality. Biscuits, nuts, and dried fruits are usually packaged in coated cellophane or monomaterial PP films, which serve primarily as oxygen barriers to preserve freshness. Finally, dried pasta is typically packaged in plastic films or paperboard cartons with transparent windows, while fresh pasta requires rigid trays combined with MAP solutions to extend shelf life. Fresh bakery products also need packaging that balances moisture retention, using materials like paper bags, LDPE, or perforated LDPE for crusty items. To protect aromas, PA films are often applied.

In addition to conventional materials, the study highlighted the increasing integration of advanced packaging technologies designed to further extend shelf-life and enhance product protection (Figure 5).

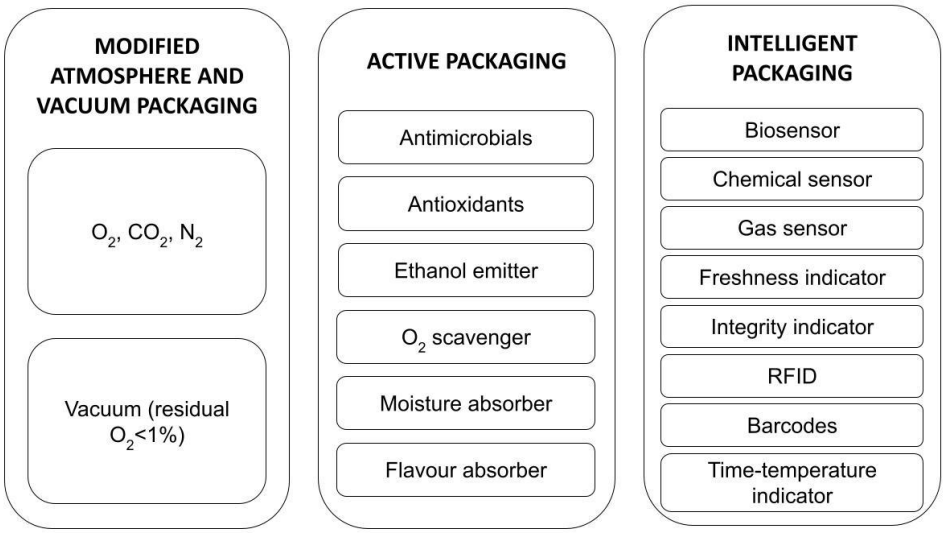

Figure 5. Selected examples of modified atmosphere, vacuum, as well as active and intelligent packaging approaches with certain use cases for cereal and snack product packaging.

For example, snacks and cereals require oxygen absorbers and MAP to prevent oxidation, especially in high-fat snacks. Furthermore, essential oils are employed to prevent mold on bread and act as insect repellents in grain packaging. MAP is particularly effective for nuts and coated fruits, while oxygen barriers such as metallized films help protect snacks prone to oxidation. In bakery products, the use of preservatives alongside MAP, typically an 80:20 CO_2 to N_2 ratio, can greatly extend shelf life, even doubling it for products like soy bread when high-barrier materials are applied. Additionally, edible films containing antimicrobial agents such as clove or oregano oils help prevent spoilage.

Furthermore, intelligent packaging systems incorporate indicators that monitor critical parameters such as temperature fluctuations, microbial activity, and product freshness, thereby providing real-time information on the quality and safety of food products. These technologies offer an added layer of assurance to both manufacturers and consumers by enabling timely interventions and reducing food waste. However, despite their promising potential, the widespread adoption of active and intelligent packaging is currently limited by several factors, including the need for further technological refinement, cost-effectiveness, and the establishment of clear regulatory frameworks to ensure safety, standardization, and consumer trust.

The findings from Publication I confirmed that the careful selection of appropriate packaging materials and storage environments plays a critical role in preserving food quality and safety, not only for cereals and snack products, but across various food categories. The study also contributed to defining the main quality degradation processes affecting these foods, which are essential for the design and execution of effective shelf-life testing. Understanding these deterioration mechanisms provides a basis for selecting appropriate test parameters. Also, it was concluded that by providing tailored protection against environmental factors such as moisture, oxygen, light, and microbial contamination, optimal packaging solutions help minimize deterioration, maintain sensory and nutritional attributes, and significantly extend shelf-life.

4.2 The stability of phenolic compounds in purees based on ASLT methodology

The aim of **Publication II** was to evaluate the stability of polyphenols in various pasteurized purees to assess the quality of these long shelf-life products during storage. Specifically, the study aimed to monitor the stability of total phenolic (TPC) and anthocyanin (ANC) content in four-grain puree with banana and blueberry (FGBB), mango-carrot-sea buckthorn puree (MCB), and fruit and yogurt puree with biscuit (FYB) and based on these indicators, assess the suitability of ASLT methodology for evaluating nutritional and colour-related changes in such products.

Initially (Table 2), MCB and FYB, containing the highest amounts of fruits, berries, and/or vegetables, had also the highest TPC, followed by FGBB, including only 45% of ingredients with phenolic content. On the other hand, FGBB showed the highest anthocyanin content, while FYB had a lower level. In the case of MCB, no anthocyanins were detected (Table 2). This is most likely due to the different polyphenolic profiles of the puree components. For example, although FGBB contained relatively few phenolic compounds—since its composition consisted mainly of banana, oil, and cereals—the blueberry fraction (8%) contributed to a concentrated anthocyanin content. In contrast, the composition of FYB was dominated by components providing phenolic compounds, such as mango (36%). Although the raspberry fraction (10%) in FYB puree was similar to the blueberry proportion in FGBB, the intrinsic anthocyanin content of raspberry is several times lower than that of blueberry (Hosseinian & Beta, 2007). Finally, MCB did contain many phenolic compounds, but none of its ingredients provided anthocyanins. Also, Table 2 shows that the transition from AL-layered packaging to AL-free material did not relevantly affect the initial phenolic contents.

Table 2. Initial total phenolic and anthocyanin content of the samples.

Product	**FGBB**		**FYB**		**MCB**	
Packaging	AL-layered	AL-free	AL-layered	AL-free	AL-layered	AL-free
TPC (mg GAE/100 g)	30.0 ± 1.7	29.2 ± 1.5	49.8 ± 1.5	50.0 ± 1.5	51.7 ± 2.6	53.0 ± 3.0
Anthocyanins (mg C3GE/100 g)	2.1 ± 0.1	2.0 ± 0.1	0.7 ± 0.1	0.6 ± 0.1	ND	ND

ND = not detected

To assess the nutritional changes of the purees during storage, the decrease of TPC was monitored at room temperature and at 40°C. The most pronounced decline in TPC under both storage conditions was observed in the FGBB puree (Figure 6a). This product contained the lowest proportion of phenolic-rich ingredients (30% banana puree, 8% blueberry puree, and 7% four-grain cereals) and had the highest pH (4.8) among the tested samples. The results showed a 63% decrease of phenolic content at room temperature and a 57% drop in ASLT for samples packaged in AL-packaging. Additionally, no statistically significant differences in polyphenol reduction were observed between AL-layered and AL-free packaged samples during storage tests across all tested products.

In contrast, the FYB and MCB purees exhibited smaller changes in TPC under both storage conditions. These formulations included higher proportions of phenolic-rich ingredients. For instance, FYB contained banana puree (37%), mango puree (36%), raspberry puree (10%), and four-grain cereals (2%), and maintained a relatively low pH

of 4.0 throughout storage. Compared to FGBB, FYB showed a more moderate decline in phenolic content, with a 41% decrease at room temperature and a 27% decrease under ASLT (Figure 6b).

The smallest decline in TPC was observed in the MCB puree, which consisted entirely of fruits, vegetables, and berries, including 52% mango, 40% carrot, and 8% sea buckthorn. This product also had the lowest pH (3.9), which may have created the most favorable conditions for preserving bioactive compounds. According to the shelf-life test results (Figure 6c), no significant loss in TPC occurred under ASLT, while at room temperature the decrease was comparable to FYB, showing a 27% reduction.

These results demonstrated that the stability of phenolic compounds is product-specific, primarily influenced by the types and proportions of ingredients used, as well as the product pH. With the latter, the results of this experiment confirmed the findings reported by previous authors. For example, Oliveira et al. (2015) studied the degradation of polyphenols in strawberry purees with different pH values, finding that at pH 3.5, 4.0, and 4.5, the total phenolic content decreased by 12%, 18%, and 21%, respectively. Similarly, Wojdyło et al. (2008) observed that in jams with a pH of 2.0–3.0, anthocyanin degradation was lower (33–35%), while the amount of anthocyanins in jams obtained at pH 3.5–4.0 were degraded by 40–48%. Therefore, understanding and maintaining the appropriate pH is important to preserve the nutritional and functional quality of fruit products during storage.

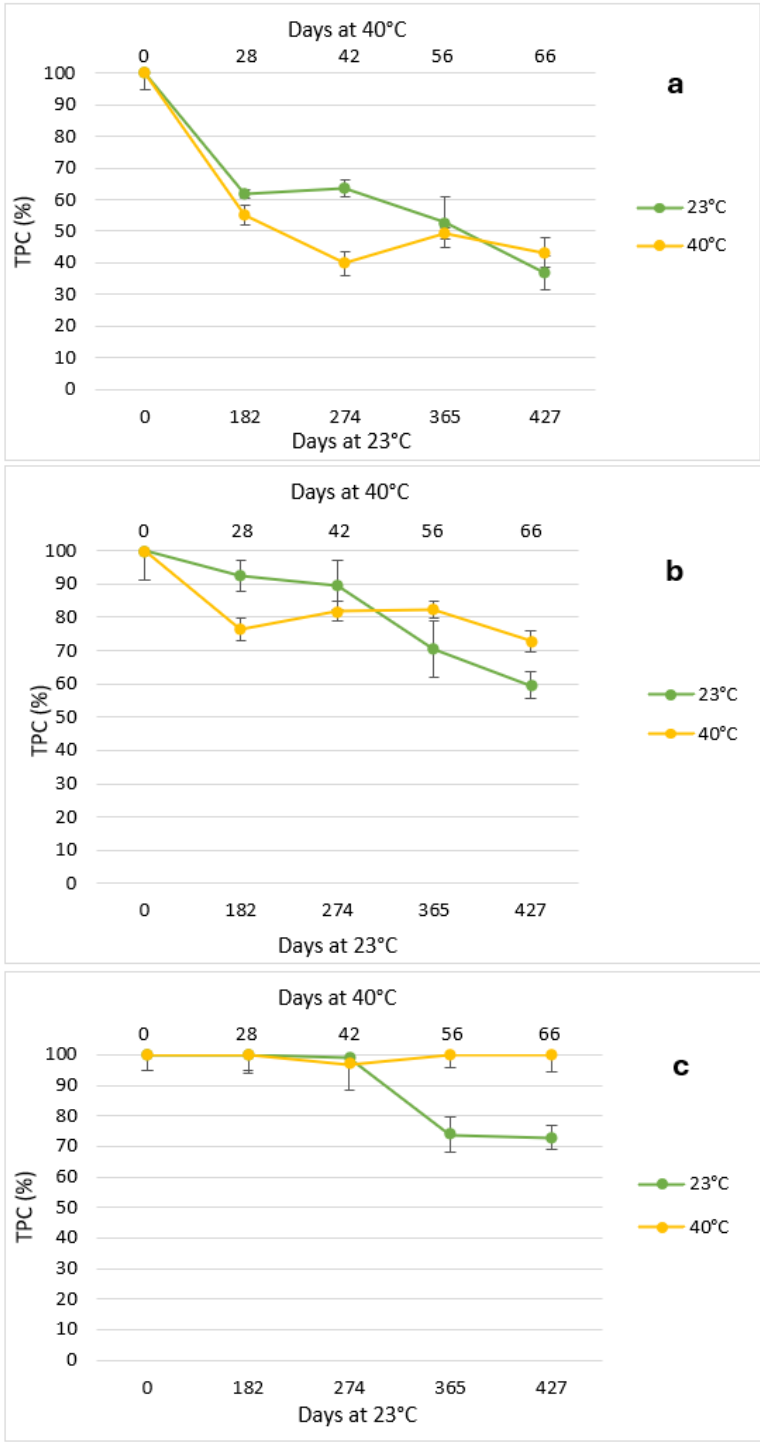

Figure 6. TPC changes (%) in FGBB (a), FYB (b), and MCB (c), at 23°C and 40°C, packaged in AL-layered doypacks.

To assess the colour-related changes of the purees through the description of a chemical marker, the change in anthocyanin content was determined in the FGBB and FYB purees at room temperature and at 40°C (Figure 7). In both formulations, anthocyanin content declined sharply during the first six months of real-time storage, with losses exceeding 70% by day 182. After this rapid initial decrease, degradation proceeded at a slower rate. Similarly to changes in TPC, the storage at 40°C accelerated anthocyanin loss most comparably with room temperature shelf-life test in FGBB puree (Figure 7a) but less in FYB (Figure 7b). In more detail, while the anthocyanin degradation in the first ASLT time point (28 days) of FYB was nearly similar to the decline in the first room temperature storage time point (182 days), the degradation in the next time points of ASLT showed a smaller decrease than in real-time, in which the anthocyanin content reached zero one year after the start of the test.

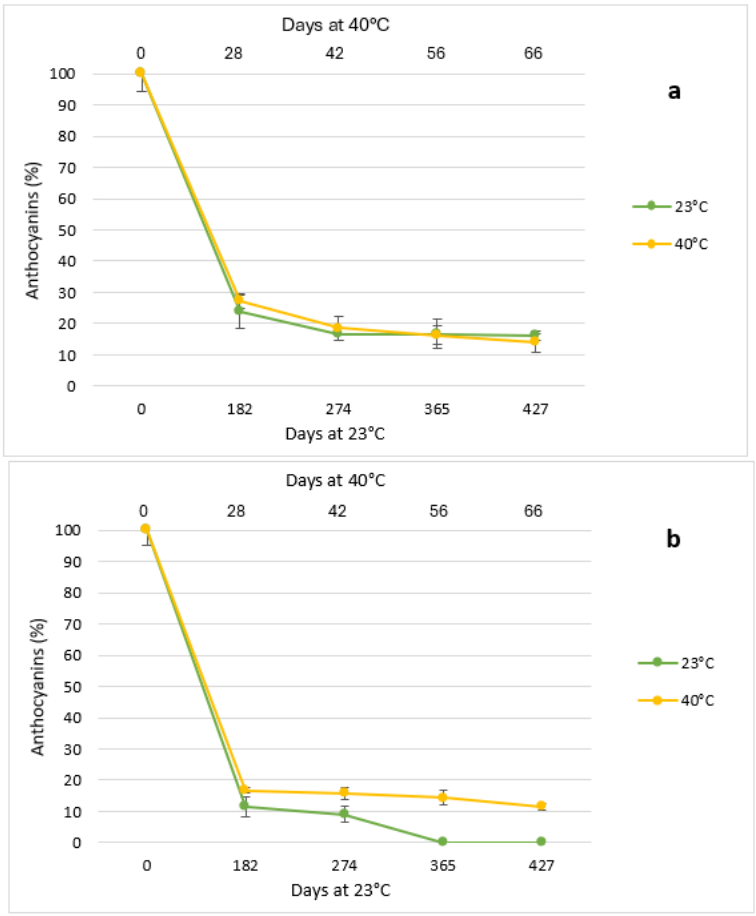

Figure 7. Anthocyanin degradation (%) in FGBB (a) and FYB (b), at 23°C and 40°C, packaged in AL-layered doypack.

To evaluate the suitability of the ASLT methodology for assessing phenolic content changes in the studied purees, the kinetic parameters of the products were calculated. As the degradation of total polyphenols and anthocyanins followed first-order reaction kinetics, their reaction rates were determined from the logarithmic concentrations plotted against time (Table 3).

Among the three products, the FGBB puree showed the clearest temperature dependence in the degradation of both total polyphenols and anthocyanins (Table 3). The reaction rate constants at 40°C were several times higher than those determined at 23°C. The relatively high R^2 values indicate that the first-order kinetic model described the degradation behaviour well, and the difference in rate constants corresponds to an approximate Q_{10} value of 3. This suggests that increasing the storage temperature by 10°C accelerates both polyphenolic and anthocyanin degradation roughly threefold. The results demonstrate that FGBB is the most temperature-sensitive of the tested formulations, and its degradation processes at 23°C and 40°C are well-correlated.

The FYB puree exhibited slower degradation and lower sensitivity to temperature compared to FGBB (Table 3). The rate constants for total polyphenol content were low at both 23°C and 40°C and the moderate R^2 values (0.65–0.80) indicate a greater variability in the data for FYB compared to FGBB. The relatively small difference in rate constants between 23°C and 40°C suggests that the assumption of $Q_{10} = 3$ overestimates the temperature effect. Therefore, $Q_{10} = 2$ better reflects the slower degradation, potentially linked to the lower pH of FYB, which provides a more stable environment for phenolic compounds. For anthocyanins, on the other hand, the levels at 40°C did not follow the same pattern as at 23°C. In more detail, while the degradation at 23°C proceeded steadily, the ANC content at 40°C remained higher than expected for the corresponding time points, with a slower apparent rate of decrease. Also, the measured concentrations indicate that a complete degradation was not reached within the testing period. This difference highlights that the current duration of the study may have been insufficient to fully capture anthocyanin stability under elevated temperatures. Therefore, extending the storage period at 40°C would be necessary to determine the actual degradation kinetics and to accurately monitor the stability of anthocyanins of this product under such conditions.

For the MCB puree (Table 3), the weakest correlation between temperatures was observed for total polyphenolic content, with minimal changes over time. This outcome likely reflects the product's lower pH and the presence of thermally stable compounds, which together contribute to enhanced phenolic stability during accelerated storage. Therefore, as no apparent temperature effect under the applied ASLT conditions was detected, it was concluded that the smallest Q_{10} factor is necessary to conduct accelerated tests with such products. Since no changes in phenolic content were observed during ASLT, no specific Q_{10} value could be calculated for this product based on this experiment. However, it can be hypothesized that the acceleration factor for this product is relatively low (likely ≤ 2), although confirmation would require an extended ASLT period. As the anthocyanin content of this product was not detected, no comparison between these two quality parameters can be given.

Overall, both total polyphenols and anthocyanins followed first-order degradation kinetics, but their temperature sensitivity differed significantly among the three products. The degradation rate increased with temperature for all samples, though to varying extents. while FGBB exhibited a strong temperature dependence ($Q_{10} = 3$), FYB showed moderate thermal sensitivity ($Q_{10} = 2$), and MCB remained largely stable under the applied accelerated storage conditions. These results confirm that both nutritional (TPC) and colour-related (ANC) quality parameters degrade according to the same kinetic principles, yet the extent of thermal acceleration must be adapted to each product's composition and pH to ensure accurate shelf-life predictions under ASLT conditions.

Table 3. Degradation parameters and Q_{10} values of total polyphenol (TPC: mg GAE/100 g) and anthocyanin (ANC: mg C3GE/100 g) degradation in FGBB, FYB and MCB purees.

Total polyphenols: FGBB										
23°C					**40°C**					**Q_{10}**
Days	**TPC**	**ln TPC**	**$k_{23°C}$ (day^{-1})**	**R^2**	**Days**	**TPC**	**ln TPC**	**$k_{40°C}$ (day^{-1})**	**R^2**	
0	30.9 ± 1.7	3.4 ± 0.05	-0.002	0.9003	0	30.9 ± 1.7	3.4 ± 0.05	-0.0123	0.7571	3
28	19.1 ± 0.4	2.9 ± 0.02			182	17.0 ± 1.0	2.8 ± 0.06			
42	19.7 ± 0.8	3.0 ± 0.04			274	12.3 ± 1.2	2.5 ± 0.10			
56	16.3 ± 2.5	2.8 ± 0.15			365	15.2 ± 0.6	2.7 ± 0.04			
66	11.4 ± 1.7	2.4 ± 0.15			427	13.4 ± 1.5	2.6 ± 0.11			
Total polyphenols: FYB										
0	56.8 ± 5.1	4.0 ± 0.09	-0.0012	0.8035	0	56.8 ± 5.1	4.0 ± 0.09	-0.0038	0.6508	2
28	52.6 ± 2.6	4.0 ± 0.05			182	43.4 ± 2.0	3.8 ± 0.05			
42	51.0 ± 4.2	3.9 ± 0.08			274	46.5 ± 1.7	3.8 ± 0.04			
56	40.1 ± 4.8	3.7 ± 0.12			365	46.8 ± 1.4	3.8 ± 0.03			
66	33.8 ± 2.3	3.5 ± 0.07			427	41.4 ± 1.8	3.7 ± 0.04			
Total polyphenols: MCB										
0	51.7 ± 2.6	3.9 ± 0.05	-0.008	0.6391	0	51.7 ± 2.6	3.9 ± 0.05	-0.0002	0.0516	Requires longer testing periods for validation.
28	53.2 ± 2.6	4.0 ± 0.05			182	51.7 ± 3.1	3.9 ± 0.06			
42	51.3 ± 1.1	3.9 ± 0.02			274	50.1 ± 4.4	3.9 ± 0.09			
56	38.2 ± 3.0	3.6 ± 0.08			365	52 ± 2.1	4.0 ± 0.04			
66	37.7 ± 2.1	3.6 ± 0.06			427	52.5 ± 2.8	4.0 ± 0.05			
Anthocyanins: FGBB										
23°C					**40°C**					**Q_{10}**
Days	**ANC**	**ln ANC**	**$k_{23°C}$ (day^{-1})**	**R^2**	**Days**	**ANC**	**ln ANC**	**$k_{40°C}$ (day^{-1})**	**R^2**	
0	2.09 ± 0.12	0.7 ± 0.06	-0.0042	0.8292	0	2.09 ± 0.12	0.7 ± 0.06	-0.0296	0.9210	3
28	0.5 ± 0.11	-0.7 ± 0.22			182	0.57 ± 0.05	-0.6 ± 0.09			
42	0.35 ± 0.04	-1.0 ± 0.11			274	0.39 ± 0.08	-0.9 ± 0.20			
56	0.35 ± 0.10	-1.0 ± 0.28			365	0.34 ± 0.06	-1.1 ± 0.18			
66	0.34 ± 0.03	-1.1 ± 0.09			427	0.29 ± 0.05	-1.2 ± 0.20			
Anthocyanins: FYB										
0	0.74 ± 0.03	-0.3 ± 0.04	-0.0109	0.8491	0	0.74	-0.3 ± 0.13	-0.0158	0.9155	Requires longer testing periods for validation.
28	0.24 ± 0.03	-1.4 ± 0.12			182	0.35	-1.0 ± 0.06			
42	0.19 ± 0.01	-1.7 ± 0.05			274	0.33	-1.1 ± 0.12			
56	0.01 ± 0.00	-4.6 ± 0.00			365	0.30	-1.2 ± 0.17			
66	0.01 ± 0.00	-4.6 ± 0.00			427	0.24	-1.4 ± 0.08			

4.3 Anthocyanin degradation and corresponding Q_{10} values of berry slices in ASLT

The aim of **Publication III** was to further investigate the applicability of ASLT for evaluating the degradation kinetics of phenolic compounds, mainly colour-giving anthocyanins, in berry-rich mueslis. Muesli products containing freeze-dried berry slices, specifically strawberries (SB), blueberries (BB), and blackcurrants (BC), were selected due to their popularity as a healthy breakfast option in Western countries.

The results showed that anthocyanins were the major phenolic compounds in these berry slices, with contents of 246.8–1086.6 mg/100 g DW, which were much higher than that of other phenolics (10.9–37.4 mg/100 g DW) (Table 4).

Table 4. Contents of total anthocyanins (ANC) and other phenolics (mg/100 g) in SB, BB, BC during ASLT and room-temperature storage test.

Storage °C	Storage time	SB		BB		BC	
		ANC	Other phenolics	ANC	Other phenolics	ANC	Other phenolics
40°C	0 days	246.8 ± 9.4	22.2 ± 2.5	1086.6 ± 60.9	37.4 ± 2.0	355.9 ± 58.3	10.9 ± 0.4
	28 days	89.1 ± 19.0	-	621.3 ± 31.2	-	292.7 ± 46.8	-
	56 days	83.7 ± 17.2	11.2 ± 0.7	436.2 ± 19.5	74.9 ± 4.5	162.0 ± 25.2	18.1 ± 0.7
	89 days	58.3 ± 9.1	12.4 ± 0.9	278.5 ± 12.1	57.1 ± 2.9	158.4 ± 24.3	18.7 ± 0.7
	120 days	57.6 ± 8.6	-	235.8 ± 10.7	-	158.4 ± 23.6	-
	169 days	52.1 ± 7.4	-	162.3 ± 6.8	-	145.1 ± 21.4	-
	197 days	49.2 ± 6.4	-	98.2 ± 3.6	-	121.9 ± 17.9	-
	365 days	49.4 ± 6.6	10.1 ± 1.1	71.3 ± 2.2	65.3 ± 3.3	87.3 ± 12.4	22.8 ± 1.1
23°C	6 months	176.3 ± 47.1	-	1022.3 ± 53.1	-	339.0 ± 55.2	-
	12 months	165.9 ± 46.2	20.8 ± 1.8	897.1 ± 49.3	61.9 ± 3.1	304.6 ± 50.4	13.5 ± 0.5

In more detail, six anthocyanins were identified in SB, where pelargonidin and its glycosides accounted for 97.9% of the initial total anthocyanin content (Table 5).

Table 5. Anthocyanin profile of studied berries at 0-point (mg/100 g).

Compound	SB	BB	BC
Cyanidin	*ND*	9.6 ± 0.7	5.0 ± 0.2
Cyanidin-3-O-glucoside	5.1 ± 0.1	20.8 ± 0.8	29.8 ± 0.5
Cyanidin-3-O-galactoside	*ND*	44.1 ± 5.8	*ND*
Cyanidin-3-O-arabinoside	*ND*	30.8 ± 3.0	*ND*
Cyanidin-3-O-rutinoside	*ND*	*ND*	135.3 ± 3.8
Pelargonidin	6.4 ± 0.2	*ND*	*ND*
Pelargonidin-3-O-glucoside	182.2 ± 20.8	*ND*	*ND*
Pelargonidin-3-O-rutinoside	17.5 ± 1.9	*ND*	*ND*
Pelargonidin-3-O-(6''-malonyl)-glucoside	23.0 ± 0.3	*ND*	*ND*
Pelargonidin-3-O-(6''-succinyl)-glucoside	12.5 ± 0.5	*ND*	*ND*
Delphinidin	*ND*	15.3 ± 1.5	4.7 ± 0.2
Delphinidin-3-O-galactoside	*ND*	83.7 ± 12.4	*ND*
Delphinidin-3-O-glucoside	*ND*	35.3 ± 0.9	49.1 ± 1.1
Delphinidin-3-O-rutinoside	*ND*	ND	129.6 ± 4.1
Delphinidin-3-O-arabinoside	*ND*	63.6 ± 7.1	*ND*
Delphinidin-3-O-(6''-coumaroyl)-glucoside	*ND*	*ND*	2.27 ± 0.0
Delphinidin-3-O-(6''-acetyl)-glucoside	*ND*	4.9 ± 0.4	*ND*
Petunidin	*ND*	4.3 ± 0.7	*ND*
Petunidin-3-O-galactoside	*ND*	79.7 ± 11.7	*ND*
Petunidin-3-O-glucoside	*ND*	53.2 ± 1.5	*ND*
Petunidin-3-O-arabinoside	*ND*	29.0 ± 2.9	*ND*
Petunidin-3-O-(6''-acetyl)-glucoside	*ND*	9.1 ± 1.1	*ND*
Peonidin-3-O-galactoside	*ND*	6.7 ± 0.5	*ND*
Malvidin	*ND*	17.8 ± 2.0	*ND*
Malvidin-3-O-galactoside	*ND*	244.7 ± 27.9	*ND*
Malvidin-3-O-glucoside	*ND*	143.1 ± 2.9	*ND*
Malvidin-3-O-arabinoside	*ND*	151.2 ± 14.9	*ND*
Malvidin-3-O-(6''-acetyl)-galactoside	*ND*	22.1 ± 4.4	*ND*
Malvidin-3-O-(6''-acetyl)-glucoside	*ND*	17.8 ± 2.0	*ND*

** ND = not detected*

BB had the highest initial content of total anthocyanins (1086.6 mg/100 g DW) (Table 4), 54.9% of which were malvidins, followed by 18.7% delphinidins, 16.1% petunidins, 9.7% cyanidins and 0.6% peonidins (Figure 10; Table 5). BC contained mostly delphinidins (52.2%) and cyanidins (47.8%), with a total initial content of 355.9 mg/100 g DW (Figure 10; Table 5).

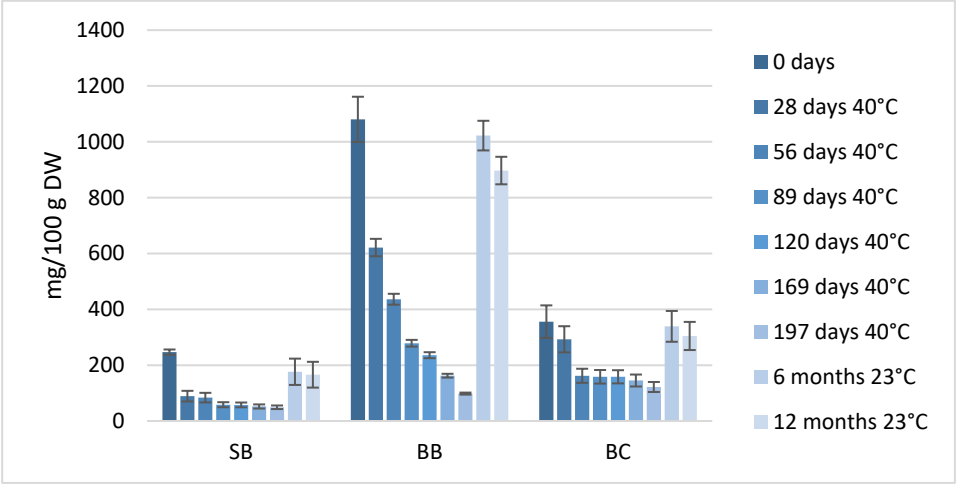

Figure 10. Total anthocyanin content during storage at 23°C and at 40°C of studied berries.

At 40°C, SB exhibited a rapid decline in total anthocyanin content, dropping by 63.9% within the first 28 days, with no significant changes observed after 89 days. BB showed a comparable initial decrease of 42.8% over 28 days, followed by a more gradual decline thereafter. In contrast, BC experienced a more delayed but rapid degradation phase, with a 36.7% reduction occurring between days 28 and 56. During storage at room temperature (23°C), SB experienced the greatest loss in total anthocyanin content over 12 months, with a 32.8% reduction. In comparison, BB and BC showed similar degradation levels over the same period, at 17.4% and 14.4%, respectively. When comparing overall anthocyanin losses under elevated temperature (40°C), the order of degradation was BB (93.4%) > SB (80.0%) > BC (75.4%) (Figure 10).

To evaluate the impact of elevated temperature on degradation kinetics, the degradation rates of total anthocyanins and initially quantitatively dominant anthocyanins were compared. Among the latter, pelargonidin 3-O-glucoside was selected for SB, malvidin 3-O-galactoside, malvidin 3-O-glucoside and malvidin 3-O-arabinoside were selected for BB, delphinidin 3-O-rutinoside and cyanidin 3-O-rutinoside for BC (Figure 11).

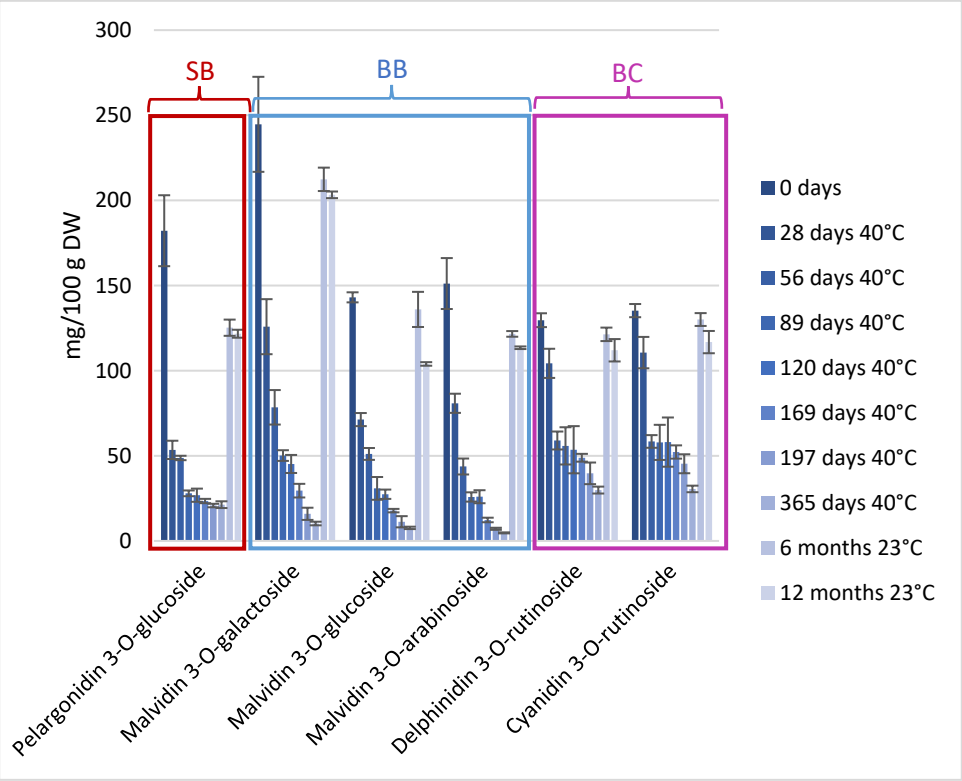

Figure 11. Degradation of quantitatively dominant anthocyanins in SB, BB and BC during storage at 23°C and 40°C.

By analysing the loss of total and specific anthocyanins over 12 months at room temperature alongside their degradation rates at 40°C, it is possible to estimate their equivalent storage durations at elevated temperatures. The results showed that based on first-order degradation kinetics, storage at 40°C for approximately 18 days (SB), 10 days (BB), and 8 days (BC) would correspond to anthocyanin degradation levels seen after 12 months at 23°C (Table 6).

Using the estimated storage durations at 40°C that correspond to anthocyanin degradation observed over 365 days at 23°C, Q_{10} values were calculated for both total and dominant anthocyanins in each berry muesli (Table 6). A Q_{10} factor of 3, commonly cited in the literature (Choi et al., 2017), was initially applied for the ASLT of berry-enriched mueslis. However, comparison between storage at 23°C and 40°C revealed that anthocyanin degradation occurred much more rapidly at elevated temperatures, with equivalent losses seen within just 8 to 18 days (Table 6). This suggests that a higher Q_{10} value is necessary to more accurately simulate long-term room-temperature degradation of colour-giving anthocyanins.

Table 6. Degradation parameters and Q_{10} values of total and quantitatively dominant anthocyanins in berry slices.

Compounds	k (day^{-1}), at 40°C	R^2, at 40°C	$t_{1/2}$ (days), at 40°C	Estimated storage time (days) at 40°C to achieve 12 months at 23°C	Q_{10}
SB					
Total anthocyanins	0.0139	0.7035	50	18	6
Pelargonidin 3-O-glucoside	0.0267	0.8641	26	13	7
BB					
Total anthocyanins	0.0142	0.9732	49	10	8
Malvidin 3-O-galactoside	0.0176	0.9706	39	8	9
Malvidin 3-O-glucoside	0.0166	0.9633	42	16	6
Malvidin 3-O-arabinoside	0.0195	0.9834	36	14	7
BC					
Total anthocyanins	0.0056	0.8115	125	8	9
Delphinidin 3-O-rutinoside	0.0063	0.8402	111	7	10
Cyanidin 3-O-rutinoside	0.0060	0.8118	116	6	11

Interestingly, although SB exhibited the highest anthocyanin loss at room temperature (32.8%), it also required the longest duration (18 days) to reach equivalent degradation at 40°C, resulting in the lowest calculated Q_{10} value (Q_{10} = 6). On the other hand, BC showed the least anthocyanin loss during ambient storage but reached comparable degradation most quickly under accelerated conditions (8 days), giving it the highest Q_{10} value (Q_{10} = 9). Also, when evaluating the quality of berry products under accelerated storage conditions based on the degradation of specific anthocyanins, it is necessary to recognize that the Q_{10} value is compound-specific, as was also found in Publication II. For instance, while the overall degradation of total anthocyanins in BB corresponds to a Q_{10} value of 8, the dominant malvidin derivatives within BB may exhibit Q_{10} values ranging from 6 to 9. A similar variability in Q_{10} values is observed for the main anthocyanins in BC, indicating that each compound may respond differently to temperature-induced degradation.

During the writing of this doctoral thesis, there was currently no directly comparable scientific literature examining the degradation kinetics of anthocyanins in freeze-dried strawberries (SB), blueberries (BB), or blackcurrants (BC), nor in berry-rich muesli products. Nonetheless, some parallels can be drawn from the limited studies on similar berry types in other products. For instance, Moldovan et al. (2016) investigated the influence of storage temperature on the total phenolic content in Cornelian cherry fruit extracts. Unlike the present findings, their reported Q_{10} value for the temperature range of 22–55°C was 1.87. Similarly, Fracassetti et al. (2013) assessed the degradation of anthocyanins in wild blueberry powder stored between 42–52°C and reported a Q_{10} value

of 1.98. These considerably lower Q_{10} values may be attributed to relatively short storage periods at ambient temperatures, during which minimal degradation of polyphenols and anthocyanins was observed. However, Publication III noted that because the phenolic degradation follows an exponential pattern, Q_{10} values are inherently dependent on the duration of storage. Furthermore, total polyphenols comprise a broad spectrum of compounds with varying stability. While anthocyanins are particularly prone to oxidative degradation, many other phenolic compounds exhibit greater structural resilience, resulting in slower overall degradation rates for total phenolics.

Despite these differences, comparable trends in half-life ($t_1/_2$) values were observed across studies. For example, the half-life of polyphenols in cherry extracts at 55°C was found to be 17.8 days (Moldovan et al., 2016), whereas in Publication III, the half-life of total anthocyanins in SB and BB at 40°C was notably longer, at 50 and 49 days, respectively. Moreover, the half-life observed for BB in Publication III (49 days) exceeded that of freeze-dried blueberry powder in the Fracassetti study, which was 39 days (Fracassetti et al., 2013). This difference may stem not only from the slight temperature difference (40°C vs. 42°C) but also from differences in the physical form of the products. These findings suggest that anthocyanins in freeze-dried berry powders may be more sensitive to thermal degradation than those retained in whole freeze-dried berries.

In conclusion, the results of Publication III showed that colour-giving anthocyanins demonstrate significantly higher degradation rates at 40°C compared to 23°C, reflecting their thermal sensitivity and tendency to degrade more rapidly under elevated temperatures. Although a Q_{10}-value of 3 is commonly used to model accelerated chemical reactions such, it may not adequately represent the degradation kinetics of anthocyanins, which undergo more rapid changes under accelerated conditions. Therefore, higher Q_{10}-values should be considered when using ASLT to evaluate the stability of anthocyanins. Also, as the ASLT model's predictive accuracy is compound-specific, adjustments should be made based on the specific behaviour of individual compounds. Overall, the results of Publication III offered valuable insights for optimizing shelf-life studies and improving quality assessment strategies for berry-containing products during storage.

4.4 The use of lipid oxidation indicators in ASLTs

To explore more methods for incorporating ASLTs in the evaluation of food deterioration during storage, an extended study was conducted. The research aimed to evaluate the use of chemical versus sensory markers in ASLT, using a range of oxidation indicators assessed in potato chips prepared with sunflower oil. In greater detail, alterations in fatty acid and volatile compound profiles, and the development of rancid odour were monitored at different storage temperatures.

Since methyl linoleate and methyl oleate had the highest contents among all fatty acids contained in the studied potato chips (Table 7), their degradation was taken under investigation. The results showed that the amount of methyl linoleate and methyl oleate dropped consistently throughout the storage test among all storage temperatures (Figure 12), undergoing degradation during the entire oxidation process, including the induction period and the formation of secondary oxidation products. Also, the findings revealed that fatty acid breakdown accelerated as storage temperature increased, showing a compliance with Arrhenius' kinetic model over the course of the study. Therefore, this process may represent a potential marker for assessing lipid oxidation during ASLT.

Table 7. Initial fatty acid profile of potato chips.

Fatty acid	Content (mg/g)
Methyl linoleate	264.94 ± 12.50
cis-9-Oleic acid methyl ester	255.09 ± 11.84
Methyl palmitate	9.69 ± 0.57
Methyl stearate	7.93 ± 0.35
Methyl arachidate	1.11 ± 0.11
Methyl palmitoleate	0.80 ± 0.05
Methyl behenate	0.18 ± 0.03
Methyl heptadecanoate	0.14 ± 0.03
cis-10-Heptadecanoic acid methyl ester	0.12 ± 0.02
Methyl lignocerate	0.10 ± 0.01
Methyl myristate	0.08 ± 0.00

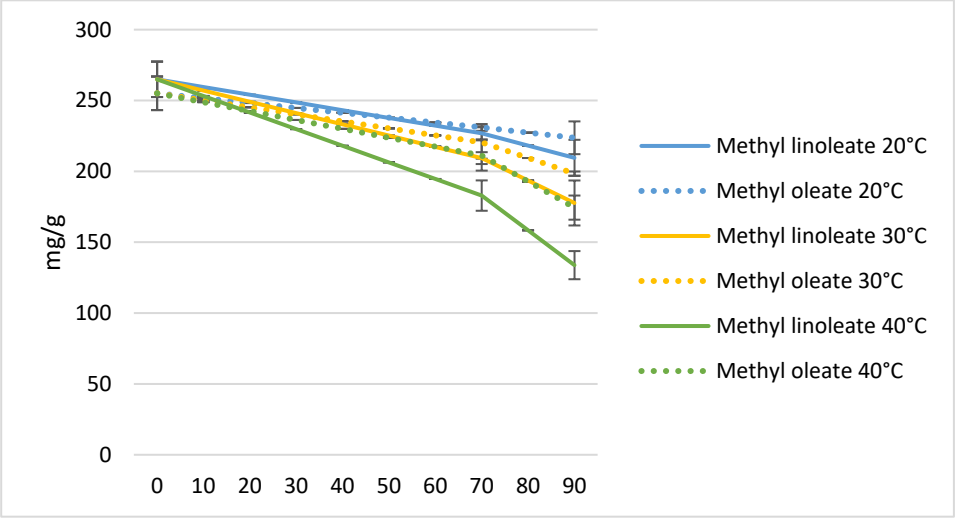

Figure 12. Methyl linoleate and methyl oleate in sunflower oil extracted from potato chips during the shelf-life test in 20°C, 30°C, and 40°C storage.

Organoleptic quality, on the other hand, is strongly influenced by volatile compounds. Therefore, the changes in volatile profile were monitored. Table 8 presents the key volatile compounds contributing to rancidity (hexanal showing the biggest amount), indicating as well that their levels elevated all through the shelf-life test.

Table 8. The main rancidiy causing volailes detected with SPME-GC-MS 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^{abc}	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}
6.94	1-pentanol	22.17 ±0.75^{i}	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^{fgh}	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^{bcdefg}	614.22 ±26.07^{abcd}	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^{abcdef}	621.90 ±44.75^{abc}	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}
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}	9.94 ±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^{cde}	22.89 ±1.06^{cd}	32.12 ±5.19^{ab}	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}
11.90	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^{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}	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^{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}	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}	52.12 ±.5.03^{cde}	54.39 ±2.65^{bcd}	45.81 ±0.38^{fgh}	45.29 ±1.05^{fgh}	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}	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^{bc}	12.30 ±2.18^{abc}	12.22 ±0.41^{abc}	13.20 ±1.05^{ab}	13.33 ±2.02^{abc}	12.67 ±0.30^{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}	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^{f}	1.05 ±0.60^{ef}	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^{abcd}	2.22 ±0.49^{ab}	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}	1.37 ±0.30^{def}	1.47 ±0.05^{def}	1.79 ±0.32^{bcd}	1.71 ±0.22^{bcd}	1.80± 0.28^{abcd}	1.44 ±0.13^{def}	1.40 ±0.36^{def}	1.65 ±0.17^{cde}	1.54 ±0.17^{de}	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}

Within each row, compounds labeled with different superscript letters (a–h) show statistically significant differences at the 0.05 level ($p < 0.05$).

Results from the HS-SPME/GC-O analysis likewise indicated that hexanal was the most strongly perceived compound (Table 9).

Table 9. Volatile profile of 90-day, 40°C-stored potato chips assessed by HS-SPME/GC-O.

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

Interestingly, during the oxidation induction period, the concentration of hexanal was lowest at higher storage temperatures (Figure 13) due to the transformation of hexanal into methyl ketones. Further literature research revealed that hexanal undergoes reactions leading to the formation of alkan-2-ones like 2-hexanone, 2-heptanone, and 2-octanone, and therefore the concentration of hexanal decreases (Grebenteuch et al., 2021). The SPME-GC-MS analysis confirmed this hypothesis, showing their increase at 30°C and 40°C storage tests (Table 8). Conversely, hexanal levels began increasing sharply once storage reached 70 days at 40°C, indicating that the induction period had ended. Regarding the changes in the volatile profile, it was concluded that hexanal content alone is not a suitable indicator for monitoring oxidation during ASLTs, since its concentration did not increase steadily. However, monitoring changes in the volatile profile remains valuable for assessing the end point of the induction phase. Furthermore, it is essential to confirm sensory results with analytical data, since in addition to hexanal, other volatile compounds also participate in the formation of undesirable off-odours. Regarding organoleptical changes, the most significant increase in rancid odour was seen for samples preserved at 40°C and mild changes at lower temperatures (Figure 14).

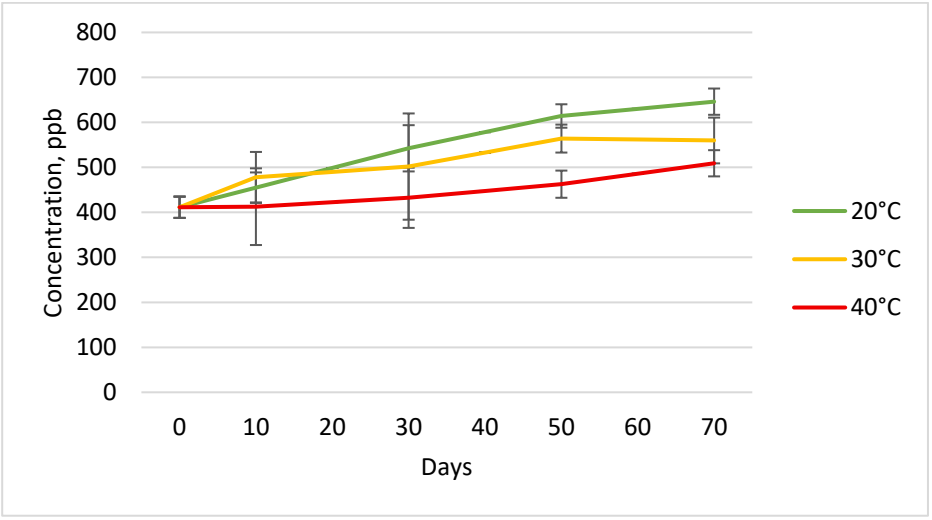

Figure 13. Hexanal development in potato chips stored for 70 days at 20°C, 30°C, and 40°C.

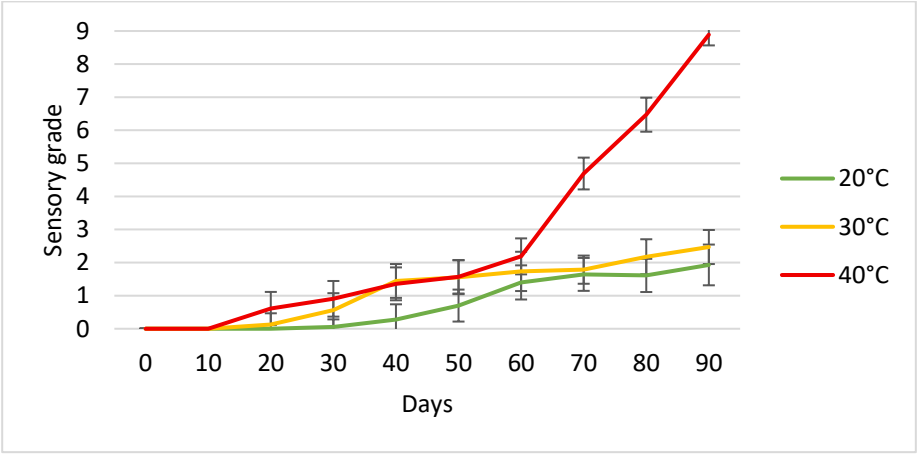

Figure 14. Rancid odor development in potato chips over 90 days at 20°C, 30°C, and 40°C.

To compare the suitability of different oxidation indicators for conducting ASLT, the experimental data were used to quantify the reaction kinetics of chosen indicators over time (Table 10). Because linoleic and oleic acids both play a role in generating volatiles linked to rancidity, their concentrations and reaction kinetics were integrated across all temperatures and time conditions. An Arrhenius plot was used to illustrate how the reaction rates of the monitored indicators vary with temperature (Figure 15).

Table 10. Reaction rates and Q_{10} values of oxidation indicators.

Storage temperature	Linoleic and oleic acid methyl esters			Rancid odor			Hexanal	
	$k_{fatty\ acids}$ (mg/g day^{-1})	R^2	Q_{10}	$k_{rancidity}$ (score/day)	R^2	Q_{10}	$k_{hexanal}$ (ppb/day)	R^2
20°C	0.9446	0.9957	1.5	0.0250	0.8998	2	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

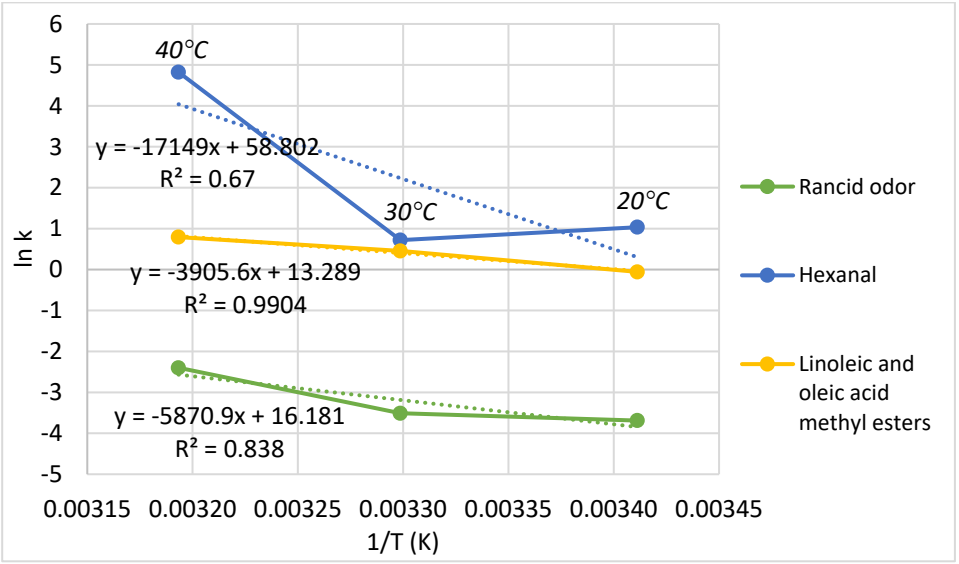

Figure 15. Arrhenius plot of monitored oxidation indicators.

The study showed that the development of rancidity and the degradation of chosen fatty acids throughout the experiment at each storage temperature followed a steady trend (Figure 15). Therefore, the acceleration factors could be calculated for these indicators (Table 10). These values indicate that for characterizing sensory changes during lipid oxidation, a Q_{10} value of 2 is suitable for this type of a product. This has also been confirmed by other authors. For instance, Agarwal et al. (2018) and Marasca et al. (2016) reported that a Q_{10} value of 2 for rancidity formation via lipid oxidation is supported by their findings. On the other hand, this study showed that when describing the rate of lipid oxidation in an ASLT based on the degradation of sunflower oil fatty acids, a Q_{10} = 1.5 should be applied. This finding is also supported by literature (Abeyrathne et al., 2021; Grebenteuch et al., 2021; Tolve et al., 2022) which states that the sensory perception of rancidity may increase disproportionately to the extent of fatty acid degradation, since the initiation phase produces hydroperoxides with minimal fatty acid loss, but the resulting intermediate compounds already start to decompose rapidly into highly odorous compounds.

On the other hand, the rate of hexanal formation displayed the greatest variations. In more detail, the reaction rates of hexanal production were mostly similar at storage temperatures 20°C and 30°C. However, the reaction rate at 40°C increased rapidly (Table 10), resulting also in an inconsistent trend on the Arrhenius plot (Figure 15). Based on these results, and being supported by literature (Calligaris et al., 2019), it was concluded that as the formation of hexanal showed a sigmoidal change, the ASLT model is not applicable for observing the development of volatile compounds responsible for rancidity. However, the analytical determination of volatile compounds during lipid oxidation serves as a useful chemical marker for assessing the end of the induction period and for describing the subsequent progression of oxidation.

5 Discussion

Based on the results of this doctoral thesis, practical guidelines can be provided for performing shelf-life assessment (with the emphasis on ASLT) in the food industry.

As stated in the first publication, the starting point in shelf-life determination is to clearly define the intrinsic (e.g. product composition, nutrient content, structure, pH and a_w) and extrinsic factors affecting the product's stability during storage. The latter includes packaging which has a vital role in determining shelf-life, as it can offer protection against environmental factors such as oxygen, moisture, and light. The choice of packaging materials, whether high-barrier films, vacuum-sealed containers, or MAP, directly affects the rate of product degradation and microbial growth. Also, proper storage conditions such as temperature, humidity and exposure to light must be established.

Moving on, knowing the intrinsic and extrinsic properties of a product, it is possible to define the main degradation processes taking place within the food during storage. These decays result from chemical (e.g. lipid oxidation, non-enzymatic degradation of polyphenols, Maillard reaction), physical (e.g. moisture loss or gain), biochemical (e.g. enzymatic degradation of lipids, proteins or polyphenols) or microbiological (growth of yeasts, moulds and bacteria) processes, identifying critical quality attributes (such as nutritional value, formation of off-flavours and off-odours, colour- or structure-related changes, and/or microbiological spoilage), defining the end of shelf-life.

Shelf-life studies can be designed as either real-time or accelerated. Real-time studies must be conducted under the actual storage conditions for the full duration of the anticipated shelf-life, mostly used for short shelf-life products which safe storage time is defined by the "use by" date. Accelerated shelf-life tests, on the other hand, enable faster identification of the end of storage time for "best before" food products with relatively long shelf-life. As the aim of this doctoral thesis was to evaluate the applicability of ASLT models for long shelf-life foods, further guidelines are provided for selecting quality indicators and acceleration factor (Q_{10}) values to enable reliable improvement and implementation of ASLTs.

The selection of Q_{10} values is one of the most critical requirements for conducting a proper ASLT experiment, as it enables the estimation of an accelerated shelf-life testing period that simulates the kinetics of changes observed under actual storage conditions (Equation 3). Considering this, the present thesis gives recommended guidelines for the use of Q_{10} values in shelf-life testing across different product categories and quality parameters (Table 11).

Table 11. Recommendations of Q_{10} values for investigated product categories.

Product category	Quality parameter	Measured value	Product	Q_{10} value	Limitations
Pasteurized fruit, berry and vegetable purees	Nutritional value	Total polyphenolic content	FGBB	3	-
			FYB	2	-
			MCB	≤2	Requires longer testing periods for validation.
	Colour changes	Anthocyanin content	FGBB	3	-
			FYB	≤2	Requires longer testing periods for validation.
Freeze-dried berries in mueslis	Colour changes	Total anthocyanin content	Strawberry	6	-
			Blueberry	8	-
			Blackcurrant	9	-
High-fat snacks	Nutritional value	Fatty acid degradation	Sunflower oil-based potato chips	1.5	-
	Sensory properties	Rancidity with sensory analysis		2	-
		Volatile compound (hexanal) formation		-	Not applicable for use in ASLT models.

The outcomes of this study show that assessing the degradation of polyphenols, as bioactive compounds of nutritional significance, during accelerated storage can be effective and may help evaluate changes in nutritional value over the product's shelf-life. Moreover, accelerated storage tests enable the assessment of estimated colour changes of purees via the evaluation of anthocyanin degradation. In more detail, the results demonstrate that when the objective is to assess either nutritional modifications (expressed as total polyphenol content) or colour alterations (expressed as anthocyanin content) in pasteurized purees, both quality parameters follow a comparable trend under ASLT conditions, with their degradation kinetics being characterized by similar Q_{10} values within the product (Table 11). However, it can also be seen that the choice of Q_{10} for conducting accelerated shelf-life tests may vary within a product category, depending on the product characteristics. While the nutritional and colour-related changes for FGBB puree were described with $Q_{10} = 3$, the same quality parameters for FYB puree should be assessed with the assumption of $Q_{10} = 2$. This suggests that the stability of phenolic compounds is product-specific, primarily influenced by the types and proportions of ingredients used, as well as the product pH. Therefore, not all purees with seemingly similar compositions require the same experimental parameters for ASLT. The author suggests that to both confirm the findings of the present work and further investigate the conditions influencing the selection of parameters for an ASLT model of a specific puree, additional research should be conducted on an individual product basis. This would

involve determining the specific phenolic profile of each puree and performing shelf-life tests with a puree having different pH values.

In long shelf-life berry mueslis, the quality deterioration of freeze-dried berries is also often due to colour loss. To model this in accelerated shelf-life test, the content of colour-contributing anthocyanins was analysed over time as a chemical marker. As shown in Table 11, when conducting ASLTs of such products, and assessing colour-related chemical markers, such as anthocyanin content, higher acceleration factors of 6-9 should be applied, depending on the berry. However, when comparing the findings from the second and third publications, some differences in phenolic degradation became apparent. While the purees showed a pH-dependent, inhibited polyphenol degradation at 40°C, indicating the need to apply Q_{10}-values of 2-3, freeze-dried berries had a significantly faster polyphenol degradation during ASLT, corresponding to higher acceleration factors. This may result from the differences in the processing methods of the products. During freeze-drying, ice crystals form within the cell walls, disrupting the cell structure. Such damage can break covalent bonds that bind polyphenols to cellular components, making them more vulnerable to degradation. In contrast, purees, with their more intact cell structure, tend to protect polyphenols by limiting their exposure to oxygen and enzymes. Furthermore, the purees were pasteurized at a higher temperature, which may have inactivated enzymes responsible for polyphenol breakdown, thereby slowing degradation compared with freeze-dried berries. This highlights the importance of considering processing technologies, and their potential influence on storage-related processes, when designing ASLT studies, particularly those investigating polyphenol degradation.

Finally, recommendations for Q_{10} values can also be provided for high-fat snack products, such as potato chips, depending on the quality indicator and the specific objective of the assessment. This extended study confirmed that different quality indicators follow distinct mechanisms that must be considered during ASLT. For example, when assessing the sensory perception of rancidity in a high-fat product such as potato chips under accelerated testing, a Q_{10} value of 2 should be applied. However, from a nutritional perspective, a Q_{10} = 1.5 is more appropriate for describing the degradation of fatty acids (Table 8). On the other hand, it is not possible to provide a recommended acceleration factor value for the formation of rancidity-causing volatile compounds (such as hexanal) in the evaluation of lipid oxidation as it showed a sigmoidal change and is not applicable for use in ASLT models. The extended study also demonstrated the importance of selection between chemical and sensory markers for ASLT studies. Chemical markers, such as fatty acid degradation, or the accumulation of specific volatile compounds, offer quantitative and objective measures of lipid oxidation. They are particularly useful when the aim of acceleration is to understand the chemical stability of nutritional components or to compare oxidative processes between similar products. However, chemical markers do not always align with consumer-perceived quality loss. In such cases, sensory analysis provides a more reliable indicator of shelf-life because it directly reflects consumer rejection thresholds. A further complication arises when considering intermediate markers such as formation of volatiles and as previously discussed, depending solely on these markers may yield unreliable or poorly predictive outcomes. To address these challenges, several strategies can be adopted. First, ASLT models should clearly define the objective, before selecting indicators. Second, the combined use of chemical and sensory endpoints can provide a more comprehensive view of deterioration, with chemical markers offering insight into degradation mechanisms and sensory data binding the model to organoleptical relevance. Third, statistical or kinetic models that include

nonlinear changes, such as sigmoidal progression of volatile formation, may improve predictability compared to classical Arrhenius-based approaches. Finally, multi-indicator shelf-life modelling, in which different Q_{10} values are assigned to distinct quality attributes, can allow simultaneous tracking of both sensory and chemical stability.

Overall, choosing key quality parameters and Q_{10} values for conducting an ASLT is based on aligning the modelled outcome with the intended definition of "end of shelf-life." The selection of an appropriate Q_{10} factor for ASLT is not universal but depends critically on the product characteristics and its processing effects, the degradation pathway under investigation, and the defined endpoint of shelf-life. The fundamental assumption behind using Q_{10} in ASLT is that the rate of a quality-related reaction follows temperature-dependent kinetics assessable by the Arrhenius relationship. Within this framework, a single Q_{10} value may be applied, but its validity depends on which quality indicator is considered the key determinant of shelf-life. If the primary objective of ASLT is to model nutritional stability, chemical markers reflecting the degradation of specific compounds (e.g., polyphenols or fatty acids) are most relevant. If the aim of the ASLT is to give insight into the deterioration of colour-contributing chemical markers, the rates of anthocyanin degradation can be observed. However, when the goal is to assess both of the aforementioned quality parameters in a single product, the study of pasteurized purees showed that the same assumptions for ASLT (Q_{10} values) can be applied, although products in different categories may require individual validation. On the other hand, when the end of shelf-life is determined by sensory perception, sensory analysis becomes the primary criterion. In this doctoral study, potential ASLT models were proposed for different product groups, considering possible limitations. These proposals were guided by the specified objectives and highlight the importance of aligning the selected Q_{10} value with the intended definition of product acceptability (Table 11). As a practical outcome, knowing these validated Q_{10} values allows food producers to calculate the duration of an accelerated shelf-life test that reflects the changes in the selected quality parameter under real-time conditions.

The findings of this thesis revealed several critical aspects that the author wishes to emphasize in order to provide improved guidelines for more reliable performance of accelerated shelf-life tests. Firstly, the aim of the shelf-life test must be clearly defined, as this guides the selection of quality markers that directly represent the degradation process limiting shelf life. Secondly, the choice of an appropriate Q_{10} factor is similarly dependent on the selected indicator and the key degradation kinetics. Thirdly, product-specific differences and processing methods also play a central role in shaping ASLT outcomes. The research showed that variations in pH or polyphenolic profile can substantially influence degradation rates. Similarly, processing techniques, such as pasteurization vs. freeze-drying, can alter structural integrity and the tendency of key compounds to degrade — with freeze-drying generally accelerating degradation and requiring the use of higher acceleration factors in ASLT. Such differences highlight the need for Q_{10} selection and experimental design to be product-specific, rather than generalized across a product category. Finally, the importance of conducting accelerated tests over a moderately longer period to ensure reliable results and validation of the chosen Q_{10} value for each ASLT model through comparison with real-time shelf-life data is essential to ensure predictive reliability.

6 Conclusions

This doctoral research demonstrated that effective ASLT requires careful consideration of product-specific characteristics, processing effects, and the selection of appropriate quality indicators. Q_{10} values must be tailored to the product, degradation pathway, and defined endpoint of shelf-life, with chemical markers used for nutritional or mechanistic assessment and sensory analysis applied when consumer perception defines acceptability. The study showed that product compositions and processing technologies significantly influence the degradation rates, highlighting the need for individualized ASLT design and validation against real-time data.

Publication I confirmed that understanding product-specific deterioration mechanisms is key to effective shelf-life management. Tailored packaging, from low- and high-barrier materials to advanced strategies such as active and intelligent packaging options, can preserve quality, maintain sensory and nutritional attributes, and extend shelf-life across different product categories.

Publication II showed that ASLT reliably tracked both the nutritional (polyphenol) and colour-related (anthocyanin) changes in pasteurized purees, but the stabilities were highly product-specific, influenced by ingredient composition and pH. While the Q_{10} values for both chosen quality indicators were Q_{10} = 3 for higher-pH puree like FGBB, lower-pH products like FYB and MCB required Q_{10} = 2 or lower for proper application of ASLT.

Publication III demonstrated the impact of product processing technology on the stability of colour-related quality indicator (anthocyanins) during shelf-life. The study showed that anthocyanins in freeze-dried berries degrade faster during storage than in pasteurized purees, with kinetics varying by berry type and compound. The commonly used Q_{10} = 3 underestimated degradations, requiring higher values (Q_{10} = 6–11) for accurate accelerated testing.

Finally, the extended study on sunflower oil-based potato chips showed that combining chemical and sensory markers enables comprehensive monitoring of lipid oxidation. Fatty acid degradation provided a reliable chemical indicator (Q_{10} = 1.5), sensory rancidity corresponded to Q_{10} = 2, while hexanal formation was unsuitable as a sole marker but useful for identifying the end of the induction period.

Summary

This thesis provides an integrated understanding of the complex factors influencing long shelf-life food stability across diverse product categories, ranging from low-moisture cereals and snacks to fruit-based products and lipid-rich savouries. The research highlighted that food quality deterioration is governed by multifaceted mechanisms including moisture migration, lipid oxidation, and the degradation of bioactive compounds such as polyphenols and anthocyanins. Recognizing these product-specific vulnerabilities is essential for designing effective preservation strategies. Packaging also emerges as a critical element in shelf-life extension, with the selection of materials and technologies tailored to the unique stability challenges of each food matrix. Whether through moisture and oxygen barriers, modified atmosphere packaging, or emerging active and intelligent systems, packaging solutions significantly mitigate environmental impacts and slow down quality loss. However, economic and technological barriers remain for widespread adoption of advanced packaging innovations.

Accelerated shelf-life testing is a powerful tool for predicting product degradation, but its reliability depends on careful selection of quality indicators, Q_{10} values, and product-specific considerations. Limitations include the variability in degradation kinetics between products and components, the influence of processing, and non-linear behaviour in some markers, which can reduce predictive accuracy. Despite these challenges, ASLT provides valuable insights into nutritional, colour, and sensory stability, especially when combining chemical and sensory markers. With proper calibration and validation against real-time data, ASLT enables efficient and mechanistically interpretable shelf-life predictions tailored to specific products and endpoints.

Ultimately, this thesis emphasizes the multifaceted nature of food shelf-life stability and the critical role of combining chemical, physical, sensory, and packaging considerations. The research emphasized that successful shelf-life prediction and product quality preservation require an integrated approach—one that accounts for specific product vulnerabilities, employs tailored packaging technologies, and uses carefully chosen quality indicators within appropriately calibrated accelerated testing protocols. By acknowledging the limitations of ASLT and addressing them through tailored experimental design and thorough validation, it is possible to enhance the reliability and applicability of accelerated methods for long shelf-life foods. This comprehensive perspective supports the development of food products that maintain safety and quality over time, meet consumer expectations, and align with sustainability goals.

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Abstract

Shelf-life assessment and applicability of accelerated shelf-life testing models for long shelf-life foods

Ensuring food quality and accurately predicting shelf-life are critical challenges in the modern food industry, directly impacting consumer safety, economic efficiency, and environmental sustainability. In an era marked by rapid population growth, climate change, and increasing consumer awareness, the demand for longer-lasting, high-quality food products is higher than ever. Meanwhile, the global food supply chain faces bigger pressure to reduce waste and comply with strict regulatory standards. Also, the alarming statistic that one-third of global food production is lost or wasted, much of it due to shelf-life mismanagement, indicates that more attention should be paid for better assessment methodologies in this area.

The aim of this doctoral research was to evaluate the applicability of accelerated shelf-life testing (ASLT) models for long shelf-life foods and to provide product-specific guidelines for selecting quality indicators and Q_{10} values for reliable shelf-life predictions. The findings demonstrated that effective ASLT requires careful consideration of product-specific characteristics, processing effects, and the selection of appropriate quality indicators. Q_{10} values must be tailored to the product, degradation pathway, and defined endpoint of shelf-life, with chemical markers used for nutritional or mechanistic assessment and sensory analysis applied when consumer perception defines acceptability. In Publication I, the preservation techniques and packaging strategies for cereal and snack products were reviewed, highlighting the crucial roles of packaging functionality and product characteristics in quality retention. Publication II confirmed that ASLT reliably tracked nutritional (polyphenol) and colour-related (anthocyanin) degradation in pasteurized purees in similar trend, with Q_{10} values adjusted to product pH (Q_{10} = 3 for higher-pH purees; Q_{10} = 2 or lower for lower-pH products). Publication III revealed the importance of product processing on the stability of colour-related quality indicator (anthocyanins) during shelf-life. This study showed that anthocyanins in freeze-dried berries degrade faster than in purees, with kinetics varying by berry type, requiring higher Q_{10} values (6–11) for accurate accelerated testing. Finally, the extended study on sunflower oil-based potato chips showed that combining chemical and sensory markers enables comprehensive monitoring of lipid oxidation, with Q_{10} = 1.5 for fatty acid degradation and Q_{10} = 2 for sensory rancidity, while hexanal formation was unsuitable as a sole ASLT marker.

To conclude, this thesis provides practical, product-specific guidelines for applying ASLT, emphasizing tailored Q_{10} values, careful indicator selection, and validation against real-time data for reliable shelf-life prediction.

Lühikokkuvõte

Säilivusaja hindamine ja kiirendatud säilivuskatse mudelite rakendatavus pika säilivusajaga toiduainetele

Toidu kvaliteedi tagamine ja säilivusaja täpne prognoosimine on kaasaegses toidutööstuses kriitilised väljakutsed, mis mõjutavad otseselt tarbijate ohutust, majanduslikku tõhusust ja keskkonna jätkusuutlikkust. Ajastul, mida iseloomustavad kiire rahvastiku kasv, kliimamuutused ja tarbijate teadlikkuse suurenemine, on nõudlus pikema säilivusajaga ja kõrge kvaliteediga toidu järele suurem kui kunagi varem. Samal ajal on ülemaailmne toidusüsteem suure surve all, et vähendada toidu raiskamist ja samal ajal järgida rangelt regulatiivseid nõudeid. Lisaks näitab murettekitav statistika, et kolmandik kogu maailmas toodetud toidust läheb raisku ning seda sageli just säilivusaja ebaõige hindamise ja haldamise tõttu. Seepärast tuleks selles valdkonnas rohkem tähelepanu pöörata paremate hindamismetoodikate arendamisele.

Selle doktoritöö eesmärk oli hinnata kiirendatud säilivuskatsete (ASLT) mudelite rakendatavust pika säilivusajaga toiduainetes ning pakkuda tootespetsiifilisi juhiseid kvaliteedinäitajate ja Q_{10} väärtuste valimiseks, et võimaldada usaldusväärsemat säilivusaja prognoosimist. Tulemused näitasid, et ASLT tõhusal rakendamisel tuleb tähelepanu pöörata toote spetsiifilistele omadustele, töötlemise mõjule ja sobivate kvaliteedinäitajate valikule. Q_{10} väärtused tuleb kohandada vastavalt tootele, kvaliteedilangust põhjustava reaktsiooni lagunemismehhanismile ja säilivusaja määratletud lõpp-punktile, kasutades keemilisi markereid toiteväärtuse või muu mehhanismipõhise hindamise jaoks ning sensoorset analüüsi siis, kui aktsepteeritavust määrab tarbija hinnang. Publikatsioon I käsitles teravilja- ja snäkitoitude säilitustehnikaid ja pakendistrateegiaid, rõhutades pakendi funktsionaalsuse ja toote omaduste tähtsust kvaliteedi säilitamisel. Publikatsioon II kinnitas, et ASLT jälgis usaldusväärselt pastöriseeritud püreede toiteväärtuse (polüfenoolid) ja värviomaduste (antotsüaniinid) langust sarnases trendis, kus Q_{10} väärtusi kohandati toote pH järgi (Q_{10} = 3 kõrgema pH-ga püree jaoks; Q_{10} = 2 või vähem madalama pH-ga püree jaoks). Publikatsioon III näitas, kui oluline on toote töötlemistehnoloogia mõju värviindikaatori (antotsüaniinide) stabiilsusele säilivuse ajal. Uuring näitas, et külmkuivatatud marjades degradeeruvad antotsüaniinid kiiremini kui püreedes, ning kiirus varieerub marjatüübi ja fenoolsete ühendite järgi, mis nõuab täpsemaks kiirendatud testimiseks kõrgemaid Q_{10} väärtusi (6–11). Viimasena näitas päevalilleõli baasil valmistatud kartulikrõpsude säilivuskatse lisauuring, et keemiliste ja sensoorsete markerite kombinatsioon võimaldab lipiidide oksüdatsiooni põhjalikku jälgimist, kus rasvhapete lagunemine jälgib mudelit Q_{10} = 1,5 ja sensoorselt rääsunud lõhna hindamisel peaks jälgima faktorit Q_{10} = 2, samal ajal kui heksanaali teke ei sobinud ASLTs jälgitavaks indikaatoriks.

Kokkuvõttes annab see doktoritöö praktilised, tootespetsiifilised juhised ASLT rakendamiseks, rõhutades kohandatud Q_{10} väärtusi, hoolikat indikaatorite valikut ja tulemuste valideerimist reaalaja andmete põhjal usaldusväärse säilivusaja prognoosimiseks.

Appendix 1

Publication I

Bauer, A.-S., **Leppik, K.**, Galić, K., Anestopoulos, I., Panayiotidis, M. I., Agriopoulou, S., Milousi, M., Uysal-Unalan, I., Varzakas, T., Krauter, V. (2022). Cereal and Confectionary Packaging: Background, Application and Shelf-Life Extension. *Foods, 11(5)*, 697. https://doi.org/10.3390/foods11050697

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Review

Cereal and Confectionary Packaging: Background, Application and Shelf-Life Extension

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Abstract: In both public and private sectors, one can notice a strong interest in the topic of sustainable food and packaging. For a long time, the spotlight for optimization was placed on well-known examples of high environmental impacts, whether regarding indirect resource use (e.g., meat, dairy) or problems in waste management. Staple and hedonistic foods such as cereals and confectionary have gained less attention. However, these products and their packaging solutions are likewise of worldwide ecologic and economic relevance, accounting for high resource input, production amounts, as well as food losses and waste. This review provides a profound elaboration of the status quo in cereal and confectionary packaging, essential for practitioners to improve sustainability in the sector. Here, we present packaging functions and properties along with related product characteristics and decay mechanisms in the subcategories of cereals and cereal products, confectionary and bakery wares alongside ready-to-eat savories and snacks. Moreover, we offer an overview to formerly and recently used packaging concepts as well as established and modern shelf-life extending technologies, expanding upon our knowledge to thoroughly understand the packaging's purpose; we conclude that a comparison of the environmental burden share between product and packaging is necessary to properly derive the need for action(s), such as packaging redesign.

Keywords: food packaging; cereals; confectionary; bakery; food quality; shelf-life; sustainable packaging; active and intelligent packaging; modified atmosphere packaging; vacuum packaging

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1. Introduction

Over the past decades, global awareness about environmental, social and economic sustainability challenges, as well as the need for immediate action to limit their negative

short- and long-term impacts, has risen considerably. With regard to environmental sustainability, challenges encompass, but are not limited to, the use of resources, land, water, energy, and generation of associated emissions and waste. In order to facilitate the transition towards a sustainable future, several (inter)national goals, commitments, and legal bases have already been initiated or applied. These include, for instance, the Paris Agreement on climate change and the United Nations Sustainable Development Goals (SDGs) on a global scale, the European Green Deal including the New Circular Economy Action Plan, as well as the Farm to Fork Strategy on European level and numerous implementations into national law systems [1–6].

Regarding food, it is well-agreed in the scientific community and beyond, that a great share of negative environmental impacts such as global anthropogenic greenhouse gas emissions or waste originate from food systems [7–9]. These systems are defined as the whole of actors and activities involved, from production to the disposal of food products of different origins, as well as herewith associated natural, social, and economic environments [10]. Moreover, they are composed of subsystems (e.g., farming) and connected to other systems (e.g., energy). A complex network in which changes (e.g., policies) made in one sector may also affect others. Against this background, different international efforts have been taken to achieve sustainable food systems, which will provide present and future generations with a secure supply of safe food [11].

Packaging is strongly associated with food, allowing, amongst other functions, containment, protection, and transportation of contents, and thus can be seen as an integral part of food systems [12,13]. Nevertheless, nowadays it is the subject of intense debates and even stricter legal requirements, mainly due to massive circularity gaps including, for example, unsatisfactory end-of-life scenarios such as limited recyclability or (marine) litter [14,15]. However, the simple omission of packaging is hardly possible, since a well-chosen packaging system frequently shows positive (indirect) effects on the total environmental sustainability of a food system by, for example, reducing food losses and food waste or increasing transport efficiency [16]. Therefore, when aiming at developing sustainable packaging solutions, it is important to apply a holistic and interdisciplinary approach over the whole life cycle of both food and its corresponding packaging [17].

Since packaging offers a service to the food product and does not fulfil an end in itself, it is often worth starting a packaging development or a redesign process from the food perspective. By gaining profound knowledge of the food product itself, together with the intrinsic and extrinsic factors that affect quality along the food supply chain, further packaging requirements can be defined and considered in the innovation process [12,13,17].

Due to their high environmental impact, the focus of research and development activities is often on (animal protein-rich) foods such as meat or milk [18–20]. Despite their high nutritional value that shouldn't be underestimated, cereal and confectionary products are rather underrepresented, regarding their impact in health but also in economic and environmental sustainability [21–27]. For instance, about 50% of daily required carbohydrates are consumed through bread in industrialized countries. Further, cereals are also an important source of proteins, minerals, and trace elements [28]. Expressed in figures, retail sales of bread alone were expected to reach about 92 billion euros in Europe in 2021 [29]. On the other hand, confectionary products reached a production volume of 14.7 million tons with an annual turnover of 60 billion euros along with an export value of 9.2 euros and an import value of two billion euros in Europe (EU28) in 2019 [30].

In more detail, the present review aims at building a comprehensive basis for future sustainable packaging development activities in the area of cereal and confectionary products by:

- Presenting relevant information on packaging functions and properties of packaging materials,
- detailing product group specific decay mechanisms and frequently used packaging solutions,
- and highlighting packaging-related shelf-life extension technologies.

The text is therefore structured as follows: After the introduction, a general background on food packaging is discussed, followed by product group specific decay mechanisms and packaging solutions. Finally, packaging measures that can extend the shelf-life are presented (see also Figure 1).

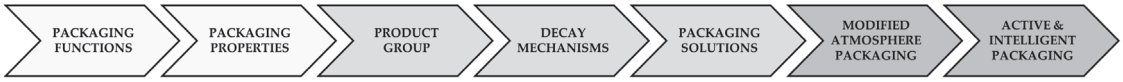

Figure 1. Outline of discussed topics, based on the review's aims.

2. Packaging

2.1. Packaging Functions

No matter how diverse individual products and packaging solutions may be on the market, it is well-agreed in relevant literature that the main functions of packaging can be broken down into a few. Next to the concept of primary and secondary functions, where the former describes in particular the technical functions like storage and transport, and the latter describes functions related to e.g., communication, a more holistic concept is frequently mentioned in the packaging literature. This concept describes the four basic functions of food packaging as (i) containment, (ii) protection, (iii) convenience, and (iv) communication [12,13,31–33].

Although the containment function is often overlooked, it can be considered one of the most essential, since it prevents product loss and contamination and facilitates storage, transportation, and distribution. There are only a few exceptions, where containment and thus packaging is not needed. Such examples are relatively large, chunky products that are often regionally produced and consumed within a short period of time or that show long shelf-life [12,13,31].

The protection function is often recognised as well as highlighted and can be indeed considered as the most important aspect of packaging. It limits or excludes intrinsic as well as extrinsic physical, chemical, and biological factors that may have negative influences on the quality of the respective food product. In the best case, the packaging is even capable of extending the shelf-life of the product. Therefore, it is of upmost importance to match the food product's properties and requirements along the supply chain with packaging to achieve optimal results. Both under- and over-packaging should be avoided since this may result, on one hand, in food losses or waste and, on the other hand, in excessive packaging [12,13,31].

Further, the convenience function refers to the practical aspects or user-friendliness of packaging. As an example, easy-to-open or -empty, microwave- or heat-able, resealable, or portion packaging can be named. These features are more and more implemented in package designs, since they allow to specifically address target groups (e.g., children, elderly, single-households, on-the-go lifestyle) and therefore frequently influence the market success of a product [12,13,31].

Last but not least, the communication function allows for information transfer and marketing. While the former allows to display legally required (e.g., product name, ingredients, shelf-life), necessary (e.g., barcodes), or voluntary (e.g., certificates, cooking recipe) information, the latter enables to transfer an often unique brand image (e.g., form, colour, shape), which may be of great recognition value [12,13,31].

It is worth mentioning that a successful package on the market does not only need a strong product in terms of quality but also an effective packaging, which in a clever way combines the above described four functions of containment, protection, convenience and communication. Otherwise, it may result in a short-term success (weak product and effective packaging), a situation where the potential is not achieved (strong product and ineffective packaging), or even failure (weak product and ineffective packaging) [31].

2.2. Packaging Properties

From a technical point of view, the functions containment and protection are closely linked to the right selection of packaging materials which consequently poses a key decision in the development process. The available material classes cover mainly glass, metal, paper/board, (bio)plastic, as well as composite materials (laminated, coextruded, blended). Composites can consist of two or more components combined to form, for example, multilayer materials (e.g., plastic-coated cardboard) which frequently show superior functional properties (e.g., barrier) and reduced weight [31], but on the downside also reduced recyclability [34,35]. Touching upon the topic of recyclability, many packaging solutions face obstacles, if it is at the stage of collection, sorting, or in general limited technical recyclability. Not even the use of mono-materials guarantees actual recycling, as it is the case for PET trays versus PET bottles (bottles are highly likely to be recycled). On the other hand, specific combinations of compatible materials, even high barrier films, for example, metallized polyolefins, might be considered recyclable in the appropriate infrastructure [36,37]. Summing up, it can be stated that each of the named materials show advantages and disadvantages (see Table 1) and the decision for a specific material must be based on the prevailing requirements (e.g., product, supply chain, use, end-of-life). Support is often provided by material specifications and declaration of compliance documents. However, it is recommended to test the materials in question under respective conditions by means of a field or laboratory test. This ensures that deviations from the target value can be recognized at an early stage in the development process [12,13,31,38,39].

Table 1. Overview of the properties and applications of most widely used materials for packaging.

Packaging Material		Barrier			Heat Seal-Ability	Mechanical, Physical and Chemical Properties	Application	Reference
		Oxygen	Moisture	Light				
Plastic	Low-density polyethylene (LDPE)	Very low	High	Low	Yes	Toughness, flexibility, resistance to grease and chemicals, temperature range −50 – +80 °C	Bags, flexible lids and bottles	[12]
	Linear low-density polyethylene (LLDPE)		High			Toughness, extensibility, resistant to grease, temperature range −30 – +100 °C	(Strech) wrap	
	High-density polyethylene (HDPE)		Extremely high			Toughness, stiffness, resistance to grease and chemicals, easy processing and forming, temperature range −40 – +120 °C	Bottles, cardboard liners, tubs, bags	
	Polypropylene (PP)	Low	High	Low	Yes	Moderate stiffness, strong, resistant to grease and chemicals, temperature range −40 – +120 °C	Bottles, cardboard liners, tubs, microwavable packaging, bags	
	Polyethylene terephthalate (PET)	Good	Good	Low	Yes	Stiffness, strong, resistance to grease and oil, temperature range −60 – +200 °C	Bottles, jars, tubs, trays, blisters, films (bags and wrappers)	[12,40]
Glass	Transparent	Absolute		Low	No	High temperature and pressure stability, brittle, chemical resistance, microwave-able	Bottles, jars	[12,40–42]
	Green			Good				
	Brown			High				
Metal (aluminium, tinplate, tin-free steel)		Absolute			No	High temperature stability	Bottles, cans, tubs, caps	[12,40]
Paper and board		Extremely low		High – extremely high	No	Mechanical stability	Boxes, liners	[12,40,41]

The key properties of packaging materials of interest are physical and mechanical strength, barrier, migration, as well as hygiene. Regarding the physical and mechanical strength, it can be noted that static as well as dynamic stress challenges the packages along the supply chain from packing, storage, and transport to consumer use. Examples for static stress are stacking and increased pressure (vacuum or modified atmosphere packaging—MAP), as well as pointed or angular products. Dynamic stress on the other

hand may be caused by the production process (e.g., printing, forming, filling) or transport (e.g., vibration). The right selection of the material, but also the shape of the packaging, therefore plays a vital role in the success of a primary, secondary or tertiary package (see also Figure 2) [12,13,38,43].

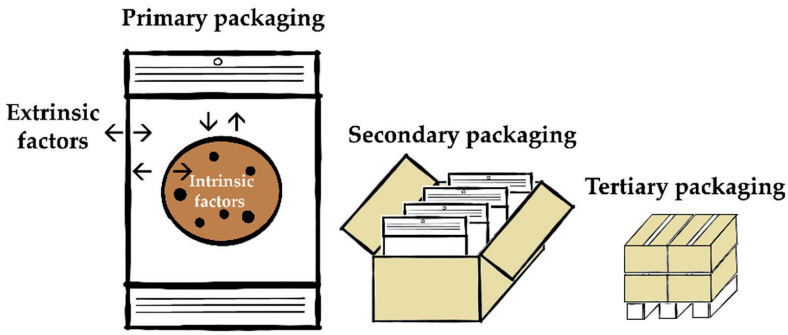

Figure 2. Schematic packaging levels of fine bakery ware (example: chocolate chip cookie), adapted from [12,13,31].

Another key characteristic of materials to be considered is the barrier property. Especially, the barriers against oxygen (O_2) and water vapour (H_2O) transmission are determinant since these can exhibit significant influences on product quality and safety. The former for example can promote oxidation reactions, loss of quality-determining ingredients (e.g., vitamins), and growth of spoilage and pathogenic microorganisms. The latter can influence structural changes such as hardening, agglomeration, or softening of products and promote microbial growth (see Section 3.2). Additionally, barriers against carbon dioxide (CO_2) and nitrogen (N_2), which are the often-used gases in MAP, as well as aroma components, are decisive. Depending on the use case and product requirement, material with an appropriate barrier, i.e., permeation characteristics, should be chosen. Complementary to the above described, the barrier against other substances like fat may be considered [12,13,38,44]. Furthermore, electromagnetic radiation (light) has to be taken into consideration, since oxidative or other chemical reactions as well as structural changes may be induced or accelerated, thus impairing product quality [12,41,45–47].

What is important regarding chemical safety is the migration of compounds from packaging materials into the food. Migration describes the mass transfer of substances from a packaging material into the food product or vice versa. As for the permeation, the driving force behind this phenomenon is the concentration gradient. Additionally, factors such as material, storage temperature, relative humidity, and time play an influencing role [38,39,48].

Against common perception, possible migration of, for example, additives, are not only present in plastic packaging materials. Migration can also be found in other (primary or secondary (recycled)) materials such as glass (e.g., silicates), metal (e.g., corrosion of the metal, additive migration from organic coatings), paper and board (e.g., fillers, contaminations like mineral oils) and may, next to the packaging material itself, find its origin in packaging aids (e.g., labels, closures, coatings) or even set-off processes (e.g., printed and role-to-role processed or stapled materials) [12,13,38]. To ensure safety of food contact materials (including packaging), several legal requirements are in place in the European Union and beyond [39,48–53]. It should be noted that in addition to the migration from the packaging material to the food, migration processes from the food to the packaging can also be observed. This process is also called sorption or scalping and may cause alteration of the product (e.g., flavour loss) as well as reduced reusability of packaging containers due to the re-release of previously migrated substances [12,13].

In addition to chemical safety, packaging materials also play a role in the hygiene and biological safety of food products. Depending on the material used, a barrier against

contamination, microorganisms and animals (e.g., food pests) can be given. To achieve a high standard of hygiene, it is crucial to utilize materials that pose a sufficient barrier and that are free from contamination. Further, it is important to use materials that do not support microbial growth. Lastly, it is important to recognise, that most packaging materials carry a low microbial count when freshly produced due to often high process temperatures (e.g., melting of glass). So, the microbial burden is often a result of recontamination during finishing processes, storage, and application, which can sometimes make it necessary to implement decontamination measures prior to the filling process [38,54].

3. Cereal and Confectionary Products

Against the above-summarized background, food packaging can be seen as a mediator between product and the environment, capable of significantly influencing food quality, safety, and shelf-life [12]. Regarding cereal and confectionary products, the following text aims at summarizing and categorizing the product group, presenting an overview of category specific decay mechanisms, as well as respective packaging solutions.

3.1. Categorization of Cereal and Confectionary Products

As shown by Belitz et al. [28], cereal and confectionary products cover a wide and diverse range of food products. They summarized different products in two groups, namely cereals and cereal products. The first group is mainly made from important staple foods such as wheat, rye, rice, barley, millet, oats and corn. These are used to produce different kinds of products. For example, Smith et al. [55] made the following division: "...unsweetened goods (bread, rolls, buns, crumpets, muffins and bagels), sweet goods (pancakes, doughnuts, waffles and cookies) and filled goods (fruit and meat pies, sausage rolls, pastries, sandwiches, cream cakes, pizza and quiche)".

The group of confectionery products are mainly sugar-based products that, in contrast to cereal products, are predominantly consumed as a "treat" rather than a full meal. These include products such as chocolate, hard candy, and pralines [56,57]. In addition to sweet confectionery, savory snacks can also be found on the market. According to Robertson [13], these include "...a very wide range of products, including potato and corn chips, alkali-cooked corn tortilla chips, pretzels, popcorn, extruded puffed and baked/fried products, half-products, meat snacks and rice-based snacks" [13,58]. In addition to that, there are combinations of sweet and savory snacks like chocolate covered pretzels or sweet popcorn [59].

In the available literature and other sources including statistics, codices and regulations, different approaches to properly (sub)categorize cereal and confectionary products can be found [59–61]. Taking a food and shelf-life perspective, it is reasonable to cluster products that exhibit similar characteristics or spoilage mechanisms. In the European Union, where there is a strong food law [62] in place, a comprehensive list can be, for example, found in the guidance document to Annex II of regulation (EC) No 1333/2008 on food additives [59,63]. For the field of cereals and confectionary, the four groups of confectionary, cereals and cereal products, bakery wares, and ready-to-eat savories and snacks are of special interest. While confectionary is further subdivided into cocoa and chocolate products, other confectionery products including breath freshening micro-sweets, chewing gum as well as decorations, coatings and fillings, cereals and cereal products are divided into whole, broken or flaked grain, flours, milled products and starches, breakfast cereals as well as pasta, noodles, batters and pre-cooked or processed cereals. For bakery wares, a classification into bread and rolls and fine bakery wares is given. Last but not least, savories and snacks are broken down into potato-, cereal-, flour- or starch-based snacks as well as processed nuts. For each of the above-mentioned subgroups, a comprehensive list of product examples is given in the mentioned document [59]. The present review adopts this categorization approach and structures relevant information on cereal and confectionary shelf-life, packaging, and shelf-life extension strategies accordingly (Figure 3).

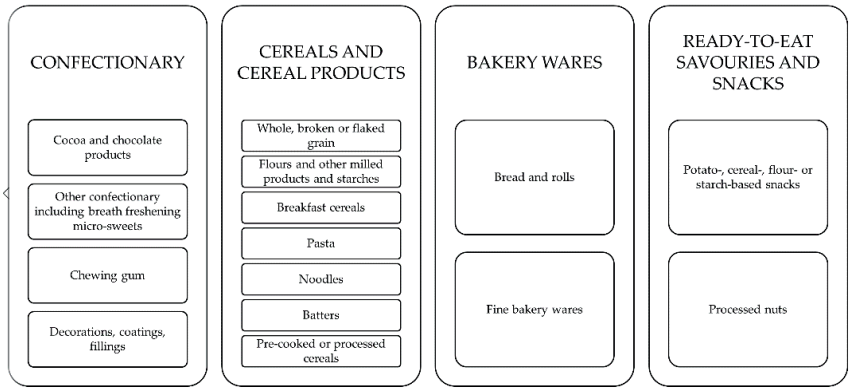

Figure 3. Representation of the followed product categorization. Adapted from [59].

3.2. Decay Mechanisms and Shelf-Life

It is well-established that intrinsic as well as extrinsic factors influence the quality of food and thus its shelf-life [13], which can be defined as the period of time a food maintains its safety and/or quality under reasonably foreseeable conditions of distribution, storage, and use [12,64–66]. Intrinsic factors include, amongst others, pH, water activity (a_w), initial microbial population, redox potential value (Eh), and nutrient content and therefore determine the nature of decay mechanisms of a food product. On the other hand, extrinsic factors determine how fast decay mechanisms proceed. Typical examples are atmosphere, climatic conditions, and illumination. Packaging itself acts as mediator or separator between intrinsic and extrinsic systems [13,67]. The following paragraphs highlight the main challenges of quality maintenance of cereal and confectionary products but do not go into detail about the physical, chemical, or biological bases of these mechanisms (e.g., oxidation). This information can be found in the relevant scientific literature [13,67,68].

Focusing on cereal and confectionary products (see Table 2), moisture content (MC) and water activity (a_w) are some of the most important quality-affecting parameters. Kong and Singh [69] define, that the a_w value is "…the vapour pressure of water above a sample (p) divided by that of pure water at the same temperature (p0); i.e, $a_w = \frac{p}{p0}$. It describes the degree to which water is free or bound to other components". They state that this is related to "…the composition, temperature, and physical state of the compounds" [69,70]. This is of importance regarding the potential growth of microorganisms as they depend on free water presence [71].

Table 2. Water activity and moisture content of confectionery products, breakfast cereals, snacks, and bakery products.

Product category	Subcategory	Product	Water Activity [a_w]	Moisture Content [%]	Reference
Confectionery	Cocoa and chocolate products	Chocolate	0.42–0.60	1.2	[72]
	Other confectionery including breath freshening micro-sweets	Hard candy	0.25–0.40	2.0–5.0	[73,74]
		Fudge, toffee	0.45–0.60	6.0–18.0	
		Nougat (white, dark)	0.55	8.00–10.0	[13,75]
		Jelly, liquorice	0.50–0.75	8.0–22.0	[73,74]
		Marshmallow	0.60–0.75	12.0–22.0	
		Marzipan	0.75–0.80	–	[13]
	Chewing gum	Chewing gum	0.40–0.65	3.0–6.0	[73,74]

Table 2. *Cont.*

Product category	Subcategory	Product	Water Activity [a_w]	Moisture Content [%]	Reference
Cereals and cereal products	Whole, broken, or flaked grain	Oats, grains, cereals	0.34–0.70	8.8–9.2	[13,72]
	Breakfast cereals	Cornflakes	0.25–0.38	1.7–3.5	
		Puffs	0.17–0.20	0.48–1.70	
	Fresh pasta	Fresh pasta	0.91–0.98	≥24	
	Dry pasta	Dry pasta	0.33–0.57	5.4–8.3	
Bakery wares	Fine bakery wares	Sponge cake, muffins	0.84–0.95	21.0–40.0	[76,77]
		Croissant crust	0.59–0.61	8.0–10–0	
		Croissant crumb	0.92–0.94	30.0–33.0	
		Biscuits	0.60–0.63	1.5–3.0	[72,78]
		Wafers	0.13–0.15	2.1	[72]
		Cookies	0.18–0.64	1.4–11.7	
	Bread and rolls	Flat bread (no yeast)	-	33.0–35.0	[79]
		Sourdough bread, yeast bread crumb	0.91–0.95	29.0–40.0	[72]
		Sourdough bread, yeast bread crust	0.88–0.94	26.0–32.0	
		Bagel crust	0.96	38.5	
		Bagel crumb	0.92	31.0	
Ready-to-eat savouries and snacks	Potato-, cereal-, flour- or starch-based snacks	Popcorn	0.07	0.28	
		Chips	0.09–0.27	0.3–1.3	
		Crackers, grissini, sticks, pretzels	0.05–0.54	1.1–5.4	
	Processed nuts	Nuts, seeds, nibs	0.15–0.75	0.5–3.1	

With an a_w lower than 0.75, a large proportion of the products listed in Table 2 falls into the group of low-moisture or dried foods that additionally exhibit low (e.g., cornflakes) or high (e.g., crisps) fat content. In this group, water uptake and thus loss of, e.g., crispness, which occurs, e.g., in potato chips and breakfast cereals after gaining moisture at a range of 0.35 to 0.5 a_w, is the main decay mechanism [12,13,69,80]. Other mechanisms include loss of aroma (e.g., flavoured products) or aroma uptake from the products' surrounding due to the often porous structure of the food products. Further, structural changes such as loss of integrity due to e.g., mechanical damage (e.g., breakage), softening, or caking may occur. While microbial growth is the basis for both, low and high fat types, oxidative mechanisms, which may lead to off-odours and -tastes and subsequently to quality loss in terms of overall acceptance, are often linked to the fat content and thus tend to increase with the same [12]. Examples that can be named are nuts, chips, biscuits, and cookies. All in all, this product group can, however, be described as rather stable and therefore storage under dry and ambient conditions is recommended and possible. For example, breakfast cereals and dry pasta stay stable under temperate conditions for 6–18 months and 48 months, respectively [72,81]. Confectionary products like pulled sugar are stable for 6–9 months under temperate conditions (e.g., ~20 °C) [68].

Other products, including chocolate for example, can be allocated to compact foods with high fat content, a group mainly susceptible to the uptake of unwanted flavours and some (often minor) water exchange (uptake or loss) processes [12]. The latter can induce so-called blooming effects [13]. Sugar bloom on the one hand is often provoked by humid

storage or rapid temperature changes and leads to the loss of surface gloss. Fat bloom on the other side is also known to cause quality related issues visible as a fine whitish layer [82]. Growth of microorganisms is, however, of minor importance in this product group. Storage under temperate or chilled conditions is therefore possible for up to 12–24 months [57].

Microbial growth is of major concern in the group of ready-to-eat and ready-to-cook convenience food products (e.g., fresh pasta). At this point, in addition to spoilage microorganisms, pathogenic microorganisms play an essential role [65,83]. Further, water loss and structural changes can be named. Additionally, oxidation can significantly gain importance regarding shelf-life. Accordingly, chilled storage is often preferred [13,67].

The area of bakery products can be divided into fresh bakery wares and ready-to-bake products. The first group (e.g., bread) shows high a_w values (>0.8) and thus short shelf-life, which is heavily influenced by water exchange processes that are often interlinked with structural changes (softening of the crust and drying of the crumb). Connected to this, starch retrogradation, which is the main mechanism of staling, can be highlighted [69]. Further, loss of moisture and hardening with a_w values below 0.5–0.7 [13,69,80] quickly result in low sensory acceptance of the products. While oxidation and rancidity play a minor role in this food category, uptake of flavours as well as microbial spoilage play a more elaborated role in this product group. The latter point is mainly driven by the often visible growth of moulds and yeasts on the food surface. Characteristic microorganisms are *Penicillium roqueforti*, *Hansenula anomala*, *Pichia anomala*, *Candida guilliermondii*, *C. parapsilosis*, *Saccharomyces cerevisiae*, *S. exiguus*, *S. unisporus*, *S. bayanus*, *S. pastorianus*. Additionally, *Clostridium* and *Bacillus* genera are known bacteria potentially affecting bakery wares (spore-forming), with e.g. *Bacillus* spp. causing "rope" or "ropy spoilage" (*Bacillus amyloliquefaciens*, *Bacillus subtilis*, *Bacillus pumilus*, *Bacillus cereus*) [71,84,85]. Oxidation and rancidity play a minor role in this product category. Accordingly, the average shelf-life of fresh bread and cake under ambient conditions is often less than one week [86]. In some cases, chilled or frozen storage is advisable. The group of ready-to-bake rolls show very similar decay mechanisms. However, due to the higher water content, drying and spoilage is even more pronounced. In the case of frozen products, these mechanisms are delayed. A special focus has to be laid on water exchange (freezer burn) and structural damage [87].

3.3. Product Group Specific Packaging

Responding to the above-mentioned predominant decay mechanisms of cereal and confectionary products, the following section aims at highlighting common packaging concepts and material choices (compare also Table 1).

Chocolate packaging has to provide a good barrier against aroma, gas (especially O_2 and H_2O) as well as light. This is conventionally achieved by using aluminium foil of different thickness to wrap the product. Since aluminium alone cannot be heat sealed, the per se excellent barrier of the material is, however, interrupted at, e.g., overlapping areas or gaps. Hence, diffusion (mass transfer) of aroma, gas and other molecules (e.g., mineral oil components) to the product cannot be excluded. Additionally, the originality of the product, an important factor of food safety, may not be ensured [13,67]. For this and other reasons (e.g., communication), many described packaging concepts (still) include an additional packaging layer, namely paper or paperboard [13,27,88–92].

Today, more and more multilayer materials can be found on the market. For example, laminates of LDPE (low density polyethylene) and aluminium allow for heat sealing of the aluminium by at the same time keeping the superior barrier and dead-fold properties of aluminium. Further, multilayer materials including paper or other aluminium replacing barrier materials (e.g., polyvinylidene dichloride (PVdC)) are available. Possible build-ups may include LDPE/aluminium/paper or LDPE/PVdC, respectively [13]. Nowadays, a shift towards packaging made (solely) from (oriented) PP, which exhibits, due to a stretching process, inter alia, improved mechanical and barrier properties, is notable [21,92]. Additionally, cold sealing, is more and more adopted, since it avoids exposing sensitive products, such as chocolate, to elevated temperatures during heat sealing. This alternative

is made possible by applying cold-seal adhesives on the intended sealing areas of the packaging film and pressing of two of the sealing areas together [31].

Individually packed chocolate products, such as chocolate coated bars or pralines, are often bought for hedonistic reasons (e.g., treats, gift function) and thus the communication function (design) of these packages is frequently at the forefront [13,56]. While the functions of containment and protection are already met, these packages often use excess packaging materials and/or layers and for example consist of a (e.g., polyethylene terephthalate (PET)) tray with individual cavities, (e.g., aluminium) wrapping of the individual pieces, a (e.g., paperboard) box, (e.g., polyethylene (PE) or polypropylene (PP)) overwrapping and packaging aids (e.g., labels, stickers). Glass or metal is also used in some cases [13].

Many confections, such as hard candies, gums, toffees and caramels are likewise (twist) wrapped individually. This is either for technical reasons such as provision of an adequate (H_2O) barrier and thus avoidance of moisture loss or uptake, resulting in e.g., drying or agglutination of the product pieces, hygienic reasons or distinction from other products. As for chocolate, tightness of the package should be in the ideal case assured [73]. Due to their in general good barrier properties and sealability, the market dominating polyolefins (PE and PP) as well as PET [93] are also frequently used in this product category (e.g., multipacks) [21,94]. If elevated barriers are needed, different multilayer materials are also adopted. Further, glass and metal packaging can be found on the market and traditional materials include waxed paper, waxed glassine and waterproof, plasticized cellulose fibre [57]. Plain paper and board are, however, hardly used as a primary packaging material, since products tend to stick to the material. The packaging types in this product category are manifold and include, for example, trays, flow packs, boxes (for example cardboard and metal) and jars [13].

Other products such as biscuits, (processed) nuts and fruits are traditionally packaged in regenerated cellulose (trade name Cellophane) fibres (RCF). Therefore, RCF is usually coated with either LDPE or PVdC copolymer and often with a layer of glassine in direct contact with the product if it contains fat. Currently, this combination of materials is replaced by PP, either as plain or pearlized OPP film, coextruded OPP (OPPcoex) film, or acrylic-coated (Ac) on both sides. Plain OPP films require a heat seal coating to improve sealability while coextruded OPP provides superior seal strength. If a high O_2 barrier is required, then acrylic-coated OPP (AcOPP) is used. One side is sometimes coated with PVdC copolymer rather than Ac. In addition, Ac and PVdC copolymer-coated OPP films provide a superior flavour and aroma barrier compared with that of uncoated OPP. Biscuits are often packed in PP and additionally a cardboard box, acting as secondary packaging [13,25].

In comparison to other products, the dry and low in fat group of cereals and cereal products, (such as whole, broken, flaked or milled) grains (e.g., wheat and rice) show rather low packaging demands. Mostly used are paper bags, flexible plastic bags (e.g., PE [95]), as well as cardboard boxes [96,97]. There are also variations of these packages, for example inner flexible plastic bag and a secondary cardboard box. If paper is used and high barriers are needed, LDPE liners for example can be applied [13], also to avoid mineral oil migration [98]. Rigid laminates with paper content and plastic lids usually known in snack product packaging, are also available. Flours for example are commercially packaged in bags or bulk bins [13]. In addition to that, woven PP bags are commonly used in developing countries. However, Forsido et al. [99] discussed that the low moisture barrier led to chemical, physical, sensorial, and microbial changes of flour. Another successful approach for flour packaging that was used for decades, was bags made from cotton twill [13].

The barrier requirements for breakfast cereals packaging are set higher than in the above-mentioned group since crispness, formation of off-flavours, loss of aroma and vitamins or breakage are more critical for consumer acceptance [13]. Consequently, the inner packaging/primary packaging level of these products is a plastic bag, mostly HDPE (high density polyethylene), giving a sufficient water vapour barrier since moisture vapour trans-

mission rates less than or equal to 15 g/m^2-day-atm are often required. Sealant polymers such as EVA (ethylene vinyl acetate), ionomer, mPE (metallocene polyethylene), or blends are used for low temperature seals, form-fill-seal packaging, and easy opening seals [95]. In order to increase barrier characteristics, HDPE is also coextruded with a thin layer of EVA or PA (polyamide) and EVOH (ethylene vinyl alcohol) polymers [95,100]. Other O_2 barrier materials for breakfast cereals are PVdC and coated polypropylene-low density polyethylene [101]. In addition, PP-bags are common liners. The secondary packaging/outer packaging is most frequently a fibreboard box [13,22]. Alternative packaging concepts include coated paperboard, plastic cups, as well as metal boxes and glass jars [13,102].

Dried pasta is often packaged in paperboard carton, containing a plastic window. At the moment, most pasta products are packaged in plastic films, such as PE or oriented polypropylene [13,103–107]. For fresh pasta/noodle products, packaging solutions might be different, as appropriate barriers (gas and/or water vapour) and/or MAP (e.g. CO_2:N_2 20:80% MAP for pasta) is needed [107,108]. The selection of packaging materials for fresh pasta products can also depend on whether or not the product is pasteurized (thus, the package must be able to withstand the pasteurization conditions) and whether or not the product is to be heated in its package (the package must be able to withstand either heating in boiling water or microwave conditions) by the consumer. For products which are not pasteurized nor intended to be heated in their package, a rigid tray of PVC-LDPE sealed with PA-LDPE film is common. When microwave heating is used, the rigid tray is usually made from crystalline polyethylene terephthalate (PET-C), or polystyrene-ethylene vinyl alcohol copolymer-LDPE (PS-EVOH-LDPE) laminate, and the film may be based on PVdC copolymer-coated PET, OPET-EVOH-LDPE, or PP [109].

Packaging of fresh bakery products such as bread is a moisture balancing act. On one hand, moisture needs to be contained to prevent drying of the product and on the other hand, moisture has to be released from the product to avoid softening of the crust and microbial spoilage. Since there is a wide range of products and product characteristics, also a wide range of packaging solutions can be found. Frequently, paper-based materials, LDPE, LLDPE, HDPE bags as well as OPP, either as plain, pearlized, OPPcoex, or Ac/OPP/Ac films are used [13,95,110–114]. The bags are usually closed either with a strip of adhesive tape or a (plastic) clip in order to reduce moisture loss [111,113,115]. EVA polymers are also used for sealability and optics [95]. Perforated LDPE bags are used (for crusty products) in order to prevent the formation of a leathery consistency of the crust due to moisture migration from the crumb [115]. If aroma and taste barriers are needed, PA is used [95]. Vacuum packaging including the use of respective barrier packaging materials is only used in some exceptions (e.g., flat breads) in this product category due to mechanical impairment of the often soft products. MAP rich in CO_2 is whereas more frequently used (e.g., sliced bread, convenience applications). For example, CO_2:N_2 60:40% MAP for bread, cakes, crumpets, crepes, fruit pies and pita bread. This is also the case for ready-to-bake products, which are intended to have a longer shelf-life [13].

Packaging for fried snack foods such as potato or tortilla chips, which exhibit, due to their production process, low moisture and high fat contents, preliminarily aims at providing a barrier against gases (H_2O and O_2) and light to avoid loss of crispness and increased oxidation/rancidity levels of the product [95]. Hence, these products are mainly packaged in high barrier multilayer films containing aluminium foil or metallisation (e.g., PET/Alu/LDPE; PETmet/LDPE; BOPP/BOPPmet) [31,94,116]. In addition, barrier polymers such EVOH or PVDC can be found in these materials. Further, rigid multilayer paper solutions with aluminium (for example spiral wound paper-board cans) or metal cans are also used. Since extruded and puffed snack foods exhibit lower fat levels and thus primarily rely on a package that provides a barrier against water vapour; these products are less often packaged in metallized materials. An example is OPP/LDPE/OPP [95]. In both scenarios, and whether flexible or rigid packaging is adopted, modified atmosphere packaging is frequently used. For example, the package is usually flushed with an inert gas (N_2) before closing [116]. Additional mechanical protection of the often fragile products

and dry storage is recommended. This might lead to the use of secondary packaging, such as cardboard boxes [31].

4. Shelf-Life Extension

As can be seen from the above text, choosing the right packaging material concept can have a positive effect on quality maintenance and therefore shelf-life of cereal and confectionary products and food in general. Where particularly sensitive products (e.g., high a_W value, high fat content or oxidation potential) are present (e.g., fresh pasta, fried snacks) or an elevated shelf-life has to be achieved (e.g., ready-to-bake rolls, fine bakery wares), modern packaging concepts such as modified atmospheric packaging or active (AP) and intelligent packaging (IP) are used (combined abbreviation: AIP). Manifold different approaches can be found regarding MAP, AP, and IP, each with different relevance for the discussed product subgroups, cereals and cereal products, confectionary, bakery wares and ready-to-eat savouries and snacks. However, for an impression of these, Figure 4 depicts selected examples.

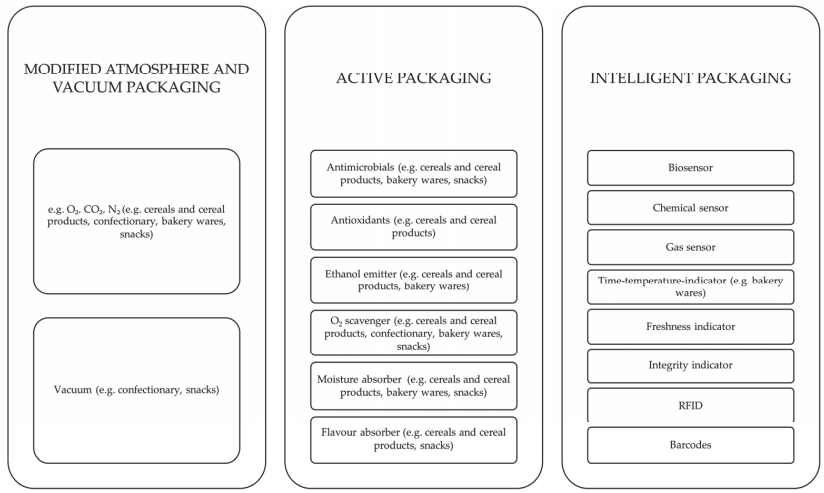

Figure 4. Selected examples of modified atmosphere, vacuum, as well as active and intelligent packaging approaches with certain use cases for cereal and confectionary packaging. Adapted from [13,108,117–140].

Using these approaches, other product preservation actions (e.g., heating, use of preservatives) may be reduced, which supports attempts to reach a healthier diet (e.g., reduction of salt) or a clean label (e.g., avoidance of excess additives) [141] These allow specifically addressing other remaining challenges in the chemical, biological, mechanical, and physical fields [12,13]. Thus, they are also often implemented in the hurdle technology, a concept of combining diverse adverse factors or treatments to control microbial growth in food products [13,142]. According to studies found, also biobased and/or biodegradable packaging material is experimentally combined with AIP approaches. These materials offer new opportunities, for example in making use of different barrier properties, that allow a certain shelf-life extension [134,135]. Examples for MAP and AP with traditional as well as biobased/biodegradable packaging materials can be found in Table 3.

Table 3. Effects of packaging material selection, active packaging (AP) and modified atmosphere packaging (MAP) on shelf-life extension of cereal and confectionary products. Abbreviations: m = month; d = day; RH = relative humidity; RT = room temperature.

Category	Product	Packaging Material	AIP/MAP Applied	Storage	Shelf-Life	Reference
Confectionary	Dark chocolate with hazelnuts	Alu (commercial)	Air	20 °C in dark	8 m	[119]
		PET/LDPE	Vacuum or N_2		8–9 m	
		PET-SiOx/LDPE			11 m	
		PET/LDPE or PET-SiOx/LDPE	Oxygen absorber		≥ 12 m	
Cereals and cereal products	Muesli with chocolate and apricots	Paper bag: PAP + PP window	Air	20 °C, RH 55 %	2 m	[143]
		Pouch: PAP/Alu/PE			9 m	
		Can:PAP/Alu + LDPE lid				
	Fresh pasta	PS tray + PVC film	Air	8 °C	20 d	[120]
		PA/EVOH/LLDPE	CO_2:N_2 22:78% MAP		40 d	
	Fresh pasta filled with cheese	Tray: EVOH/PS/PE wrapped in film: EVOH/OPET/PE	Air	4 °C	7–14 d	[108]
			CO_2:N_2 50:50% MAP		42 d	
	Gluten-free fresh filled pasta	Tray: PETFilm: antifog PET film	Air	4 °C	14 d	[121]
		Tray: EVOH/PS/PEFilm: EVOH/OPET/PE	CO_2:N_2 30:70% MAP		42 d	
Bakery wares	Sponge cake	PA/LLDPE	Combinations of oxygen scavengers with / without ethanol emitter	30 °C, RH 60%	≤42 d	[139]
		PVDC/PA/cPP				
	Sliced wheat bread	PET-SiOx/LDPE	Bread	20 °C	4 d	[130]
			Bread + preservatives		6 d	
			Ethanol emitter		24 d	
			Ethanol emitter + oxygen absorber		30 d	
	Ciabatta bread	OPA/PE	Air (control)	21 °C	5 d	[122]
			Air + ethanol spray		11 d	
			CO_2:N_2 10:90% MAP		12 d	
			MAP + ethanol spray		13 d	
			Air + ethanol emitter		25 d	
			MAP + ethanol emitter		30 d	

Table 3. *Cont.*

Category	Product	Packaging Material	AIP/MAP Applied	Storage	Shelf-Life	Reference
	Wheat bread	HDPE/PE	-	25.8 °C, 275.5 lx, RH 31.2%	2 d	[144]
		Unpackaged bread	-		3 d	
		HDPE/Nanoparticles/PE	Ag-TiO_2		>6 d	
	Calcium-enriched wholemeal bread	PA/PE bag + cardboard box	CO_2:N_2 60:40% MAP	20 °C	24 d	[145]
	Whole wheat bread	PA/PE	N_2	RT	2–3 w	[123]
	Part-baked flat bread (Sangak)	PA/PE	Air	25 °C	9 d	[124]
			CO_2:N_2 20:80% MAP		18 d	
			CO_2 100% MAP		21 d	
	Sliced wheat bread	Tray: APET/EVOH/PEAntifog-film: PA/PE	Air without potassium sorbate & with 0.15% potassium sorbate	20 °C, RH 60%	14 d	[125]
			N_2 100% MAP, CO_2:N_2 30:70% MAP, CO_2:N_2 50:50% MAP, CO_2:N_2 70:30% MAP, CO_2 100 %MAP;with & without potassium sorbate		21 d	
			Air with 0.30% potassium sorbate		>21 d	
	Bread	Plastic bag	E-Poly-L-Lysine Biofilms1.6/3.2/6.5 mg of E-Poly-L-Lysine /cm^2	RT for 7 days inoculated with *A. parasitus*	+1 d	[131]
			E-Poly-L-Lysine Biofilms6.5 mg of E-Poly-L-Lysine /cm^2	RT for 7 days inoculated with *P. expansum*	+3 d	
	Sliced wheat bread	PP/PET/LDPE	Star anise oil, thymol	25 °C inoculated with *P. roqueforti*	14 d	[132]
	Bread	Starch-based bionanocomposite film	Chitosan, grapefruit seed extract	25 °C, RH 59%	20 d	[133]
	Sliced white pan bread	PP bag	–	30°C	3 d	[134]
		PBAT-PLA bag			≥21 d	
			Trans-cinnamaldehyde			
	Bread	BOPP	–	25 °C, RH 75%	3 d	[135]
		PLA			6 d	
		PLA-PBSA bag	Thymol		7–9 d	

4.1. Modified Atmosphere Packaging (MAP)

Leaving quality sensitive products exposed to atmospheric conditions (gas composition of N_2, O_2, Ar, CO_2, traces of other gases) can trigger undesirable changes such as quality-related oxidative decay or growth of (non)pathogenic aerobic microorganisms. On the contrary, modifying the atmosphere inside a packaging can help maintain the quality of a product over an elevated timeframe. Consequently, common mitigation strategies include the reduction of packaging headspace and, thus, total available atmosphere or even removal of the atmosphere (to a value below one percent), which in turn results in vacuum packaging. To maintain these conditions over time, it is necessary to assure an appropriate containment function of the packaging by choosing packaging materials with an appropriate gas barrier and proper sealing. Challenges in this case are often the structure of the products and the corresponding residual oxygen in the packaging in the case of e.g., pores and the collapse of the product in the case of e.g., a soft structure [13,125,146].

A more advanced modification can be found in a so-called modified atmosphere packaging, MAP [147]. Here, an active modification takes place in a two-step process, where first the initial atmosphere is removed (vacuum) and then replaced with a specific artificially composed atmosphere before closure of the barrier packaging. Commonly, in product-dependent concentrations used, colourless and odourless gases in MAP mainly encompass CO_2 and N_2. Due to its formation of hydrated carbonate species in aqueous phase CO_2 is valued for its bacteriostatic and fungistatic effect, which increases with increasing concentration. Due to the solubility in water and fat, formation of under-pressure in the package and, consequently, possible collapse of the latter is possible. To avoid this and to act as a filler gas, the inexpensive and inert N_2 is applied. Hence, passively, also this gas contributes to quality maintenance of the product. Furthermore, O_2 is a frequently used gas but of little relevance for the cereal and confectionary sector. Its field of application is mostly in meat (e.g., bright-red colour preservation via high-oxygen MAP) and fish products and to lower extent in plant products [145,148,149]. More recently, permitted noble gases such as argon are subject to research but not broadly applied on cereal and confectionary products [150,151]. Depending on the chosen MAP gas composition, food shelf-life can increase manifold (50–400%) and with this advantage along the supply chain can be recorded (e.g., less food waste, longer remaining shelf-life, less frequent production and transport). However, disadvantages linked to MAP, in general encompass the need for more sophisticated packaging materials and filling equipment, costs for gas and increased packaging volume [13].

Regarding the food categories at the centre of the present review, confectionary products are less frequently in the centre of research and application of MAP than cereals and cereal products, bakery wares or ready-to-eat savouries and snacks (see Table 3). One case of MAP use, however, is reported by Mexis et al. [119], for dark chocolate with hazelnuts. The authors found, that when conventionally used aluminium packaging together with storage under surrounding atmosphere was replaced with a PET/LDPE or PET-SiO_x packaging and vacuum or N_2, the shelf-life (dark storage at 20 °C) was increased from 8 to 8–9 and 11 months, respectively. Also Kita et al. [152], investigated the effects of different packaging types and shelf-life extension strategies for chocolate coated products (fruits and nuts). They analysed air, vacuum and MAP ($N_2 \geq 98\%$) of coated cherries, figs, hazelnuts and almonds in long term storage conditions in three different types of packaging. PP film closed with a clip was chosen for air, PP film sealed for vacuum and metallized sealed film for MAP. They resumed that the best packaging solutions for the chosen chocolate coated products, ensuring quality (for example bioactive compounds, antioxidative activity) were, on one hand, air and vacuum packaging for fruits, vacuum packaging for hazelnuts and MAP for almonds.

In the category of cereals and cereal products, and in more detail in fresh pasta, MAP often contains elevated amounts of CO_2 (up to 80%) and corresponding low N_2 values (balance) [13,108,120,121]. For instance, Lee et al. [120] conducted a comparative study on fresh pasta packaged under air (PS tray with PVC film) and under CO_2:N_2 78:22% MAP

(PA/EVOH/LLDPE). As a result, the shelf-life was doubled from 20 to 40 days at a storage temperature of 8 °C. Even higher rates of shelf-life increase for fresh filled pasta were shown in two other studies [108,121]. In the first case, samples included fresh pasta filled with cheese in a sealed tray (EVOH/PS/PE) with a barrier film (EVOH/OPET/PE) and two different atmospheres (air; CO_2:N_2 50:50% MAP). Quality maintenance was increased from 7–10 days up to 42 days [108]. Similarly, in the second case, gluten-free fresh pasta was packaged in trays (control: PET; test: EVOH/PS/PE) sealed with films (control: PET; test: EVOH/OPET/PE). Shelf life under air was compared to CO_2:N_2 30:70% MAP. Here, an increase from 14 to 42 days was notable [121].

Turning to bakery wares such as (pita)bread, cakes, crumpets, crepes, (fruit)pies, Robertson [13] reports a frequent use of CO_2:N_2 60:40% MAP. However, in the scientific literature, a more diverse application of CO_2:N_2 MAP can be seen. For example, Rodriguez et al. [126] investigated extending the shelf-life of bread using MAP packaging in a combination with preservatives. The research referred to bread slices packaged in a 60 µm bag. The results showed that in the samples without added preservative, and CO_2:N_2 50:50% MAP, the increases in shelf-life were 117% and 158% (at 22–25 °C and 15–20 °C). For the samples with calcium propionate addition and in N_2 100% MAP, shelf-life was increased by 116%. Furthermore, calcium propionate addition and CO_2:N_2 20:80% MAP increased the shelf-life by 150% and 131% at 22–25 °C and 15–20 °C. When the CO_2 concentration was increased to 50%, the increased shelf-life of the samples with added preservative was 167% at 22–25 °C. For the same settings at 15–20 °C the increase was even 195%. Fernandez et al. [149], conducted a similar research with soy bread. They as well used different settings of MAP and preservative adding but expanded the question of packaging options. They used two multilayer packaging solutions, high and medium barrier. The high barrier was LLDPE/PA/EVOH/PA/LLDPE, whereas the medium barrier solution was LLDPE/PA/LLDPE. As controls, LDPE and air atmospheres were used. The combination of high barrier packaging in CO_2:N_2 50:50% or CO_2:N_2 20:80% MAP without calcium propionate addition extended the shelf-life of the samples by at least 200%.

Turning to ready-to-eat savouries and snacks (e.g., crisps) Sanches et al. [128] investigated inter alia the effects of different packaging atmospheres under 40 °C and room temperature on multiple crisp samples, linked to lipid oxidation. They included marketed products under unknown MAP concentrations, air, N_2, vacuum and oxygen scavengers in the analysis. Reflecting changes in the fatty acid profile of the crisps, it was resumed that changes in the package's atmospheres, mostly cutting out oxygen, was crucial for the shelf-life of the crisps. Vacuum packaging options would also allow stable lipid profiles, however, they are not suitable for easily breakable crisps. Del Nobile [129] was similarly questioning the optimal packaging for crisps, however, focused on finding the best headspace gas composition for two different multilayer film packages (metallized PP and PVdC coated PE) through simulated storage. He proposed that N_2 combined with water vapour would lead to a shelf-life extension up to 80%.

4.2. Active and Intelligtent Packaging (AIP)

While MAP is firmly established in the market, active and intelligent packaging has not yet reached its full potential in food packaging applications but is at the threshold of more widespread use in the European market and subject to intense research and development activities [153–155]. Accordingly, the following paragraphs aim at outlining the concept of AIP and highlighting applications most relevant for cereal and confectionary packaging.

Just as conventional packaging applications, AIP define as food contact materials as given in Regulation (EC) No 1935/2004. While conventional packaging has to be sufficiently inert not to transfer substances to the food in quantities that endanger human health or bring an unacceptable change of the food product (composition, organoleptic properties), AIP are intentionally designed not to be inert. This allows them to actively maintain or even improve the quality or shelf-life of food products [39]. Hence, AIP deliberately includes "active" components that are either aimed to be released to the food or that aim at absorbing

substances from it. This justifies the division of active packaging into so-called releaser and absorber systems. However, a clear distinction is made to traditional substance releasing materials (e.g., wooden barrels) in food contact. The use of active substances aimed to be released to the food must also comply with the Directive 1333/2008 on food additives and should be authorized accordingly by applicable community provisions [63]. Furthermore, specific requirements regarding labelling and information, avoidance of misleading consumers as well as safety assessment and authorisation is given [39]. In addition to Regulation (EC) No 1935/2004, Commission Regulation (EC) No 450/2009 gives specific rules for the use of AIP (e.g., community list of allowed substances for use and evaluation of these) [39,156].

In response to major challenges in food quality and safety [12,13], key technologies in the area of active packaging are emitters (e.g., CO_2, ethanol, antimicrobials, antioxidants) and scavengers (e.g., O_2, CO_2, ethylene), absorbers (e.g., H_2O, flavour and odour), self-venting packages, microwave susceptors, and temperature control packaging [13,40,157–165]. Intelligent packaging on the other hand refers to packaging that monitors the food product and provides information about its condition [39]. Related key technologies are mostly indicators and sensors (e.g., time, temperature) and linked processing and communication systems (e.g., (printed) electronics). Further, tamper evident packaging and anti-counterfeiting applications exist [163,166].

Due to their effectiveness, the growth forecasts for AIP in the coming years are high, but it must be emphasised that the sustainability of such sophisticated packaging solutions should be evaluated case by case [167]. In addition to the actual reduction of food losses and food waste, factors such as, e.g., the recyclability of AIP, which may include metal-based components, should be evaluated [153,163,168,169].

Going into detail about cereal and confectionary packaging (see also Table 3), an application example for oxygen absorbers is in sliced bread. Where O_2 concentration decreased below 0.1% within a few days of packaging, microbial shelf-life was shown to be extended. It was reported that there was no effect on sensory quality [170]. Oxygen absorber can also be used in combination with MAP. In 2003, Del Nobile et al. [127] showed that the application of CO_2:N_2 80:20% MAP in the packaging of durum wheat bread prolonged the shelf-life from 3 to about 18 days at 30 °C. However, if the packaging film itself possesses a high barrier against oxygen, neither the use of scavengers nor MAP are necessary to achieve the desired shelf-life of white bread [171]. Finally, an oxygen scavenger system, consisting of a multilayer coextruded bag associated with an oxygen scavenger, was tested in different storage conditions (accelerated storage, room temperature, refrigerator), for its effect on preservative-free tortillas shelf life. The results indicated a protective effect of the packages including the oxygen scavenger system. Specifically, the weight and thickness of flour tortillas under room temperature conditions could be maintained, opposed to respective decreases detected in control packages (consisting of LDPE/LLDPE). In parallel, yeast and mold growth were hold back in the packages containing the oxygen scavenger versus control (room temperature and accelerated storage). Under refrigerated conditions, a shelf-life up to 31 days was estimated, however, independed of the use of oxygen scavengers [172].

It has been also shown that the use of ethanol emitters extend shelf-life even without establishment of an additional modified atmosphere. For ciabatta, a shelf-life of 16 days, at 21 °C could be obtained, packaged in air atmosphere and ethanol emitter addition [122].

Antimicrobial, antifungal, and antioxidative agents as active food packaging include multiple research topics. Options include the applications of essential oils, edible films, and nanocomposites, which are often used with products susceptible to microbiological degradation, e.g., sliced bread. For example, oregano essential oil has been observed to be a successful application against yeasts and moulds in sliced bread. It was applied in the form of antimicrobial sachet at concentrations of 5, 10, and 15% (v/w) at room temperature [136]. In addition to that, methylcellulose edible films produced with clove and oregano essential oil have displayed antimicrobial activity against spoilage fungi in bakery products and have improved sliced bread shelf-life to 15 days, at 25 ± 2 °C [137].

Also, cinnamaldehyde was used as an active ingredient to increase the shelf-life of sliced bread. It was incorporated in gliadin films (5%), which allowed to keep the quality of the product for 27 days of storage at 23 °C [173]. Next to having antimicrobial effects, essential oils are also antioxidative agents that can be included in packaging material like HDPE, LDPE, EVA. Zhu et al. [138] for example tested this approach with sesame essential oils for the packaging of oat cereals. However, there are also biological threats that could shorten the shelf-life of cereal and confectionery products. Essential oils from garlic, black pepper, ginger, fennel, and onion already have been tested as insect repellents for grain packaging. All these tested essential oils were characterized by significant fumigant insecticidal properties. For example, allyl mercaptan deriving from allium plants added as a sachet with rice flour, was proven as potential protective active packaging against *S. oryzae* contamination leaving sensory properties unaffected [174]. In general, the incorporation of essential oils in packaging materials is a growing sector [175,176]. One background can be that they are waterproof, so it could be the ideal material for the incorporation into a film, which will turn it from a conventional packaging material to an active one, increasing both its value and its functionality [175].

One further option of active packaging is the targeted use of composites at the nanoscale, whether organic (oils/proteins/carbohydrates) and/or inorganic, e.g., clays. This topic is of interest as active agents might have different properties in smaller scales. Materials of which at least one of its external dimensions belongs to the nanoscale (1 to 100 nm) are considered nanomaterials [177,178]. They are characterized for their unique properties such us high surface-area-to-volume ratio, fine particle size, and high reactivity [179]. One common area of research interest is represented by publications including essential oils. For example, bio-nano-composite films prepared with corn starch incorporated with chitosan nano-clay, and further enriched with a variety of ratios of grapefruit seed extracts have been studied. It was shown that this solution was capable of inhibiting fungal proliferation for a period of 20 days, compared to that of 6 days in bread packaged samples with synthetic plastic, indicating a successful active packaging approach to extent the shelf-life of bakery products [133]. Furthermore, two different formulations mainly consisting of essential oils from several plants were evaluated for their potential antifungal properties in maize grains. Specifically, in a recent study, bioactive EVOH films including various essential oils have been characterized. Cinnamaldehyde, citral, linalool and isoeugenol were investigated to decrease the activity of *A. steynii* and *A. tubingensis* strains. It was shown that the ochratoxin A production by these strains in partly milled maize grains could be reduced significantly. The inhibitory effect was the highest in EVOH with cinnamaldehyde, followed by isoeugenol and citral [180]. In parallel, EVOH copolymer films incorporated with essential oils from *Origanum vulgare*, *Cinnamomum zeylanicum* and/or their major active constituents have been studied. The results showed that carvacrol and cinnamaldehyde were effective in decreasing *Aspergillus flavus* and *A. parasiticus*-induced aflatoxin production in maize, respectively. Overall, cinnamaldehyde showed the highest inhibitory effect, followed by combinations of EVOH with essential oils from *Origanum vulgare*, *Cinnamomum zeylanicum* and carvacrol [181].

Next to these highly discussed organic nanoparticles, inorganic particles like Ag (silver) and TiO_2 (titan dioxide) have also been applied to packaging solutions, for example cereal products, due to their antimicrobial effects [182–185]. However, there is a concern on potential risk of nanoparticles migrating into food, although limited data showed that obtained values were within the limits set by the legislation [185–189]. It was shown that Ag-TiO_2 nanocomposite incorporated in HDPE considerably extended shelf-life and microbiological safety of bread in comparison with control sample stored in an open atmosphere or in HDPE bags [144]. Not only the characteristics of plastic packaging can be optimized by the inclusion of nanoparticles. The modification of paper with Ag-TiO_2-SiO_2 (silicon dioxide) or Ag/N-TiO_2 composites can improve the papers material characteristics. It was shown that such paper was capable to extend the shelf-life of bread

by 2 days in comparison to the control, in both ambient (18–20 °C) and refrigerated (0–4 °C) conditions [190].

Research in optimizing packaging with nanostructures goes even further to high-tech materials. An example is a packaging material with a montmorillonite layer. It was shown that montmorillonite composite polyamide 6 nano-fibres placed over PP films, increased the shelf-life of bread by 2 days at room temperature, due to inhibition of microbial growth [191].

Intelligent packaging, on the other hand, is a special packaging technique aiming to monitor the quality of the packaged food and to predict or measure the safe shelf-life better than a best before marking date [122,130,171,192–194]. It provides functions beneath the ones considered as conventional e.g., protection and containment and is used to monitor the condition and provide quality information of packed foods to the consumers [158]. Different indicators, such as time-temperature, microbial growth, product freshness, pack integrity etc., are used as intelligent packaging systems. High temperatures and/or temperature fluctuation are often correlated with food deterioration as result of detrimental biochemical reactions combined with microbial growth. Depending on the food sensitivity specific intelligent indicators can be applied to specific food products. The time-temperature indicator measures the change that imitates the targeted quality characteristics with the same behaviour under the same time-temperature exposure. The pH and enzymatic indicators can also give information about the quality of food [195]. Commercially available time-temperature indicators can be used to monitor quality changes of many perishable and semi-perishable foods. Among other products, these indicators have been applied to canned fruitcake for 10 days' storage at constant (12, 25 and 37 °C) temperatures. Sensory analysis, as quality characteristic of the product, was correlated with indicator response [140,196].

Reflecting the above chapters and findings, it can be summarized and confirmed that, if chosen correctly, cereal and confectionary packaging, as well as food packaging in general can make a valuable contribution to maintaining the quality and safety of food [12,13,17]. Accordingly, it can also help to prevent food losses and waste, an important point when it comes to making our food systems more sustainable [11,16]. This point is also taken up in the SDGs and influences current political efforts such as the European Union's Green Deal [2,3,6].

However, packaging redesign or optimizations should not simply be carried out without evaluating the effects on ecological, social, and economic sustainability as objectively as possible. This is the only way to avoid possible hidden trade-offs [17].

In addition, close cooperation between a wide range of disciplines is required. In this context, and among others, material science, sustainability science and social sciences, and humanities can be mentioned in addition to food science and technology. The latter in particular has, however, an important enabling function [197,198]. The future focus here could be on the points of promoting (i) diverse and sustainable primary produce, (ii) new processes and systems for sustainable manufacture, (iii) reduction of food and material waste along the supply chain, (iv) safety and traceability, (v) affordable and balanced nutrition, (vi) healthy diets as well as (vii) digitalization. MAP and AIP are important approaches in this context, which are particularly present in the points (ii), (iii) and (iv) [198].

5. Conclusions

The ongoing discussion about packaging optimization towards the enhancement of the sustainability of certain products, asks for a profound review of the status quo in specific food groups. Cereal and confectionary were found to be underrepresented in recent publications addressing this topic, despite their global economic and ecologic importance. To take the right steps aspiring more sustainable production and consumption of goods, it is essential for practitioners along the food supply chain to thoroughly understand packaging functions (containment, protection, convenience, communication), properties

(physical and mechanical strength, barrier, migration, hygiene), product group specific decay mechanisms, used packaging solutions, and shelf-life extension strategies.

Commonly available packaging solutions vary in material selection (glass, metal, plastic, paper), as well as in shape (rigid, semi-rigid, flexible) and size. Therefore, each packaging solution offers unique benefits and limitations regarding its optimization potential. Important decay mechanisms mediated by packaging in cereal and confectionary products and snacks include inter alia oxidative mechanisms and changes in moisture content. Especially for products for which quality is easily impaired through such mechanisms, packaging solutions and technologies extending the shelf-life need to be considered as ways to improve the products´ sustainability. This, in combination with a proper material selection, includes the applications of MAP and AIP (e.g., scavengers, indicators, active ingredients) as well as novel approaches (e.g., nanotechnology).

However, sustainability improvement includes different other aspects. After the proper understanding of the packaging's purpose in these certain product categories and subcategories, the question of burden shares between the environmental impacts of the food product itself in comparison to its packaging must be considered along the whole life cycle. Thus, further research is deemed necessary to investigate data from related Life Cycle Assessment (LCA) studies and to combine the findings with the current status quo, in order to derive proper redesign steps for cereal and confectionary products. However, LCA is by default limited to environmental analysis and does not cover all sustainability dimensions. The inclusion of economic and social aspects would finally provide a holistic picture on how to attain more sustainable products.

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Appendix 2

Publication II

Saarniit, K., Lang, H., Kuldjärv, R., Laaksonen, O., Rosenvald, S. (2023). The Stability of Phenolic Compounds in Fruit, Berry, and Vegetable Purees Based on Accelerated Shelf-Life Testing Methodology. *Foods, 12(9)*, 1777. https://doi.org/10.3390/foods12091777

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The Stability of Phenolic Compounds in Fruit, Berry, and Vegetable Purees Based on Accelerated Shelf-Life Testing Methodology

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Abstract: Evaluating the stability of polyphenols in fruit, berry, and vegetable purees helps to assess the quality of these products during storage. This study aimed to (1) monitor the stability of total phenolic content (TPC) in four-grain puree with banana and blueberry (FGBB), mango-carrot-sea buckthorn puree (MCB), and fruit and yogurt puree with biscuit (FYB); (2) study the effect of aluminum-layered vs. aluminum-free packaging on the changes in TPC; and (3) assess the suitability of accelerated shelf-life testing (ASLT) methodology to evaluate the stability of polyphenols. The samples were stored at 23 °C for 182, 274, 365, and 427 days. The corresponding time points during ASLT at 40 °C were 28, 42, 56, and 66 days, calculated using Q_{10} = 3. The TPC was determined with Folin–Ciocalteu method. The results revealed that the biggest decrease in TPC took place with high-pH FGBB, which contained fewer ingredients with bioactive compounds. Minor changes were seen in FYB and MCB, which had lower pH values, and contained a larger amount of ingredients that include polyphenols. In addition, the choice of packaging material did not affect the TPC decrease in each puree. Finally, it was concluded that the ASLT methodology is suitable for studying the TPC changes in such purees, but the corresponding Q_{10} factors may vary and should be determined based on the chemical profile and ingredient list of the product.

Keywords: total phenolic content; Folin–Ciocalteu assay; pasteurized purees; packaging; accelerated shelf-life test

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1. Introduction

Consumption of fruits, berries, and vegetables in regular and sufficient amounts is one of the widely approved key parts of achieving a well-balanced diet. In addition to providing vital dietary fiber, fruits, berries, and vegetables also consist of health-beneficial bioactive compounds such as antioxidants and polyphenols [1]. However, the amount of these compounds in food can decrease with applying heat during processing [2], for example, when producing pasteurized purees [3]. In addition, it has been stated that storage time also has a significant effect on the quantity of polyphenols [4,5]. Therefore, it is important to evaluate the stability of phenolic compounds in pasteurized purees to assess the quality of these long-shelf-life products during storage.

Fruit, berry, and vegetable purees are considered good sources of bioactive compounds [6,7]. These compounds include polyphenols, which are secondary metabolites synthesized by plants. Polyphenols have physiological and morphological importance for plants, protecting them against UV radiation, mechanical damage, and microbial infection [8]. Various plants contain different amounts of polyphenols, depending on the genetic background, growing, and climatic conditions [9,10]. For example, blueberries (*Vaccinium*

ssp.), sea buckthorn (*Hippophae rhamnoides* L.), and raspberries (*Rubus idaeus* L.) are widely known to contain high amounts of health-beneficial phenolic compounds [7,11,12]. The total content of polyphenols in blueberries ranges from 48–302 mg/100 g of fresh fruit weight [7] and they are considered important to monitor during the shelf-life of blueberry products [13]. More specifically, blueberries contain bioactive compounds such as anthocyanins, flavonols, and phenolic acids [14–16]. In addition, raspberries are a good source of anthocyanins [17]. Sea buckthorn, also named as seaberry, has excellent antioxidant properties, mainly due to its high total phenolic content (TPC) which can range from 11–964 mg GAE/100 g [9,12]. Furthermore, fruits contain phenolic compounds that form an important part of their chemical quality. For example, bananas consist of phenolic acids and flavonoids. The TPC of bananas varies in the range of 7–475 mg GAE/100 g, depending on different cultivars and growing conditions [10]. Mango, a popular exotic fruit, also contains various phenolics such as phenolic acids, flavonols, and anthocyanins [18,19]. As well as phenolic-rich berries and fruits, vegetables and cereals are also consumed as health-beneficial sources of bioactive compounds. For instance, the main phenolic compounds in carrots are phenolic acids [20]. In cereals, the TPC depends on the grain type, growing, and processing conditions [21]. For example, the TPC in wheat bran fractions is 750–1082 mg GAE/100 g [22].

Several methods are used to assess the TPC in different matrixes. For example, Folin–Ciocalteu (F–C) assay is one of the most widely used methods to quantify total polyphenols in fruit juices and beverages. In this method, a redox reaction between the F–C phenol's reagent and the reducing compounds in the sample takes place. However, this assay has its limitations as the reagent not only reacts with polyphenols but also with other compounds in the sample, including ascorbic acid, reducing sugars, SO_2, etc. As a result, these compounds are also unintentionally quantified as polyphenols. In addition, it is suggested that the F–C assay gives an overview of the total antioxidant capacity and, as phenolics represent antioxidants in most plants, it shows an approximate TPC as a result. Nevertheless, the F–C assay can still be used to evaluate the TPC of samples when polyvinylpolypyrrolidone (PVPP) treatment is applied to separate polyphenolic and non-polyphenolic compounds [23]. Therefore, the F–C assay is still widely implemented to measure the TPC in most food samples. In addition, it also has some considerable benefits compared to other similar methods. For example, the F–C assay does not require an overnight incubation time for the preparation of reagents and the results are easily repeatable. This makes the straightforward method simple to perform, and, in addition, it is inexpensive [24,25].

As the market share of fruit, berry, and vegetable purees is continuously increasing [26], these healthy and convenient products with a high content of bioactive compounds must reach consumers in the best possible condition. In addition, as consumers are becoming more aware of sustainable packaging, industries must provide it to keep up with the demand, ensuring there is no loss in product quality and storage time [27]. However, as the purees need barriers against light and gases to maintain their quality during storage [28,29], packages including aluminum are still often used. Aluminum provides excellent barriers and, at the same time, is stable over a wide range of temperatures, not generating toxic releases when exposed to food. On the other hand, the production of aluminum is an environmentally burdensome process. For example, the global warming potential (GWP) of a metalized PET is 0.197 kg CO_2 equivalent [30], while the GWP of a pure PET bottle is 32% less burdensome [31]. In addition, the GWP of the aluminum foil itself is 0.382 kg CO_2 equivalent [30]. Therefore, removing the aluminum layer from multilayered packaging has a positive effect on the environment and it also makes the recycling of the package easier [32]. Regarding barrier needs, aluminum can be replaced with plastics which provide similar barriers against oxygen, water vapor, or gases. For example, oriented polyamide (OPA) is often used as a good oxygen barrier material (OTR = 18 $cm^3/m^2/day$) [33].

To monitor important quality attributes during shelf-life and to determine the end of the storage time of food products efficiently, there is demand from the food industry for fast

and reliable methods [34,35]. For this purpose, an accelerated shelf-life test (ASLT) could be used. ASLT allows for the acceleration of the quality deterioration of food products without changing the order of reactions taking place in standard conditions [36]. This methodology enables the faster launch of long shelf-life food products to the market [37]. Furthermore, this approach can be used to evaluate the effect of changes made in the recipe, technology, and/or packaging materials on the quality of the product during storage [35]. The chemical and physical reactions occurring in the product during shelf-life are accelerated by changing storage conditions [38]. These include temperature, oxygen, light, and relative humidity. A higher storage temperature is the most frequently used factor as it affects the kinetics of the reactions the most [37]. The methodology of ASLT is based on the Arrhenius equation (Equation (1)), which shows the effect of temperature on the reaction rate:

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

where k is the kinetic rate constant, k_0 is the exponential factor representing the collision frequency of the reacting molecules, E_a is the activation energy (J), R is the universal gas constant (8.3144 J/mol·K), and T is the absolute temperature (K) [37,39].

Based on the reaction rates of chemical or physical processes in the product, it is possible to find the acceleration factor Q_{10}, which is defined as the number of times a reaction rate changes with a 10 °C change in temperature [40]. Each quality process has its characteristic Q_{10} factor [40] which is calculated to conduct reliable ASLTs [41]. The Q_{10} factor is derived from the Arrhenius equation as follows (Equation (2)):

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\frac{10}{T_2 - T_1}} \quad (2)$$

where k_1 and k_2 represent the reaction rate at temperatures T_1 and T_2 [42].

The storage stability of phenolic compounds in berry, fruit, and vegetable products has been previously studied by several authors. For example, Srivastava et al. [43] studied the effect of different conditions on blueberry extract. The results showed that the effect of storage was smaller than the impact of the thermal treatment. In addition, Castrejón et al. [44] showed a decrease in the content of total phenols, antioxidants, and anthocyanins in blueberries even during ripening. Patras et al. [45] investigated the decrease and kinetic modeling of anthocyanins in strawberry jam during storage. In this case, the degradation of anthocyanins followed first-order kinetics where the reaction rate increased with an increase in the temperature. The same result was shown by Celli et al. [46] who studied the degradation of anthocyanins in freeze-dried microencapsulates from lowbush blueberries. Andersson et al. [47] studied the effect of storage time and temperature on the stability of TPC in beverages prepared with sea buckthorn berry puree, concluding that the largest decrease in TPC occurred immediately after production and later no significant change was observed. However, as far as the authors know, there is no clear information in the literature about the suitability of ASLT methodology for fruit, berry, and vegetable purees.

Therefore, the aims of this study were to (1) monitor the stability of phenolic compounds in different fruit, berry, and vegetable purees; (2) study the effect of AL-layered vs. AL-free packaging on the changes in TPC; and (3) assess the suitability of accelerated shelf-life testing methodology to assess the changes in phenolic content in these purees.

2. Materials and Methods

2.1. Purees and Packaging

The samples of packaged purees were supplied by a local producer (Salvest AS, Tartu, Estonia). Three different organic purees were used in this study: four-grain puree with banana and blueberry (FGBB), mango-carrot-sea buckthorn puree (MCB), and fruit and yogurt puree with biscuit (FYB). The ingredients and nutritional compositions of 100 g of purees, labeled on the packages, are given in Table 1.

Table 1. The nutritional composition of four-grain puree with banana and blueberry (FGBB), mango-carrot-sea buckthorn (MCB), and fruit and yogurt puree with biscuit (FYB) in 100 g of product.

Nutritional Composition	FGBB	MCB	FYB
Ingredients	Water, banana puree (30%), blueberry puree (8%), four-grain cereals (rye, oat, wheat, barley) (7%), and rapeseed oil	Mango puree (52%), carrot puree (40%), and sea buckthorn puree (8%)	Banana puree (37%), mango puree (36%), yogurt (15%), raspberry puree (10%), and biscuit (2%) including wheat flour, butter, and water
Energy (kcal/kJ)	62/262	62/262	88/368
Fat (g/100 g)	1.4	0.0	1.3
Unsaturated Fatty Acids (g/100 g)	0.0	0.0	0.8
Carbohydrates (g/100 g)	11.0	13.0	16.0
Sugars (g/100 g)	3.8	11.0	11.0
Protein (g/100 g)	1.2	0.6	1.3
Salt (g/100 g)	0.0	0.0	0.0

The purees were packaged in two types of doypack pouches where one version included an aluminum (AL) layer and the other one was AL-free (Gualapack S.p.A, Castellazzo Bormida, Italy). In addition, the doypacks included materials like polyethylene terephthalate (PET), oriented polyamide (OPA), and polypropylene (PP). In more detail, the doypack composition with AL-layer consisted of 12 µm PET/9 µm ALU/15 µm OPA/75 µm PP. The doypack without the AL-layer consisted of 12 µm PET/15 µm OPA/70 µm PP. The spout material of both packages was PP. The oxygen and water vapor transmission rates for both doypacks were <1 $cm^3/m^2/24$ h and <1 $g/m^2/24$ h, respectively.

The packaged purees were heat treated with the internal temperature being 108 °C for 31 min for FGBB, 103 °C for 43 min for MCB, and 103 °C for 17 min for FYB.

2.2. Reagents and Standards

Folin–Ciocalteu reagent (Sigma-Aldrich, Taufkirchen, Germany), gallic acid monohydrate (Sigma-Aldrich, Germany), sodium bicarbonate (Sigma-Aldrich, Germany), poly(vinyl polypyrrolidone) (PVPP) (Sigma-Aldrich, Germany), acetone (Sigma-Aldrich, Germany).

2.3. Design of Shelf-Life Tests

Purees packaged in doypacks were stored in a carton board box at room temperature (23 °C) and in a climate chamber at 40 °C and 50% of relative humidity (Memmert UN750, Büchenbach, Germany). The samples were stored in the dark to simulate the most likely condition applied in the warehouse. As the expected shelf-lives of the samples at room temperature were 12 months, the testing time points were chosen based on this to describe possible changes taking place before and after the expected end of storage. Therefore, the testing points for room temperature storage were 0-point (immediately after production), 182 days (6 months), 274 days (9 months), 365 days (12 months), and 427 days (14 months). For the ASLT at 40 °C, the storage time for each corresponding analysis point was calculated, taking into account the Q_{10} factor (Equation (3)).

$$Accelerated\ aging\ time\ (AAT) = \frac{Desired\ real\ time\ (RT)}{Q_{10}^{\left(\frac{T_{AA}-T_{RT}}{10}\right)}} \quad (3)$$

where AAT is the accelerated aging time at accelerated aging temperature (T_{AA}) and RT is the real storage time at real storage time temperature (T_{RT}) [48].

As the literature states, the Q_{10} for almost all food products is approximately 3 [49]. Therefore, the time points of the ASLT which corresponded to 6, 9, 12, and 14 months in room temperature storage were calculated to be 28, 42, 56, and 66 days at 40 °C. At each time point, 2 sample replicates from both storage conditions were taken for analysis.

2.4. pH Analysis

The pH was measured using a pH-meter (Mettler-Toledo International Inc., Columbus, OH, USA). The analysis was done by inserting a pH-electrode into a previously homogenized sample. Two measurements were performed for both sample replicates.

2.5. Analysis of Total Phenolic Content

The content of total phenolic compounds was determined using the F–C method as described by Yap et al. [50]. The extraction of total phenolic compounds from different food matrices was performed as described by Sulaiman et al. [51] with some modifications, and the polyvinylpolypyrrolidone (PVPP) treatment was performed as described by Bridi et al. [23] with some modifications.

Briefly, 1 g of sample was weighed into 15 mL high-speed centrifuge tubes, 5 mL of 70% acetone was added, and mixed thoroughly. Sample extracts were rotated for 60 min using rotator Stuart SB3 (TEquipment, Long Branch, NJ, USA). Sample extracts were centrifuged (21,000× *g* at 18 °C for 10 min), filtered with a microfilter (CHROMAFIL Xtra PET-20/13, 0.2 µm), and diluted with acetone up to 5 times, if necessary.

To separate polyphenols and non-polyphenolic derivatives (sugars, ascorbic acid, and sulfite) from the samples and, therefore, to see the amount of interfering compounds, a pretreatment with polyvinylpolypyrrolidone (PVPP) was used. The PVPP was suspended in milliQ water and was well shaken before being added to the filtered sample. PVPP treatment was applied as follows: 0.5 mL of PVPP suspension (40 g/L) was added to 0.5 mL of filtered sample and the mixture was rotated for 10 min using rotator Stuart SB3 (TEquipment, USA). After PVPP treatment, the samples were centrifuged (21,000× *g* at 18 °C for 10 min), filtered with a microfilter (CHROMAFIL Xtra PET-20/13, 0.2 µm), and diluted with acetone up to 5 times, if necessary.

The content of TPC was determined using the F–C method. For this, 20 µL of filtered and diluted sample extracts (PVPP treated or untreated) were mixed with 100 µL of 0.2N F–C reagent. After 5 min, the reaction was stopped by adding 80 µL of 7.5% sodium carbonate solution. After stopping the reaction, the samples were incubated for 30 min at 37 °C. After incubation, the absorbance of the samples was measured with a BioTek Synergy H1 multi-mode microplate reader (Agilent Technologies, Inc., Santa Clara, CA, USA) at a wavelength of 765 nm. A 70% acetone solution was used as an absorbance blank. The results were expressed as gallic acid equivalent (GAE). TPC of the sample was calculated as a difference between before and after PVPP pretreatment in mg/g of the gallic acid equivalent (mg GAE/g).

2.6. Statistical Analysis

Statistical significance testing was performed in R 4.2.2 (The R Foundation for Statistical Computing, Vienna, Austria) using package "emmeans" 1.8.3. The TPC response variable was modeled by a cubic B-spline of time data plus packaging. The model fit was evaluated visually and using the adjusted coefficient of determination. The significances were calculated across time points and packaging for each different product and each different storage temperature by using pairwise t-test comparisons between the estimated marginal means. The confidence level was set to 0.95 and adjusted using the Bonferroni method. *p*-values were adjusted according to the Benjamini–Hochberg method [52]. The significance level for compact letter displays was set to 0.05.

3. Results and Discussion

3.1. pH

The initial pH values of the purees differed marginally. For example, in the 0-point, MCB had the lowest pH value with 3.9 in both packages. The initial pH of FYB was similar, with the value being 4.0 also in both doypacks. However, FGBB with fewer acidic ingredients showed the highest pH value of 4.8 in both packages. During both storage tests, the pH values of the purees did not change.

3.2. Effect of Packaging Material on the Changes in TPC

The results of initial TPCs from each puree at 0-point showed that there were no statistical differences, whether the puree was packaged in AL-layered or AL-free packaging. However, there were slight distinctions during the storage tests. For example, when the decrease of TPC in FGBB puree was slightly bigger in AL-free packaging at both 23 °C and 40 °C, the results were the opposite for the FYB puree in which the TPC decreased faster in AL-layered packaging at both storage temperatures.

In more detail, by the end of the tests, the phenolic content in FGBB puree decreased by 65% and 60% in AL-free packaging at 23 °C and 40 °C, respectively, while in AL-layered doypacks, the decrease was 63% at 23 °C and 57% at 40 °C (Figure 1a). On the other hand, the TPC of FYB puree decreased by 41% in AL-layered packaging at the 23 °C storage test and 27% during the ASLT. In AL-free packaging, the decrease in FYB was 37% at room temperature and 19% at 40 °C storage (Figure 1b). In addition, the decrease of TPC in the MCB puree, packaged in AL-free packaging and stored at 23 °C, was also slightly bigger (37%), while in AL-layered packaging, the decrease was 27% in the same storage conditions (Figure 1c). However, as seen from Figure 1 and Supplementary Materials (Table S1), there were no statistical differences between the results at each time point during both storage tests, whether the purees were packaged in AL-layered or AL-free doypacks.

It is known that aluminum is used to enhance packaging materials with its good barriers, including providing a high barrier against light [33]. At the same time, it has been shown that the storage stability of polyphenols can be easily affected by light from the surrounding environment [53]. Therefore, it is concluded that fruit, berry, and vegetable purees should be packaged in opaque materials. However, the storage tests in the current experiment were conducted in environments without light and, as no statistical differences were seen based on the results, it is concluded that in this case, the packaging choice did not affect the decrease in the TPC.

3.3. Comparison of Changes in TPC of Three Purees

The highest content of phenolics in the samples before storage was found in the FYB and MCB purees (Supplementary Materials, Table S1). The FYB contained mainly banana, mango, and raspberry, which are known to have high contents of phenolic compounds [10,54,55]. For example, the initial content of TPC in FYB was 49.8 mg GAE/100 g in AL-layered doypack, and 50.0 mg GAE/100 g in AL-free packaging (Supplementary Materials, Table S1). The MCB puree also showed the high phenolic content of mango, carrot, and sea buckthorn [55–57]. For this puree, the initial contents of TPC were 51.7 mg GAE/100 g and 53.0 mg GAE/100 g for AL-layered and AL-free doypacks, respectively. At the same time, FGBB showed the lowest initial content of TPC with 30.9 mg GAE/100 g and 29.2 mg GAE/100 g in doypacks with AL and without AL-layer, respectively. This is probably because while the FYB and MCB purees contained almost 100% fruits, berries, and/or vegetables, FGBB consisted of only 45% of ingredients with phenolic content.

In more detail, the biggest changes in the TPC during both storage tests took place with FGBB, in which a rapid change already occurred in the first time point (Figure 1a). This puree contained the lowest amount of fruits, berries, or vegetables and also had the highest pH compared to other purees. Previously, it has been argued by Narita et al. [58] that phenolic compounds are more stable under acidic pH conditions, which in part explains why the decrease of TPC in FGBB was significantly bigger during both storage tests, compared to the FYB and MCB purees. However, Friedman [2] has also stated that the stability of phenolic compounds not only depends on pH but also on the structure of the specific compound. For example, the FGBB puree consisted of 30% banana puree, 8% blueberry puree, and 7% four-grain cereals. According to the literature, these ingredients contain various polyphenols which may have different stabilities during storage. For example, bananas and four-grain cereals can contain ferulic acid [10], which may degrade during storage due to its carboxyl group [59]. However, ferulic acid may also be bound to other compounds in the matrix, such as reducing sugars or other polymeric structures [60],

making the phenolic component more stable during storage [61]. Next to banana, FGBB also consisted of blueberries, which, according to the literature, may contain chlorogenic acid, which can be stable in acidic conditions and high temperatures [16]. In addition, blueberries may include stable glycolysed flavonols such as quercetin-based and myricetin-based galactosides and glucosides [14,62]. However, blueberries can also contain anthocyanins such as cyanidins, which are sensitive to higher temperatures [15] but are more stable at lower pHs [63]. Therefore, the possible anthocyanins in FGBB may be less stable due to the high pH of the matrix. In addition, anthocyanins can also exist in unstable free forms when the matrix has undergone processes such as heat treatment or storage at ambient temperatures. On the other hand, it has been stated by Mäkilä et al. [64] that otherwise relatively unstable anthocyanins can form more stable compounds during storage through polymerization, co-pigmentation with other phenolic compounds, and further degradation to hydroxybenzoic acids. Based on this discussion, it is hypothesized that the FGBB puree contained ingredients that may have included polyphenols with different stability throughout storage. However, the FGBB puree had the highest pH, consisting of nearly 50% of water, making the matrix the least favorable for phenolics to maintain stability during storage.

Similarly to FGBB, the FYB puree also contained banana as the main ingredient. In more detail, FYB consisted of 37% banana puree, 36% mango puree, 10% raspberry puree, and 2% four-grain cereals. Overall, this product had a lower pH throughout storage and showed a smaller decrease in TPC than FGBB in both storage conditions (Figure 1b). Similarly to the FGBB puree, it is hypothesized that FYB could also contain ferulic acid originating from bananas and four-grain cereals [59]. However, in addition to this tropical fruit, FYB also contained mango in a large proportion. For example, based on the literature, mango may include various phenolics such as phenolic acids, flavonols, and anthocyanins [18,19]. While gallic acid and quercetin derivatives in mango may be more stable [15,16,63], anthocyanins and catechins might degrade more easily during storage [15,18]. As well as these components, FYB also contained raspberries in smaller quantities. These acidic berries can contain cyanidins and ellagitannins, which are both temperature-sensitive compounds [15,17]. Based on this discussion, it is concluded that the FYB puree may have contained both stable and less stable bioactive compounds. However, the puree included more fruits and berries than FGBB, and therefore the pH of the matrix was also lower, which might have contributed to the compounds being more stable during storage.

Finally, the smallest changes in TPC during storage were seen in the MCB puree (Figure 1c) with the lowest pH. Similarly to FYB, this product also contained mango but in a larger amount. More specifically, the MCB puree consisted of mango (52%), carrot (40%), and sea buckthorn (8%). Based on the literature, it is speculated that this puree may contain possibly stable phenolic acids and flavonoids that might be originating from the mango [15,16,18,20]. However, the puree may also contain compounds in smaller quantities that may be less stable, for example, catechins [15,18,65] from mango and sea buckthorn and salicylic acid from sea buckthorn [66]. Based on this discussion, it is hypothesized that MCB may also have contained both stable and less stable phenolic compounds. However, even more importantly, the MCB puree consisted only of fruits, berries, and vegetables and had the lowest pH, which may have created the most advantageous environment for keeping the bioactive compounds stable throughout storage.

3.4. Effect of Storage Temperature and Following Linear Regression Models of TPC Changes

Overall, the biggest decreases in the TPC in each puree occurred during storage at 23 °C (Figure 1, Supplementary Materials, Table S1). However, there are considerable differences when comparing the results between purees at both storage temperatures. For example, with the FGBB puree, the decrease during storage at 23 °C was 63% in the AL-layered doypack and 65% in AL-free packaging. In comparison, by the end of the ASLT, the TPC decreases in the FGBB puree were slightly smaller, with 57% in AL-layered and 60% in AL-free packaging (Figure 1a).

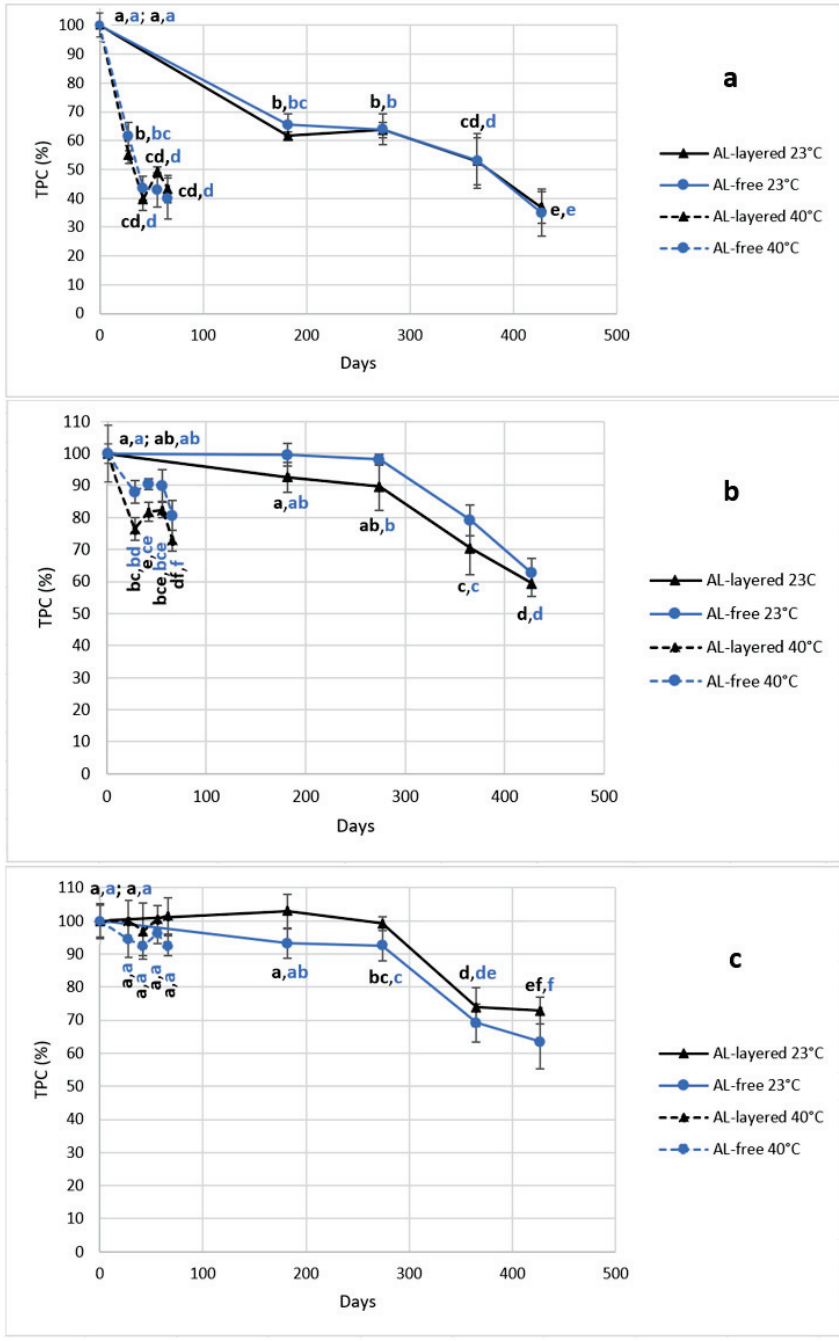

Figure 1. TPC changes in FGBB (**a**), FYB (**b**), and MCB (**c**), at 23 °C and 40 °C. The significances are calculated across time points and packaging for each different product and each different storage temperature by using pairwise *t*-test comparisons between the estimated marginal means. The 0-point results are statistically different for FYB (**b**), where 23 °C = group ab, ab, 40 °C = group a, a.

However, for the other purees, the results were not as similar in a comparison of different storage temperatures. For instance, while the TPC in the FYB puree decreased by 41% and 37% by the end of the room temperature storage test in AL-layered and AL-free packaging, during storage at 40 °C, the decrease in both packaging materials was only 27% and 19%, respectively (Figure 1b). Furthermore, during the ASLT, no significant changes in the TPC were found in the MCB puree in either packaging. However, during the storage at 23 °C, the TPC decrease in the same puree was more similar to FYB, with 27% in AL-layered and 37% in AL-free packaging (Figure 1c).

Therefore, the storage temperature had different effects on the total phenolic content based on the puree and its properties. As stated in the literature [2,58], phenolic compounds are more stable under acidic pH conditions, and the stability of phenolics depends on the specific compound and its structure. The experiment results are in accordance with the literature, showing that the phenolic content is more stable in matrixes with a lower pH. In addition, the literature [45,46] states that the rate of degradation of phenolic compounds increases with an increase in the temperature. However, there were minor or no changes in the FYB and MCB purees during the ASLT, showing that the ingredients in these purees may have contained compounds which could be more stable at higher storage temperatures.

Considering the previous discussion, linear regression models of the changes in the TPC can be presented based on the effect of storage temperatures. This is necessary in order, in the future, to conduct accurate ASLTs with similar purees. To assess whether the chosen acceleration factor (Q_{10} = 3) is suitable for conducting an ASLT with each puree, the correlation coefficients of TPC at both storage temperatures are represented on Figure 2.

Unlike for the MCB and FYB purees, the comparative changes in the TPC between 23 °C and 40 °C storage tests were most similar for the FGBB puree (Figure 2a). For example, with FGBB in AL-layered packaging, the correlation coefficient for the decrease in TPC between both storage temperatures was 0.7874. In AL-free packaging, the coefficient was even higher. Since FGBB had the highest pH and consisted of nearly 50% water, it also might have had the least favorable matrix for phenolics to maintain stability during storage. Therefore, it was clearly seen that the changes in both storage conditions took place rapidly and comparably. Although the TPC decrease at room temperature in the FGBB puree was still slightly larger (by 5–6%) than during ASLT, it can be said that the chosen acceleration factor (Q_{10} = 3) is suitable for conducting an ASLT with the FGBB puree.

For the FYB puree, the decrease in TPC during the ASLT was approximately 1.5 and 2 times smaller for AL-layered and AL-free packaging, respectively, compared to room temperature storage. This difference is also reflected in the regression model between the results of both storage conditions. The correlation coefficients of the TPC in the FYB purees packaged in AL-layered and AL-free doypacks at 23 °C and 40 °C are remarkably lower than for the FGBB puree (Figure 2b). As the changes in FYB at a higher storage temperature were smaller, it can be said that the chosen acceleration factor (Q_{10} = 3) was overrated for the FYB puree and was initially expected to reflect a faster decrease than actually took place. Therefore, it is concluded that to conduct an accurate ASLT with FYB, the acceleration factor should be smaller than Q_{10} = 3.

No significant changes in TPC took place with MCB at 40 °C throughout the ASLT, showing that the ingredients in this puree may have contained compounds which could be more stable at a higher storage temperature. In addition, the decrease was also the smallest at room temperature storage, compared to other purees. This outcome is also reflected in the regression models where the coefficient for MCB in AL-layered packaging was 0.3787, and for AL-free packaging it was even lower (Figure 2c). As no significant changes took place during the ASLT, it is concluded that the chosen Q_{10} factor (Q_{10} = 3) was also overrated for the MCB puree. Therefore, this product requires the use of a smaller acceleration factor and, consequently, a longer period of storage time at 40 °C to reflect the changes taking place during real-time storage.

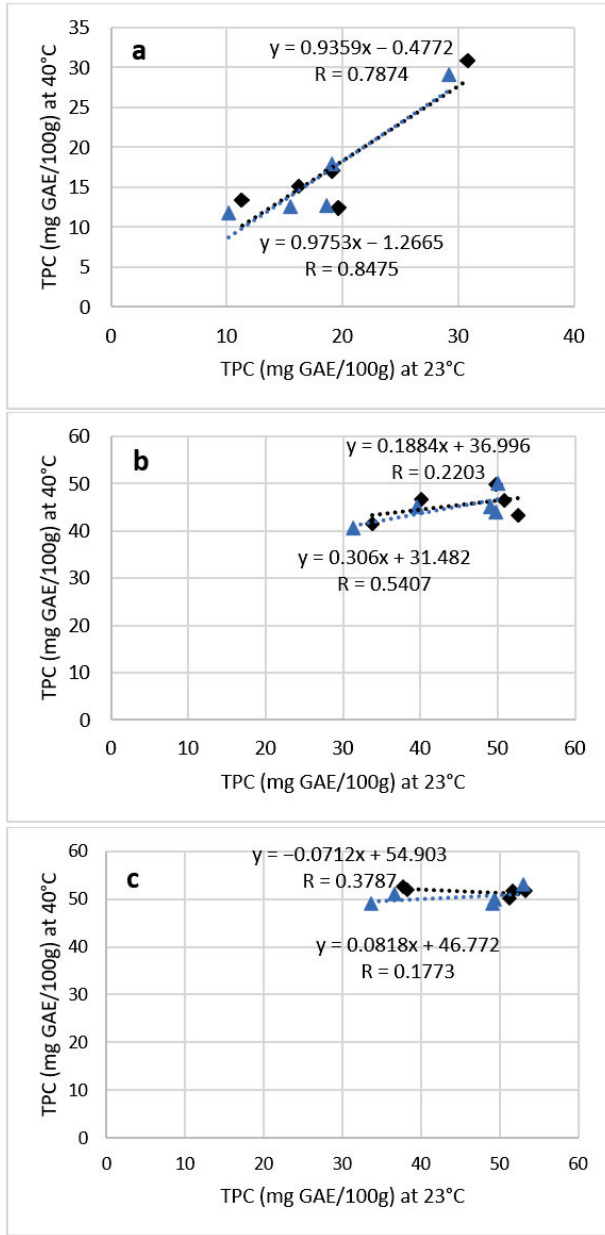

Figure 2. Linear regression models of TPC in FGBB (**a**), FYB (**b**), and MCB (**c**) at 23 °C and 40 °C (rectangle = AL-layered, triangle = AL-free).

4. Conclusions

The results revealed that the stability of phenolic compounds in different fruit, berry, and vegetable purees is product specific, mostly depending on the ingredients used, the amount of these ingredients, and the pH. The most significant decrease in TPC took place with the FGBB puree, with the highest pH and the smallest amount of ingredients containing phenolic compounds. On the other hand, minor changes in TPC took place with the FYB and MCB purees. It was discussed that the FYB puree may have contained

both stable and less stable bioactive compounds. However, the pH of the matrix was also lower, which might have contributed to the compounds being more stable during storage. The smallest decrease in TPC was found for the MCB puree. In this case, the puree consisted only of fruits, berries, and vegetables and had the lowest pH, which may have created the most advantageous environment for keeping the bioactive compounds stable throughout storage.

The results showed that the choice of packaging material did not affect the TPC decrease in each puree. However, this conclusion assumes that the products are mostly stored in dark conditions throughout the supply chain. Therefore, the effect of AL-layered vs. AL-free packaging on the content of total phenols may be different when conducting the tests in environments exposed to light.

To study the suitability of ASLT methodology for assessing the phenolic content changes in these purees, linear regression models were presented. The results showed that the decrease in TPC during 23 °C and 40 °C storage tests was most similar for the FGBB puree. This was also reflected in the highest correlation coefficients for the FGBB puree samples. On the other hand, the correlation coefficients for FYB were lower due to smaller changes during ASLT. With the MCB puree, no significant changes in the TPC took place at 40 °C, resulting in the lowest correlation coefficients. Therefore, the chosen acceleration factor (Q_{10} = 3) was suitable for the FGBB puree but not for the FYB and MCB purees. As a result, it is concluded that the ASLT methodology is suitable for studying the TPC changes in such purees, but the corresponding Q_{10} factors may vary and should be determined based on the chemical profile and ingredient list of the product.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/foods12091777/s1, Table S1. Changes in TPC (mg GAE/100 g) of four-grain puree with banana and blueberry (FGBB), mango-carrot-sea buckthorn puree (MCB), and fruit and yogurt puree with biscuit (FYB) during storage tests at 23 °C and 40 °C.

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Appendix 3

Publication III

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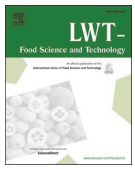

Storage stability of berry mueslis with special focus on phenolic compounds

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ABSTRACT

To investigate stability of phenolic compounds in food products during storage, real-time (RT, at 23 °C) and accelerated shelf-life tests (ASLT, 40 °C) were conducted on modified-atmosphere-packaged strawberry, blueberry, and blackcurrant mueslis. Monitored with LC-MS and HPLC, a clear variation was observed in the phenolic profile of the berry mueslis in both tests, including 29 anthocyanins, 40 flavonols, 16 phenolic acids, and 2 flavan-3-ols. The contents of these phenolic compounds changed differently during storage. Unlike other phenolics, the contents of all identified anthocyanins were significantly decreased in the tests. The modified atmosphere package of the mueslis did not retard anthocyanin degradation at 40 °C. The largest decrease occurred in the first 56 days of ASLT, when 54–66 % of total anthocyanins were lost. The degradation was highly associated with structural features of anthocyanins, including substitution on both anthocyanidins and sugar moieties. Pelargonidin 3-*O*-glucoside, malvidin 3-*O*-arabinoside, and malvidin 3-*O*-galactoside had higher degradation rates (k = 0.0267, 0.0195, and 0.0176 day^{-1}, respectively) than others. Acylation on the sugar moieties also significantly enhanced storage stability of anthocyanins. Our results suggested that the stability of bioactive phytochemicals in food products should be considered when estimating the health-promoting function and sensorial property of the products.

1. Introduction

Berries have been widely applied in the food industry to provide products with unique flavors, delightful colors, and potential health-promoting benefits (Saarniit et al., 2023). As studied for decades, the beneficial effects of berries on human health are mainly attributed to their secondary metabolites, phenolic compounds in particular (Becker Pertuzatti et al., 2021; Ntemiri et al., 2020). Berry-derived phenolic compounds have a wild diversity in chemical structures, presenting mostly as anthocyanins, tannins, flavonols, flavan-3-ols, and hydroxycinnamic acids (Tian et al., 2017). As a major groups of berry phenolics, anthocyanins have been reported as protective effects against the oxidative stress-associated diseases, such as cancers, and cardiovascular or neurodegenerative diseases (Liang et al., 2024). The berry-derived anthocyanins can also lower the incidence of obesity by reducing fatty acid synthesis through inhibiting fatty acid synthase (Singh et al., 2020). In addition to anthocyanins, other minor phenolic groups in berries also contribute to human health as reported extensively (Saarniit et al., 2023).

Yet, berry phenolics degrade during the shelf-life of food products, resulting in a decrease in their bioactivities. Phenolic degradation is dependent on storage conditions such as temperature, light, or oxygen content (Singh et al., 2020). Our previous research suggests that the degradation rate of phenolic compounds is also highly influenced by the type of food matrix. Some food matrix provides an acidic condition that is optimal for phenolic compounds to retain their intact structures (Saarniit et al., 2023). The structural features of berry phenolics also play an essential role in their stability. For example, anthocyanidins are more stable after glycosylation and methylation on their basic structures (Zhao et al., 2017). The improved stability is attributed to the decreasing numbers of hydroxyl groups and increasing numbers of methoxy groups in the B ring of anthocyanidins (Liu et al., 2018). Moreover, the interaction among phenolic compounds or between phenolics and other components (*e.g.*, dietary fiber) is another key factor that affects phenolic degradation rate (Pico et al., 2022). Thus, instead of investigating the degradation of phenolic commercial standards, it is more

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important to study their changes within food matrices. Besides diminishing health beneficial functions, the degradation of phenolics may also cause a large shift in sensorial properties of berry-added products (Tian et al., 2017). Thus, considering the risks to food quality and consumers' acceptance, it is critical to monitor the compositional changes of berry phenolics during the shelf-life of the products.

Accelerated shelf-life testing (ASLT) is a time-efficient method for food manufacturers to assess the quality of foods with relatively long shelf-life. Compared to real-time storage tests (RT) at room temperature, ASLT speeds up the natural deterioration processes of food products without altering the sequence of reactions that occur under normal storage conditions (Calligaris et al., 2019). The acceleration can be achieved by adjusting storage conditions such as temperature, oxygen levels, light exposure, or humidity (Kilcast & Subramanian, 2000). Among which, elevating temperature is most commonly used due to their significant impact on reaction rates (Calligaris et al., 2019). As discussed in our previous study, the mechanism of ASLT relies on the Arrhenius equation, which describes the relationship between temperature and the speed of chemical reactions (Saarniit et al., 2023). The acceleration factor Q_{10} (the number of times that the reaction rate changes with a 10 °C change in temperature) is introduced to calculate the testing time points for ASLT corresponding to room-temperature storage time (ASTM International, 2021; Toledo, 2007).

Although anthocyanins are temperature-sensitive, this moderate elevating temperature (40 °C) allows for meaningful degradation analysis while avoiding unrealistic thermal stress. The temperature of 40 °C is well accepted in previous studies of anthocyanin stability as a compromise between accelerating degradation kinetics and avoiding extreme conditions that may not reflect realistic storage scenarios (De Marchi et al., 2024; Polyiam et al., 2025). To date, the ASLT is rarely used to measure the shelf-life of berry products. Most of the published results have focused only on variation in total phenolic content during ASLT period using colorimetric methods (Saarniit et al., 2023; Sadilova et al., 2006). Our research aims to systematically investigate the stability of phenolic compounds during the shelf-life of commercial food products by using both ASLT (at 40 °C) and RT (at 23 °C). Muesli products added with freeze-dried berry slices (*i.e.*, strawberries, blueberries, and blackcurrants, respectively) were chosen for their popularity as a healthy breakfast in Western countries and increasing interest gained in Asian countries (Dziki et al., 2022). Liquid chromatographic and mass spectrometric methods were applied to monitor compositional variation in anthocyanins, flavonols, flavan-3-ols, hydroxycinnamic acids, and hydroxybenzoic acids at a molecular level. Based on the changes in phenolic concentration, the degradation kinetics of major berry phenolics were determined. Statistical models of first-order kinetics, one-way analysis of variance, and calculation of Q_{10} were used to predict the influence of temperature on phenolic degradation and estimate the storage days in ASLT. As the novelties of our research, we provide new findings of the changes in phenolic profiles, degradation kinetics of anthocyanins, and statistical correlation among different phenolic compounds. These results will offer a reference for food manufacturers to ensure product quality and shelf-life.

2. Materials and methods

2.1. Chemicals

Reference standards of delphinidin, cyanidin, peonidin, petunidin, malvidin, pelargonidin 3-*O*-glucoside, quercetin, ellagic acid, *p*-coumaric acid, (+)-catechin, and *trans*-cinnamic acid were purchased from Sigma-Aldrich (St. Louis, MO, United States). The solvents of LC and MS grade, such as acetonitrile, formic acid, hydrochloric acid, ethyl acetate, and methanol were purchased from Honeywell (Espoo, Finland).

2.2. Ingredients, production and packaging of muesli samples

The muesli samples were produced using rolled oats (Balti Veski AS, Estonia), freeze-dried strawberry (*Fragaria* spp., SB), blueberry (*Vaccinium* spp., BB) and blackcurrant (*Ribes* spp., BC) slices (Freezedry OÜ, Estonia), sugar syrup (Nordic Sugar A/S, Denmark), whole milk powder (Valio OY, Finland), strawberry concentrate (Bayernwald KG, Germany), and vanilla sugar (Santa Maria AS, Estonia).

Three types of mueslis were produced. Strawberry muesli consisted of rolled oats (41.5 g/100 g), sugar syrup (21.9 g/100 g), whole milk powder (17.9 g/100 g), freeze-dried strawberry slices (14.3 g/100 g), strawberry concentrate (4.3 g/100 g), and vanilla sugar (0.2 g/100 g). Blueberry muesli contained rolled oats (43.8 g/100 g), sugar syrup (23.1 g/100 g), whole milk powder (18.9 g/100 g), freeze-dried blueberry slices (9.4 g/100 g), strawberry concentrate (4.5 g/100 g), and vanilla sugar (0.2 g/100 g). Blackcurrant muesli included rolled oats (41.5 g/100 g), sugar syrup (21.9 g/100 g), whole milk powder (17.9 g/100 g), freeze-dried blackcurrant slices (14.3 g/100 g), strawberry concentrate (4.3 g/100 g), and vanilla sugar (0.2 g/100 g). To produce the basis of the muesli, rolled oats, sugar syrup, strawberry concentrate, and vanilla sugar were mixed and baked at 130 °C for 45 min. After that, the baked basis was cooled at room temperature for 4 h. Then, the dry and cooled basis was mixed with whole milk powder and berry slices.

The muesli samples were packaged in stand-up pouches, containing 20 μm Matt-BOPP/12 μm PET/7 μm Aluminum/110 μm LDPE (Dakla-Pack Europe, Netherlands). The oxygen transmission rate of the packaging material was < 0.5 $cm^3/m^2/24$ h and the water vapor transmission rate was < 0.5 $g/m^2/24$ h. In addition, 50 mm × 57 mm of iron-based oxygen absorber (Tianhua Tech Co., Ltd, China) was added into each package.

2.3. Storage test design of muesli samples

Two storage tests were conducted. The packaged mueslis were stored at room temperature (23 °C) and in a climate chamber at 40 °C (Memmert UF110, Germany), respectively. In the test at 23 °C, the testing points of storage time were set at 6 and 12 months. For the ASLT at 40 °C, the testing time points were calculated with Q_{10} factor using Equation (1).

$$Accelerated\ aging\ time\ (AAT) = \frac{Desired\ real\ time\ (RT)}{Q_{10}^{\left(\frac{T_{AA}-T_{RT}}{10}\right)}} \quad (1)$$

where AAT is the accelerated aging time at accelerated aging temperature (T_{AA}) and RT is the real storage time at real storage time temperature (T_{RT}) (ASTM International, 2021). The Q_{10} value was set as 3 (which is a common setting for almost all food products). The time points of the ASLT were calculated to be 28, 56, 89, 120, 169, 197, and 365 days at 40 °C (Choi et al., 2017), to simulate the storage at room temperature for 0.5, 1, 1.5, 2, 3, 3.5, and 6.5 years, respectively.

2.4. Analysis of phenolic compounds

The dried berries (4 replicates for analysis of anthocyanins and 2 replicates for analysis of other phenolic compounds) were first picked from muesli samples at each time point during both storage tests and then crushed into fine powders with mortar and pestle (Supplemental Table 1). Anthocyanins and other phenolic compounds were extracted from the berries using two different methods described in our previous study with a slight modification (Tian et al., 2019). For anthocyanins, approximately 1.0 g of berry powders were mixed with acidified methanol (methanol/hydrochloric acid, 99:1, *v/v*) at a solid/solvent ratio of 1:3 (*w/v*). The extraction was assisted with ultra-sonication (at 45 kHz, for 10 min) and centrifugation (for 10 min, at 1500 × *g*). The supernatants from three-time extraction were combined and diluted to a

final volume of 10 mL with the acidic methanol. For other phenolic compounds, the berry powders (3.8 g) were mixed with 20 mL of aqueous ethyl acetate (water/ethyl acetate, 1:1, *v/v*), followed by 3 min of vortex and 15 min of centrifuge (1500 × *g*). The supernatants after centrifugation were collected and completely dried by using a rotary evaporator (at 35 °C, Heidolph, Germany). The residues were re-dissolved in 3 mL of methanol. The extracts of anthocyanins and other phenolic compounds were filtered with 0.2 mm syringe filters and stored in the freezer at −20 °C till further analyses.

The methods of identifying and quantifying phenolic compounds were described in our previous studies (Tian et al., 2017, 2019). Briefly, the identification was conducted by using a Shimadzu Ultra performance liquid chromatography (UPLC) system equipped with an SPD-M40 photo diode array detector (PDA), and a LCMS-8045 mass spectrometer (MS; Shimadzu Corp., Kyoto, Japan). LC chromatographic separation was performed with a Phenomenex Aeris peptide XB-C18 column (150 × 4.60 mm, 3.6 μm, Torrance, CA, United States). The reject volume was 10 μL. The total flow rate was set to 1 mL/min, and approximately 0.3 mL/min of samples were eluted into mass spectrometers. MS full scan and MS^2 product ion scan were operated in both ESI^+ and ESI^- mode. A Shimadzu LC-30AD liquid chromatograph system coupled with an SPD-M20A diode array detector (Shimadzu Corp., Kyoto, Japan) was used for quantitative analysis of phenolic compounds. All chromatograms were monitored at the wavelength of 520 nm (for anthocyanins), 360 nm (flavonols and ellagic acid derivatives), 320 nm (hydroxycinnamic acids), and 280 nm (flavan-3-ols). The identified compounds were quantified by external reference standards (Supplemental Table 2). Approximately 1 mg of reference compounds were dissolved in 10 mL ethanol and diluted into four different concentrations. The calibration curves were established between peak areas in the HPLC-DAD chromatogram and corresponding concentrations.

2.5. Degradation kinetics of anthocyanins

The degradation of anthocyanins during ASLT was analyzed following the first-order kinetics (Equation (2)).

$$C_t = C_0 \times e^{(-kt)} \quad (2)$$

where C_t and C_0 are the anthocyanin concentrations at Day t and Day 0, respectively. The value of *k* is the rate constant, and t is the storage time (day). The half-life value ($t_{1/2}$) of total anthocyanin content was calculated with Equation (3).

$$t_{1/2} = (\ln 1 / 2) / k \quad (3)$$

2.6. Statistical analyses

The concentration of each identified compound was calculated on the basis of dry weight of berries and the values are expressed as mean ± standard deviation (SD). The *k* values used in anthocyanin degradation kinetics and correlations between individual phenolic compounds in berry slices were calculated using Origin Pro 2018 (Origin Lab, Northampton, MA, United States). Cluster heatmap and correlation heatmap of Pearson's correlation coefficients were performed using MetaboAnalyst 6.0 (www.metaboanalyst.ca). Statistical differences among data were calculated based on one way-ANOVA and Tukey's post hoc test ($p < 0.05$) by IBM SPSS Statistics 28 for Windows (SPSS Inc., NY, United states).

3. Results and discussion

3.1. Phenolic profiles in berry slices

All the phenolic compounds were characterized by MS and MS^2. The identification was based on the MS fragmentation pattern by comparing molecule ions and typical fragment ions with previously reported data (Aaby et al., 2007, 2012; Ancillotti et al., 2017; Becker Pertuzatti et al., 2021; Clifford et al., 2006; Grace et al., 2019; Kelanne et al., 2020; Nie et al., 2017; Pico et al., 2022; Rothwell et al., 2013; Spínola et al., 2015; Tian et al., 2017, 2019; Álvarez-Fernández et al., 2015). As shown in Table 1, 29 anthocyanins were identified in the slices of SB, BB, and BC, presenting as delphinidin, cyanidin, pelargonidin, petunidin, peonidin, malvidin, and their glycosides. Other phenolic compounds from the groups of flavonols (40 compounds), flavan-3-ols (2), hydroxycinnamic acids (13), and hydroxybenzoic acids (3) were also detected from berry samples. Anthocyanins were the major phenolic compounds in these berry slices, the total contents of which (246.8–1086.6 mg/100 g dry weight basis, DW) were much higher than that of other phenolics (10.9–37.4 mg/100 g DW) (Supplemental Table 3-5).

In SB, six anthocyanins were tentatively identified. Pelargonidin and its glycosides accounted for 97.9 % of the total anthocyanin content (246.8 mg/100 g DW) (Fig. 1A). The results were consistent with the observation of anthocyanin contents of SB (216–385 mg/100 g DW) in the research of Wang and Lin (Wang & Lin, 2000). The flavanols found in SB included quercetin, kaempferol, isorhamnetin, and their glycosides. Ellagic acid and its glycosides (hydroxybenzoic acids and derivatives) were only identified in SB among three berry slices.

The total content of eleven anthocyanins in BB was 1086.6 mg/100 g DW, 54.9 % of which were malvidins, followed by 18.7 % delphinidins, 16.1 % petunidins, 9.7 % cyanidins, and 0.6 % peonidins (Fig. 1B). Among flavonols and flavan-3-ols, laricitrins and syringetins (including aglycones and glycosylated forms), as well as (−)-epicatechin were only found in BB. BC contained delphinidins (52.2 %) and cyanidins (47.8 %) with a total content of 355.9 mg/100 g DW (Fig. 1C). Myricetin and its glycosides (flavonols) were identified only in BB and BC. Our results of BB and BC suggested higher levels of anthocyanins in comparison with the data in previous studies (558 mg/100 g DW and 210–250 mg/100 g DW, respectively) (Dobson et al., 2017; Hosseinian & Beta, 2007). This large variation was probably caused by different berry cultivars.

3.2. Changes in major groups of phenolic compounds during storage

All dried berry samples in this study were subjected to the same standardized process of storage and sampling to ensure a reasonable comparison of the results. The changes of anthocyanin contents in SB, BB, and BC slices during ASLT and room-temperature storage are present in Fig. 2A–C. In the ASLT (40 °C), the total anthocyanin content showed a sharp decrease of 63.9 % in SB for 0–28 days but no significant degradation was observed after 89 days (Fig. 2A). Anthocyanin degradation in BB (42.8 % decrease in 28 days) was similar to that observed in SB, followed by a gradual decline after 28-day storage (Fig. 2B). In BC, a rapid degradation of anthocyanins (36.7 %) occurred from 28 to 56 days (Fig. 2C). Different degradation speeds are probably attributed to the stability of dominant anthocyanins with different structures (Dobson et al., 2017). During room-temperature storage, SB showed the largest decline (32.8 %) of total anthocyanin content in 365 days. The total anthocyanin degradation in BB and BC in 12 months at 23 °C was similar (17.4 % and 14.4 %, respectively). Anthocyanin degradations at room-temperature storage in our study were remarkably slower than that in the previous study (Piljac-Žegarac & Šamec, 2011). Piljac-Žegarac and Šamec found that no anthocyanins in SB were detected with colorimetric assay after 4-day storage at 25 °C. Thus, the modified atmosphere package in our study showed retard effect on anthocyanin degradation at room temperature. However, this package did not protect anthocyanin from the fast degradation at elevated temperatures. Most of the anthocyanins in BB (93.4 %), SB (80.0 %), and BC (75.4 %) degraded at 40 °C. For other phenolic compounds, the changes in the total contents fluctuated over 365 days. Generally, the total contents of other phenolics were increased in BB and BC but decreased in SB along with storage time (Fig. 2D–F). In SB, the contents of flavonols and hydroxycinnamic acids were decreased (49.3 % and 24.6 %, respectively), and

Table 1
Identification of phenolic compounds in strawberry (SB), blueberry (BB) and blackcurrant (BC) mueslis by HPLC-DAD-ESI-MS [a]

Tentative identification (abbreviation)	UV $\lambda_{typical}$ (*nm*)	$[M+Na]^+/[M+H]^+/[M-H]^-$ or other ions (*m/z*)	MS^2 (*m/z*)	Presence in			Literature
				BB	BC	SB	
Anthocyanins							
Delphinidin 3-*O*-rutinoside (**De-Rut**)	525	-/611.2/609.2	611.2 → 465.1, **303.1** 609.2 → **300.0**	–	+	–	1–3
Delphinidin 3-*O*-galactoside (**De-Gal**)	520	-/465.1/463.1	465.1 → **303.1** 463.1 → **300.0**	+	–	–	4–7
Delphinidin 3-*O*-glucoside (**De-Glu**)	523	-/465.1/463.1	465.1 → **303.1** 463.1 → **300.0**	+	+	–	1,2,4–7
Delphinidin 3-*O*-(6″-coumaroyl)-glucoside (**De-coGlu**)	530	-/611.2/609.1	611.2 → **303.1** 609.1 → **300.0**	–	+	–	1–3
Delphinidin 3-*O*-(6″-acetyl)-glucoside (**De-acGlu**)	527	-/507.1/505.1	507.1 → **303.1** 505.1 → **300.0**	+	–	–	4,6,7
Delphinidin 3-*O*-arabinoside (**De-Ara**)	524	-/435.1/433.1	435.1 → **303.1** 433.1 → **300.0**	+	–	–	4,6,7
Delphinidin (**De**)	525	-/303.1/301.0		+	+	–	2,7
Cyanidin 3-*O*-rutinoside (**Cy-Rut**)	518	-/595.2/593.2	595.2 → **287.1** 593.2 → **284.0**	–	+	–	1–3
Cyanidin 3-*O*-galactoside (**Cy-Gal**)	516	-/449.1/447.1	449.1 → **287.1** 447.1 → **284.0**	+	–	–	4,6,7
Cyanidin 3-*O*-glucoside (**Cy-Glu**)	515	-/449.1/447.1	449.1 → **287.1** 447.1 → **284.0**	+	+	+	1–10
Cyanidin 3-*O*-arabinoside (**Cy-Ara**)	517	-/419.1/417.1	419.1 → **287.1** 417.1 → **284.0**	+	–	–	6,7
Cyanidin (**Cy**)	523	-/287.1/285.0		+	+	–	2
Pelargonidin 3-*O*-rutinoside (**Pl-Rut**)	503	-/579.2/577.2	579.2 → 433.1, **271.1** 577.2 → **269.1**	–	–	+	9,10
Pelargonidin 3-*O*-glucoside (**Pl-Glu**)	501	-/433.1/431.1	433.1 → **271.1** 431.1 → **269.1**	–	–	+	8–10
Pelargonidin 3-*O*-(6″-malonyl)-glucoside (**Pl-maGlu**)	502	-/519.1/517.1	519.1 → **271.1** 517.1 → 473.1, **269.1**	–	–	+	9,10
Pelargonidin 3-*O*-(6″-succinyl)-glucoside (**Pl-suGlu**)	504	-/533.1/531.1	533.1 → **271.1** 531.1 → 499.1, 431.1, 337.0, **269.1**	–	–	+	phenol-explorer
Pelargonidin (**Pl**)	509	-/271.1/269.1		–	–	+	phenol-explorer
Petunidin 3-*O*-galactoside (**Pt-Gal**)	524	-/479.1/477.1	479.1 → **317.1** 477.1 → **314.0**	+	–	–	4,6,7
Petunidin 3-*O*-glucoside (**Pt-Glu**)	524	-/479.1/477.1	479.1 → **317.1** 477.1 → **314.0**	+	–	–	4–7
Petunidin 3-*O*-(6″-acetyl)-glucoside (**Pt-acGlu**)	530	-/521.1/519.1	521.1 → **317.1** 519.1 → **315.1**	+	–	–	4,6,7
Petunidin 3-*O*-arabinoside (**Pt-Ara**)	525	-/449.1/447.1	449.1 → **317.1** 447.1 → **314.0**	+	–	–	4,6,7
Petunidin (**Pt**)	533	-/317.1/315.1		+	–	–	
Peonidin 3-*O*-galactoside (**Po-Gal**)	517	-/463.1/461.1	463.1 → **301.1** 461.1 → **298.0**	+	–	–	4,6,7
Malvidin 3-*O*-galactoside (**Ma-Gal**)	526	-/493.1/491.1	493.1 → **331.1** 491.1 → **328.1**, 313.0, 299.0	+	–	–	5–7
Malvidin 3-*O*-glucoside (**Ma-Glu**)	526	-/493.1/491.1	493.1 → **331.1** 491.1 → **329.1**, 313.0, 299.0	+	–	–	5–7
Malvidin 3-*O*-(6″-acetyl)-galactoside (**Ma-acGal**)	531	-/535.2/533.1	535.2 → **331.1** 533.1 → **328.1**, 313.0, 299.0	+	–	–	4,6,7
Malvidin 3-*O*-(6″-acetyl)-glucoside (**Ma-acGlu**)	531	-/535.2/533.1	535.2 → **331.1** 533.1 → **329.1**, 313.0, 299.0	+	–	–	4,6,7
Malvidin 3-*O*-arabinoside (**Ma-Ara**)	525	-/463.1/461.1	463.1 → **331.1** 461.1 → **328.1**, 313.0, 299.0	+	–	–	6,7
Malvidin (**Ma**)	535	-/331.1/329.1		+	–	–	
Flavonols							
Myricetin 3-*O*-galactoside (**My-Gal**)	266, 355	-/481.0/479.1	481.0 → **319.0** 479.1 → **315.9**, 287.2, 271.1, 242.3, 214.2, 179.1, 151.0	+	–	–	6
Myricetin 3-*O*-glucoside (**My-Glu**)	256, 266 (sh), 353	-/481.0/479.0	481.0 → **318.7** 479.0 → **315.9**, 287.1, 270.7, 258.7, 242.2	–	+	–	1,2
Myricetin 3-*O*-(6″-*O*-malonyl)-galactoside (**My-maGal**)	257, 266 (sh), 356	-/567.0/565.0	567.0 → **319.1** 565.0 → **315.7**, 287.1, 270.7, 259.5, 242.2, 178.7	–	+	–	1,2
Myricetin 3-*O*-arabinoside (**My-Ara**)	266, 355	473.0/451.0/449.1	449.1 → 316.0, 287.0, 271.0, 214.5, 151.0	–	+	–	1,2
Myricetin-pentoside 1 (**My-Pent 1**)	270, 346	473.0/451.0/449.1	451.0 → **319.0** 449.1 → **316.0**, 287.3, 271.0, 259.4, 241.7, 214.2, 179.4, 151.2	+	–	–	6,11
Myricetin-pentoside 2 (**My-Pent 2**)	260, 350	473.0/451.0/449.1	451.0 → **319.4**	+	–	–	6,11
Myricetin (**My**)	252, 370	-/319.0/317.2	317.2 → 271.2, 179.0, 151.15	+	+	–	1,2,5
Quercetin 3-*O*-galactoside (**Qu-Gal**)	260, 350	-/465.0/463.1	465.0 → **303.3** 463.1 → **300.1**, 271.1, 255.0, 243.2, 151.2	+	+	–	1,4–6,8,11
Quercetin 3-*O*-glucoside (**Qu-Glu**)	257, 354	487.0/465.0/463.1	465.0 → **303.3** 463.1 → **300.0**, 271.1, 255.1, 243.0, 151.3	+	+	+	1,2,4,6,8,11,12

(*continued on next page*)

Table 1 (*continued*)

Tentative identification (abbreviation)	UV $\lambda_{typical}$ (*nm*)	$[M+Na]^+/[M+H]^+/[M-H]^-$ or other ions (*m/z*)	MS^2 (*m/z*)	Presence in			Literature
				BB	BC	SB	
Quercetin 3-*O*-glucuronide (**Qu-Gluc**)	260, 346	-/479.0/477.1	479.0 → **303.1** 477.1 → **301.1**, 271.2, 255.1, 151.3	+	–	+	5,9–11
Quercetin 3-*O*-(6″-*O*-malonyl)-glucoside (**Qu-maGlu**)	256, 266 (sh), 353	573.0/551.0/549.1	551.0 → **303.2** 549.1 → 505.1, **300.0**, 271.1, 255.1, 151.0	+	+	–	1,2,6
Quercetin-acetyl-hexoside 1 (**Qu-acHex 1**)	255, 351	529.0/507.1/505.1	507.1 → **303.2** 505.1 → **300.0**, 271.0, 255.0, 243.0	+	–	–	6,11
Quercetin-acetyl-hexoside 2 (**Qu-acHex 2**)	256, 355	529.0/507.0/505.1	507.0 → **303.0** 505.1 → **300.1**, 271.1, 255.2, 243.0, 151.4	+	–	–	6,11
Quercetin-coumaroyl-hexoside (**Qu-coHex**)	259, 355	-/611.1/609.1	611.1 → **303.4** 609.1 → 462.5, **300.2**, 271.1, 255.2, 150.9	+	–	–	
Quercetin 3-*O*-rhamnoside (**Qu-Rha**)	257, 346	471.0/449.0/447.1	449.0 → **303.0** 447.1 → **300.0**, 271.1, 255.1, 243.2, 151.2	+	–	–	6,11
Quercetin 3-*O*-xyloside (**Qu-Xyl**)	266, 353	457.0/435.0/433.1	435.0 → **303.1** 433.1 → **300.0**, 271.1, 255.1, 243.0, 151.2	+	–	–	11 phenol-explorer
Quercetin 3-*O*-arabinoside (**Qu-Ara**)	258, 353	457.0/435.0/433.2	435.0 → **303.2** 433.2 → **300.0**, 271.0, 255.1, 234.3	+	+	–	1,4,11
Quercetin-pentoside (**Qu-Pent**)	257, 352	457.00/435.3/433.1	435.3 → 303.0	+	–	–	6,11
Quercetin (**Qu**)	255, 366	-/303.0/301.2		+	+	–	1,2,4–6,11
Laricitrin 3-*O*-galactoside (**La-Gal**)	254, 356	517.0/495.1/493.1	495.1 → **333.1** 493.1 → **330.1**, 315.1, 286.9, 271.1, 258.7, 243.1, 151.1	+	–	–	6,11
Laricitrin 3-*O*-glucoside (**La-Glu**)	260, 346	517.0/495.1/493.1	495.1 → **333.0** 493.1 → **330.0**, 314.8, 287.1, 270.9, 259.2, 243.2, 151.5	+	–	–	6,11
Laricitrin-acetyl-hexoside (**La-acHex**)	260, 346	559.0/537.0/535.1	537.0 → **333.2** 535.1 → **330.2**, 314.6, 286.8, 270.9, 259.3, 151.20	+	–	–	6
Syringetin 3-*O*-galactoside (**Sy-Gal**)	261, 345	531.0/509.0/507.1	509.0 → **347.0** 507.1 → **344.0**, 329.1, 314.9, 300.9, 286.2, 272.9, 270.0, 258.0, 242.2, 151.5	+	–	–	6,11
Syringetin 3-*O*-glucoside (**Sy-Glu**)	260, 345	531.1/509.0/507.1	509.0 → **347.0** 507.1 → **344.0**, 329.1, 315.0, 301.0, 286.2, 273.1, 270.2, 257.9, 242.2, 151.5	+	–	–	4–6,11
Syringetin-acetyl-hexoside (**Sy-acHex**)	269, 350	573.0/551.0/549.1	551.0 → **347.1** 549.1 → **344.1**, 328.9, 315.2, 301.0, 287.4, 273.1, 269.8, 257.8, 242.1	+	–	–	11
Syringetin 3-*O*-rhamnoside (**Sy-Rha**)	260, 346	515.1/493.0/491.1	493.0 → **347.1** 491.1 → **344.0**, 329.0, 286.9, 272.7	+	–	–	11
Syringetin-pentoside (**Sy-Pent**)	265, 345	501.0/479.0/477.1	479.0 → **347.1** 477.1 → **344.1**, 329.4, 315.2, 301.1, 286.0, 273.2, 258.0, 242.2, 151.6	+	–	–	6,11
Syringetin (**Sy**)	265, 368	-/347.0/345.2		+	–	–	11
Kaempferol 3-*O*-rutinoside (**Ka-Rut**)	266, 353	-/595.1/593.1	593.1 → **284.1**	–	+	–	1,2
Kaempferol 3-*O*-galactoside (**Ka-Gal**)	265, 346	471.0/449.0/447.1	449.0 → **287.1** 447.0 → **284.1**, 255.2, 227.1	–	+	+	1,2,8,12
Kaempferol 3-*O*-glucuronide (**Ka-Gluc**)	265, 346	485.0/463.0/461.0	463.0 → **287.0** 461.0 → **285.0**, 255.0	–	–	+	8,10,12
Kaempferol-hexoside 1 (**Ka-Hex 1**)	265, 346	-/449.1/447.1	449.0 → **287.0**	–	+	–	8
Kaempferol-hexoside 2 (**Ka-Hex 2**)	263, 346	471.1/449.0/447.1	449.0 → **287.1** 447.0 → **284.0**, 255.0, 227.2	–	+	–	8
Kaempferol 3-*O*-(6″-*O*-malonyl)-glucoside (**Ka-maGlu**)	266, 346	557.0/535.0/533.1	535.0 → **287.1** 533.1 → **284.1**, 255.2, 227.0	–	+	+	1,9,10
Kaempferol-acetyl-hexoside (**Ka-acHex**)	267, 351	513.1/491.1/489.1	491.1 → **287.1** 489.1 → **284.1**, 255.2, 227.1	–	–	+	8,12
Kaempferol-pentoside (**Ka-Pent**)	265, 345	441.0/419.0/417.1	419.0 → **287.0** 417.1 → **284.0**, 255.0, 226.9	+	–	–	6
Kaempferol (**Ka**)	265, 368	-/287.1/285.1		+	–	–	5
Isorhamnetin 3-*O*-glucoside (**Is-Glu**)	265, 346	501.0/479.0/477.1	479.0 → **317.1** 477.1 → **314.1**, 299.1, 285.0, 271.1, 257.1, 243.0, 226.7	–	+	–	1
Isorhamnetin 3-*O*-glucuronide (**Is-Gluc**)	265, 346	515.1/493.1/491.1	493.1 → **317.0** 491.1 → **315.1**, 300.0, 270.6, 254.7, 243.1	–	–	+	8,12
Isorhamnetin 3-*O*-(6″-*O*-malonyl)-galactoside (**Is-maGal**)	255, 265 (sh), 345	587.0/565.0/563.1	565.0 → **317.0** 563.1 → 519.1, **314.1**, 299.2, 285.1, 271.0, 256.6, 243.1	–	+	–	1
Flavan-3-ols							
(+)-Catechin (**Cat**)	280	-/291.1/289.2		+	–	+	1,2,4–6,8–10,12
(−)-Epicatechin (**ECat**)	280	-/291.1/289.2		+	–	–	1,2,4–6
Hydroxycinnamic acid derivatives							
5-*O*-Cafferoylquinic acid (**5-CaQA**)	295 (sh), 328	377.1/355.1/353.2	355.1 → 163.3, 145.1 353.2 → 191.2, 135.3	+	+	–	1,6
3-*O*-Cafferoylquinic acid (**3-CaQA**)	295 (sh), 323	377.0/355.1/353.2	355.1 → 163.3, 145.1 353.2 → 191.2, 135.3	+	–	–	4–6,11

(*continued on next page*)

Table 1 (*continued*)

Tentative identification (abbreviation)	UV $\lambda_{typical}$ (*nm*)	$[M+Na]^+/[M+H]^+/[M-H]^-$ or other ions (*m/z*)	MS^2 (*m/z*)	Presence in			Literature
				BB	BC	SB	
Cafferoyl-glucose (**Ca-Glu**)	290 (sh), 327	365.0/-/341.2	341.2 → **179.2**, 161.3, 133.3	–	+	–	1,2,6
Caffeic acid (**CaA**)	290 (sh), 327	-/181.1/179.3		+	+	+	2,4–6
Caffeic acid derivative 1 (**Ca der1**)	290 (sh), 326	359.1/337.0/335.2	337.0 → 163.2, 144.9 335.2 → 179.2, 161.3, 135.3	+	–	–	6
Caffeic acid derivative 2 (**Ca der2**)	290 (sh), 325	391.1/369.1/367.2	369.1 → 163.25, 145.2 367.2 → 179.2, 161.3, 135.3	+	–	–	6
Caffeoyl-coumaroylquinic acid (**CaCoQA**)	290 (sh), 316	523.0/501.1/499.1	499.1 → 191.4, 173.4, 163.4, 161.1, 155.1135.2	+	–	–	13
Coumaroyloxymethylene-glucopyranosyloxy-butenenitrile (**Co-meGlu-B**)	313	444.0/422.1/420.2	444.0 → 260.1 420.2 → 163.4, 145.4, 119.4	–	+	–	1,2
p-Coumaroyl-glucose (**Co-Glu**)	290 (sh), 323	349.0/-/325.3	325.3 → **163.3**, 145.2	–	+	+	1,2,6,9,10
p-Coumaroyl-hexose (**Co-Hex**)	290 (sh), 323	349.0/-/325.3	325.3 → **163.3**, 145.2, 117.3	–	–	+	6,8–10,12
p-Coumaric acid (**CoA**)	295 (sh), 323	183.05/165.2/163.4		+	+	+	2,5,12
Cinnamoyl-glucose (**Ci-Glu**)	284	333.1/311.1/309.3	333.1 → 185.2, 171.4	–	–	+	8,10
Feruloyloxymethylene-glucopyranosyloxy-butenenitrile (**Fe-meGlu-B**)	328	474.0/452.1/450.2	474.0 → 290.1 450.2 → 193.1, 160.0, 151.6, 149.0, 134.3	–	+	–	1,2
Hydroxybenzoic acid derivatives							
Ellagic acid-deoxyhexose (**El-Deox**)	282, 371	-/449.1/447.1	449.1 → **303.0**, 286.9 447.1 → **300.0**	–	–	+	8–10,12
Ellagic acid-rhamnose (**El-Rha**)	282, 365	-/449.1/447.1	449.1 → **303.0**, 286.9 447.1 → **300.0**	–	–	+	12
Ellagic acid (**ElA**)	252, 368	-/303.0/301.2		–	–	+	9,10,12
others							
unknown phenolic acid 1 (**unknown 1**)	313	-/325.1/323.3	325.1 → 147.1, 119.2 323.3 → 145.2, 117.3	–	+	–	
unknown phenolic acid 2 (**unknown 2**)	311	-/325.1/323.2	325.1 → 147.1, 119.2 323.2 → 145.3, 117.4	–	+	–	
unknown phenolic acid 3 (**unknown 3**)	269, 300	343.0/321.0/319.2	319.2 → 183.3, 139.1, 115.5, 109.2	+	–	–	

[a] The literatures in this Table include: (1) Tian, Y., *et al.* https://doi.org/10.1021/acs.jafc.9b00033; (2) Kelanne, N., *et al.* https://doi.org/10.1021/acs.jafc.0c03354; (3) Tian, Y., *et al.* https://doi.org/10.1016/j.foodchem.2016.09.145; (4) Grace, M. H., *et al.* https://doi.org/10.1016/J.FOODCHEM.2018.10.101; (5) Pico, J., *et al.* https://doi.org/10.1016/J.JFCA.2022.104412; (6) Ancillotti, C., *et al.* https://doi.org/10.1007/s00216-016-0067-y; (7) Nie, Q., *et al.* https://doi.org/10.1002/jsfa.7885; (8) Spínola, V., *et al.* https://doi.org/10.1016/J.FOODCHEM.2014.09.163; (9) Aaby, K., *et al.* https://doi.org/10.1021/jf0702592; (10) Aaby, K., *et al.* https://doi.org/10.1016/j.foodchem.2011.10.037; (11) Becker Pertuzatti, P., *et al.* https://doi.org/10.1016/J.FOODCHEM.2020.127958; (12) Antonia, M. A., *et al.* https://doi.org/10.1021/jf506076n; (13) Clifford, M. N., *et al.* https://doi.org/10.1021/JF060536P; and Phenol-Explorer database, 2015, http://phenol-explorer.eu/.

flavan-3-ol ((+)-catechin) was not detected after 56 days. The content of hydroxybenzoic acids in SB was increased by 2 folds in ASLT. In contrast, the changing trends of other phenolic groups in BB and BC were opposite to the trends in SB. In BB, the contents of flavonols, flavan-3-ol and hydroxycinnamic acids after 365-day storage were increased by 1.5–1.9 folds compared to 0 day. An increase in both flavonols and hydroxycinnamic acids (2.2 and 2 folds, respectively) was also observed in BC.

In our study, an ASLT of 28 and 56 days was planned to simulate 6- and 12-month of RT, respectively. However, the total anthocyanin contents after 6- and 12-months of RT were 1.2–2 folds higher than that under the corresponding accelerated storage situation at 40 °C (Fig. 2A–C). The results were consistant with the previous study, in which the reductions of total anthocyanins at high temperatures of 60 °C and 80 °C (60–85 % degradation during 3-day storage) were significantly faster than that at 25 °C (3 % degradation for 14 days) (Fracassetti et al., 2013). Additionally, anthocyanins in different groups have shown varying degradation rates (46.5–90.0 %) in ASLT and room-temperature (2.7–33.4 %) during 12-month storage. This is attributed to the different number and position of hydroxyl and methoxy groups as well as sugar moieties linked to the anthocyanin aglycones (Liu et al., 2018).

For other phenolic compounds, the total contents in SB after 12-month storage at 23 °C were 1.9 folds higher than that after 56 days at 40 °C (Fig. 2D). On the contrary, other phenolic contents in BB and BC at room-temperature storage were 17.4 % and 25.4 %, respectively; which were lower than those in the ASLT (Fig. 2E and F). As the major flavan-3-ols identified in SB, (+)-catechin degraded significantly faster in 56-day storage at 40 °C than in the corresponding 12-month storage at 23 °C. Yet, the opposite degradation performance of flavan-3-ols (99.3 % (+)-catechin and 0.7 % (−)-epicatechin) was observed in BB, showing 6.1-folds higher content in 56-day storage at 40 °C than that in 12-month storage at 23 °C. The mechanism behind the different degradation pattern of flavan-3-ols is still unclear due to the complexity of phenolic compounds in the studied berry slices and the unveiled conversion pathway among them. One of the possible reasons is that the type and amount of added sugars (especially as sucrose and fructose) in food matrices could affect the degradation of polyphenols in berry products (Hanuka Katz et al., 2020). The effect of sugars on polyphenol degradation was due to a combination of several mechanisms, including decreased oxygen solubility, chelation of transition metal ions, and scavenging of reactive oxygen species (Hanuka Katz et al., 2020). Interestingly, this effect was also influenced by the berry variety. For example, by adding powdered sugar to SB, the content of catechin in the cultivar ELKAT (41.1 mg/kg, fresh weight) was higher than that in the cultivar *Senga sengana* (22.2 mg/kg, fresh weight) after 6-month frozen storage (Oszmiański et al., 2009). Therefore, the sugar syrup added to berry mueslis in this study might be one of the reasons that led to different degradation pattern of catechin.

3.3. Changes in individual phenolic compounds during storage

A heatmap was used to reveal the content changes in individual phenolic compounds in berry slices during storage (Fig. 3A–C). In SB, all the anthocyanins and most of the other phenolic compounds degraded

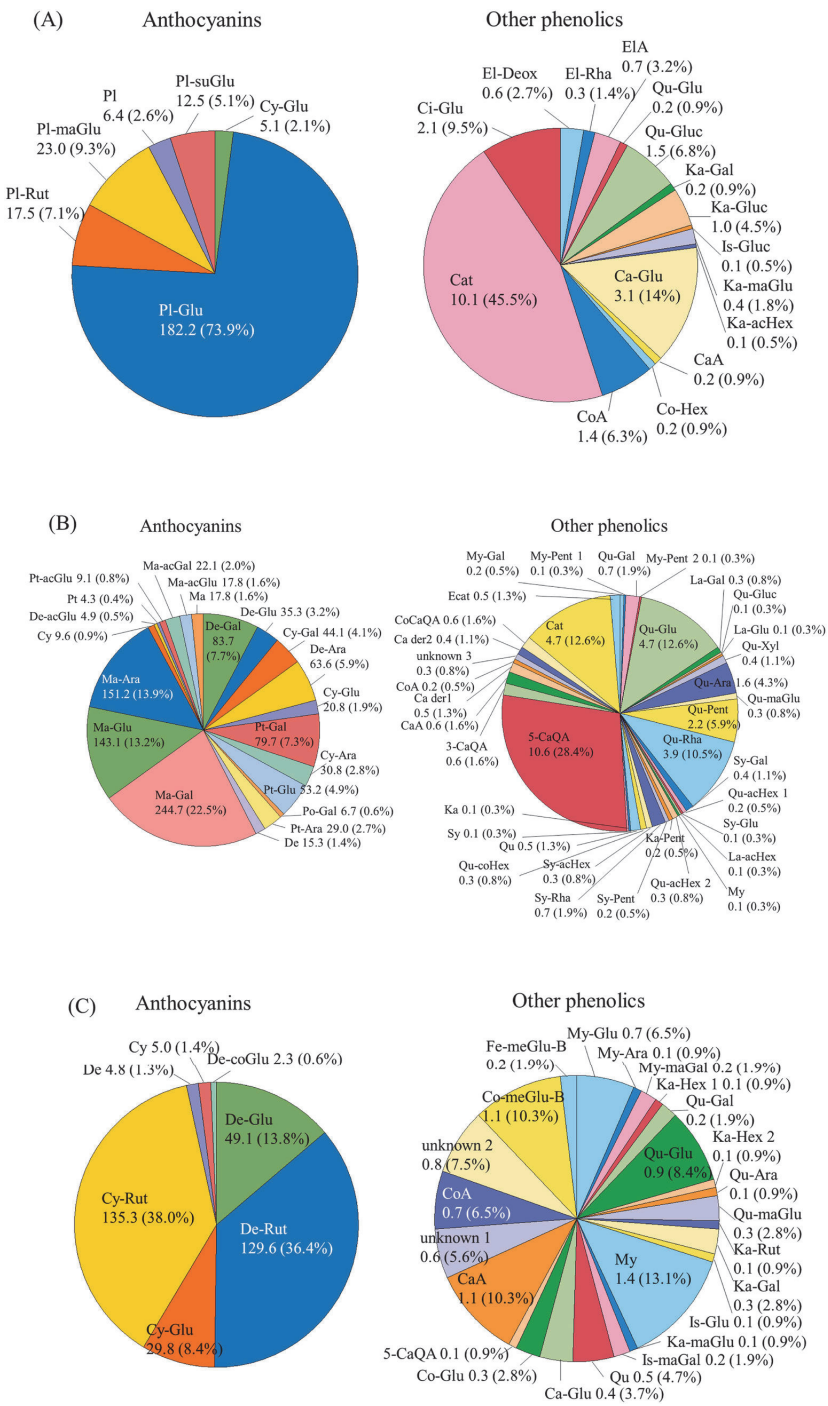

Fig. 1. Relative profiles of anthocyanins and other phenolic compounds of strawberry (A), blueberry (B) and blackcurrant (C) mueslis in Day 0. Each compound was presented as an abbreviation of compound name with compound content in the unit of mg/100 g DW (percentage of compound in total anthocyanin or total other phenolics).

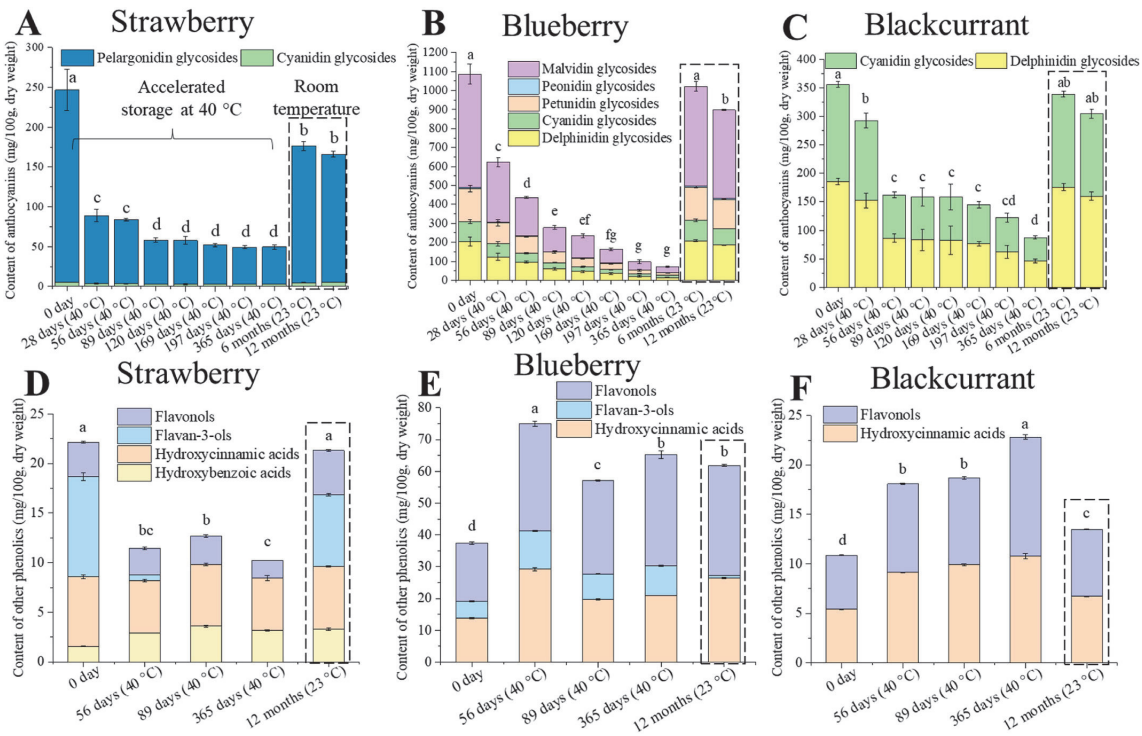

Fig. 2. Changes in the contents of anthocyanins (A–C) and other phenolic compound groups (D–F) in the studied berry slices during ASLT and room-temperature storage (room-temperature storage shown as the columns with dashed lines). Lowercase letters indicate statistical significance (Tukey' test), which was set at $p < 0.05$.

along with time in ASLT (Fig. 3A). Other phenolic compounds with significant increasing contents included isorhamnetin 3-*O*-glucuronide, kaempferol-acetyl-hexoside, ellagic acid, and *p*-coumaric acid.

In the hierarchical cluster analysis of BB, anthocyanins were separated from the categories of other phenolics. At the bottom part of the heatmap (Fig. 3B), individual anthocyanins degraded along with ASLT time. The contents of most flavonols were increased in ASLT except for quercetin 3-*O*-glucuronide, the content of which was slightly decreased. For most of the hydroxycinnamic acids, their contents were slightly increased while the contents of 3-*O*-caffeoylquinic acid and caffeic acid showed no significant difference between 0 day and 365 days.

In BC, individual anthocyanin contents were declined in the ASLT (Fig. 3C). Most flavonols and hydroxycinnamic acids were accumulated along with storage time. The exceptions included myricetin 3-*O*-(6″-*O*-malonyl)-galactoside, quercetin 3-*O*-(6″-*O*-malonyl)-glucoside, and coumaroyloxymethylene-glucopyranosyloxy-butenenitrile, the contents of which showed no significant change.

In ASLT, the degradations of the dominant anthocyanins in SB (pelargonidin 3-*O*-glucoside, 73.8 %) and BC (delphinidin 3-*O*-rutinoside, 36.4 %; and cyanidin 3-*O*-rutinoside, 38.0 %) were in proportion to the total anthocyanin content, while malvidin 3-*O*-galactoside (22.5 %) and malvidin 3-*O*-arabinoside (13.9 %) in BB had a larger decline compared to the total anthocyanins. As a result, elevating temperature to 40 °C affected individual phenolic compounds differently.

The degradation rates of anthocyanins in berry slices were also compared during 56-day storage in ASLT to the corresponding 12-month storage at 23 °C. In SB and BB, most of the individual anthocyanins and other phenolics showed higher contents in 12-month storage at 23 °C than 56-day storage at 40 °C. In BC, similar results were observed in individual anthocyanins. However, more individual flavonols and hydroxycinnamic acids in BC were detected in 56-day storage at 40 °C than in 12-month storage at 23 °C. On the other hand, some other phenolic compounds were well-fit in the accelerated storage model, showing no significant or slight difference between real time storage and corresponding simulated storage. The accelerated storage model can be applied for specific compounds such as caffeic acid and ellagic acid in SB, myricetin 3-*O*-galactoside, myricetin pentoside isomer 2 and quercetin-acetyl-hexoside isomer 2 in BB, and quercetin 3-*O*-(6″-*O*-malonyl)-glucoside, kaempferol 3-*O*-(6″-*O*-malonyl)-glucoside and kaempferol hexoside 1 in BC.

3.4. Correlation among the studied phenolic compounds

The correlation of phenolic change in berry slices in ASLT are shown in Fig. 4A–C. Generally, anthocyanins in all studied berry slices showed negative correlation to other phenolic compounds in our study. In SB, both hydroxycinnamic acids and hydroxybenzoic acids showed stronger negative correlations with anthocyanins compared to flavonols (Fig. 4A). Flavan-3-ol ((+)-catechin) positively correlated to anthocyanins and other phenolics, except ellagic acid-rhamnose, kaempferol-acetyl-hexoside, and *p*-coumaroyl-hexose. Previous study demonstrated that during degradation, sugar moieties were removed from anthocyanins (from C-ring), generating aglycones (Sadilova et al., 2006). Aglycones were further broken into smaller phenolic compounds by removing hydroxyl, methyl, and other functional groups and by aromatic rings cleavage. Phenolic acids are common degradation products from the cleavage of B-ring. Consisting with these previous findings, in our study, pelargonidin 3-*O*-glucoside was negatively correlated to two

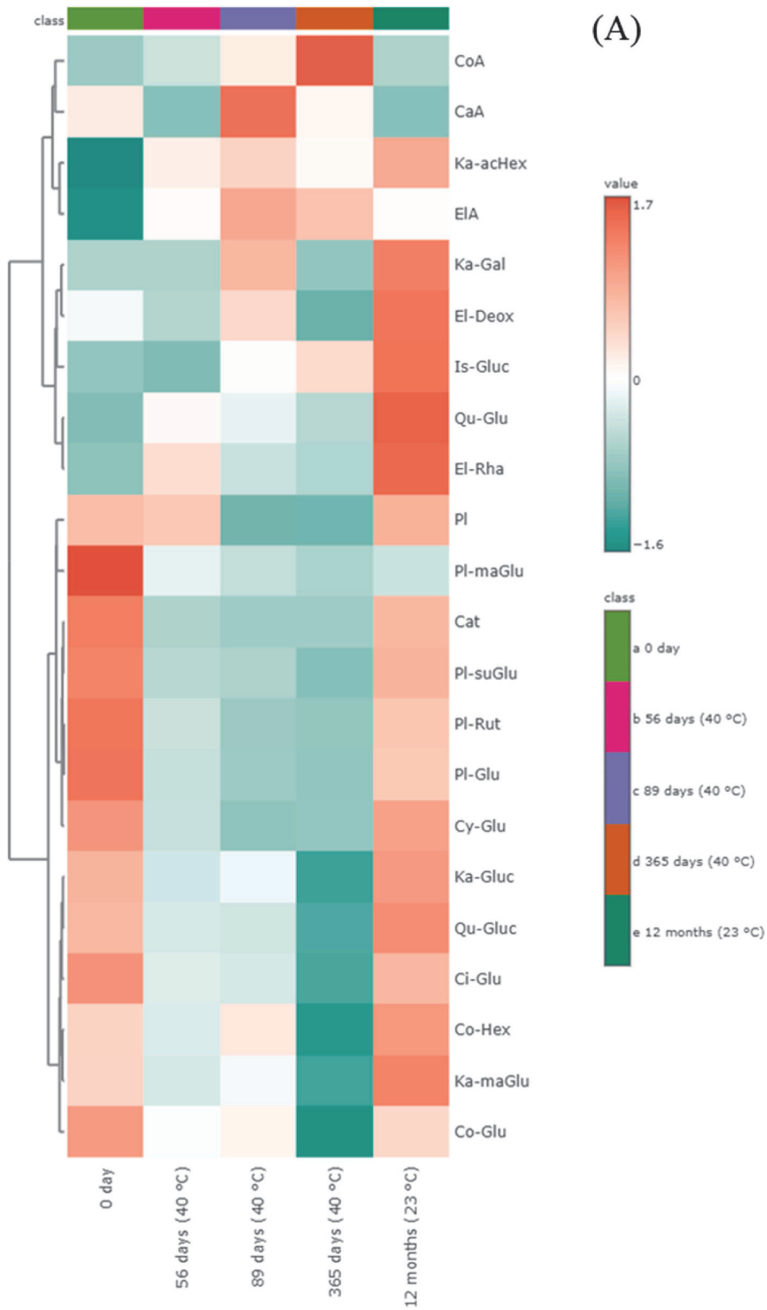

Fig. 3. Relative changes in contents of individual phenolic compounds in strawberry (A), blueberry (B) and blackcurrant (C) mueslis during ASLT and room-temperature storage. In the heatmaps, grids with a color-scale from red to white to green represent the data values from high to medium to low.

phenolic acids (*p*-coumaric acid and ellagic acid) in the studied SB, indicating the possible conversion pathway (Sadilova et al., 2006). The negative correlation between kaempferol 3-*O*-(6″-*O*-malonyl)-glucoside and kaempferol-acetyl-hexoside was probably due to the loss of carbon dioxide from flavonoid malonyl-glycosides and generating corresponding flavonoid acetyl-glycosides as mentioned in Horowitz and Asen's research (Horowitz & Asent, 1989).

In BB, flavonols showed stronger negative correlations with

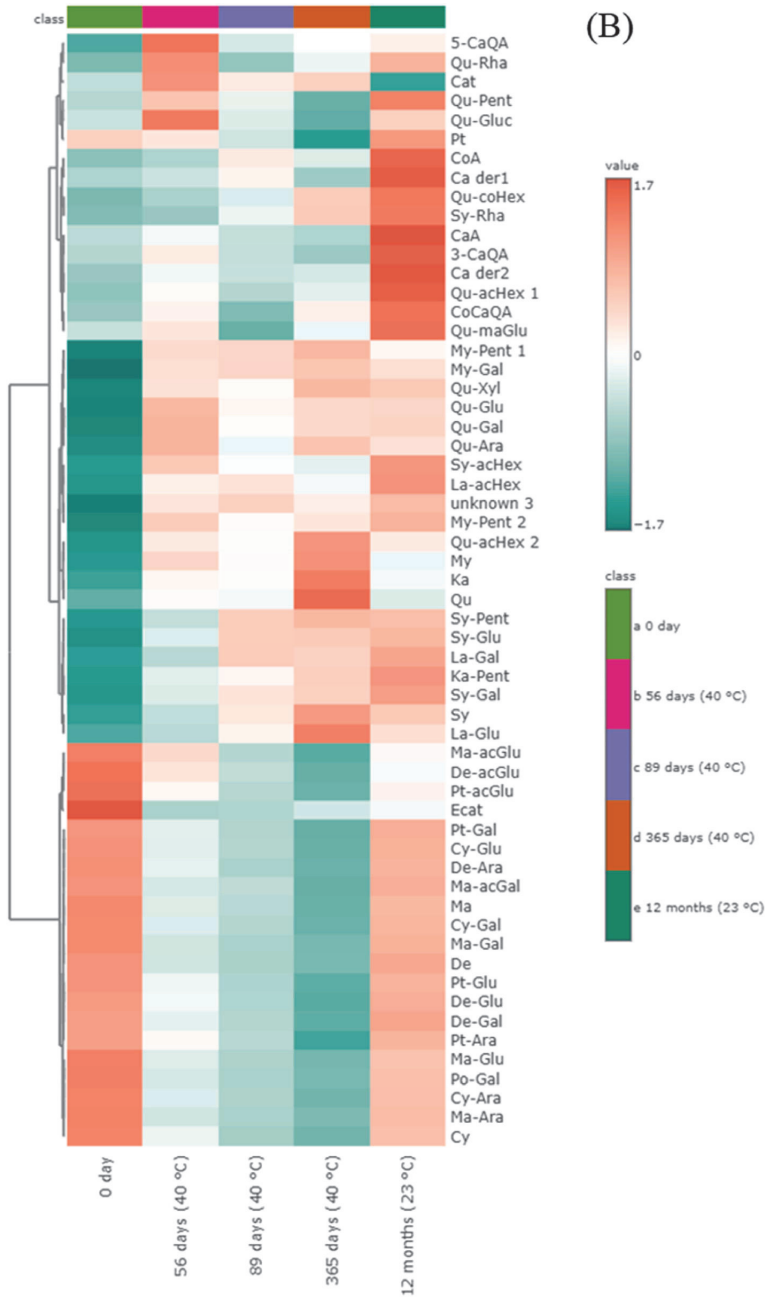

Fig. 3. (*continued*).

anthocyanins than hydroxycinnamic acids did (Fig. 4B). Consisting with the negative correlations observed in this study, quercetin glycosides were probably the degradation metabolites of cyanidin glycosides as stated in the research of Chen et al. (Chen et al., 2020). According to another study, cyanidin 3-*O*-glucoside might degrade into caffeoylquinic acid, which was consistent with the negative correlation between them in our study (Chen et al., 2020). Interestingly, (−)-epicatechin (flavan-3-ols) positively correlated to anthocyanins and negatively correlated to other phenolics. (+)-Catechin, the other flavan-3-ols in BB, correlated with anthocyanins and other phenolics in an opposite way as (−)-epicatechin did. The correlation between (+)-catechin and (−)-epicatechin was negative. The epimerization could contribute to the increase content of catechin and epicatechin degradation (Lončarić et al., 2018). In BC, anthocyanins negatively correlated to flavonols and

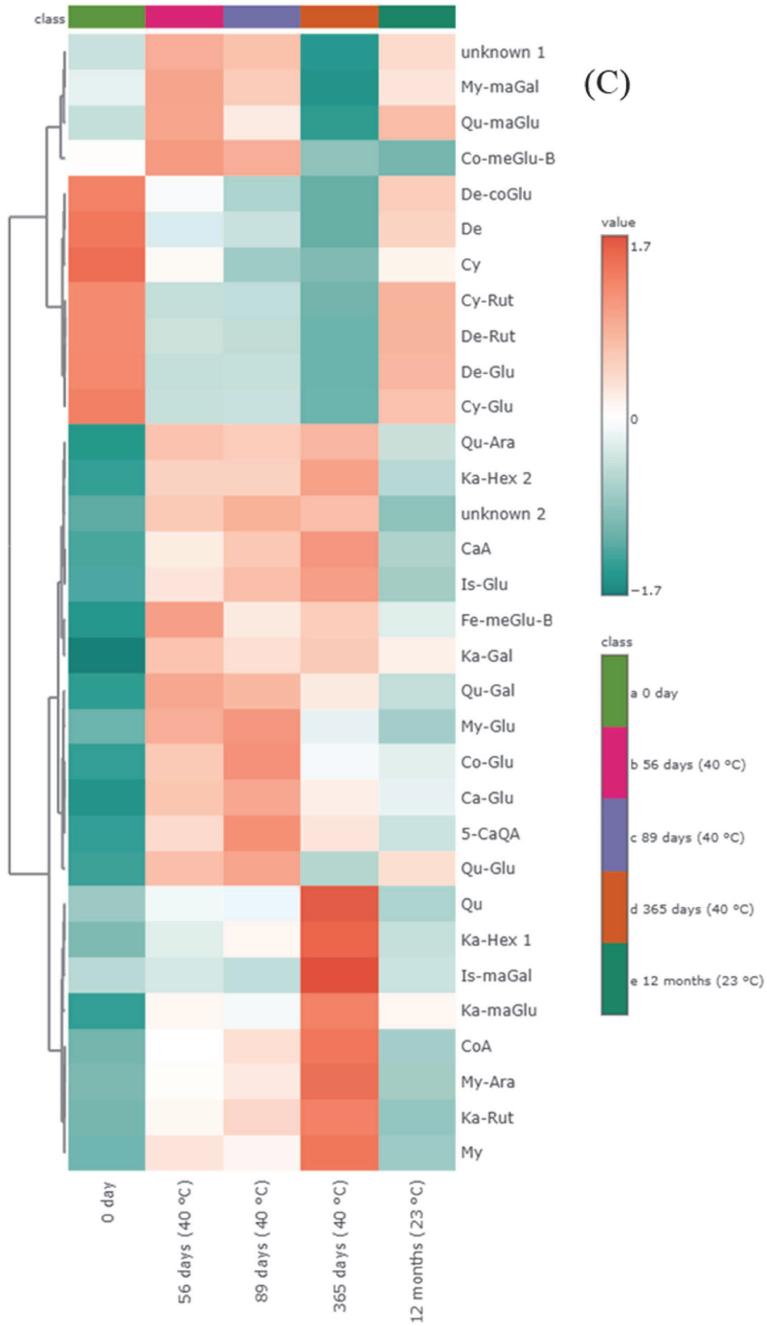

Fig. 3. (*continued*).

hydroxycinnamic acids (Fig. 4C). Flavonols positively correlated to hydroxycinnamic acids in general.

3.5. Degradation kinetics of anthocyanins in ASLT

Anthocyanins with various structures showed different degradation rates in ASLT and the rate constants were represented by the *k* values. As shown in Table 2, pelargonidin derivatives (*k* of 0.0147) degraded much faster than cyanidins (*k* of 0.0020) in SB. In BB, the degradation rate of compounds followed the descending order of malvidins (*k* of 0.0167), delphinidins (*k* of 0.0123), cyanidins (*k* of 0.0117), petunidins (*k* of 0.0115), and peonidins (*k* of 0.0115). Delphinidins (*k* of 0.0056)

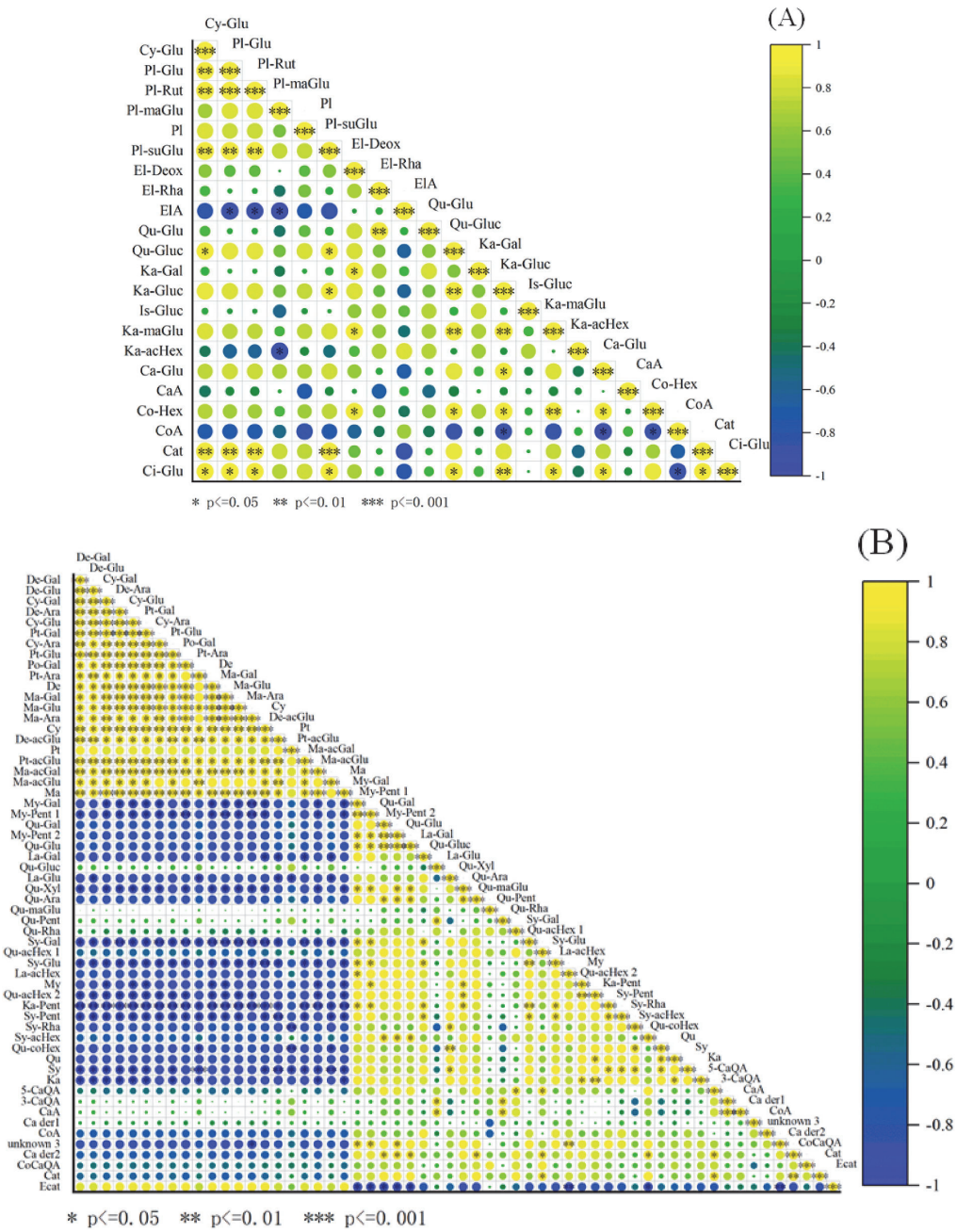

Fig. 4. Correlations between contents of individual phenolic compounds in strawberry (A), blueberry (B) and blackcurrant (C) mueslis in ASLT. In the correlation heatmaps, yellow and blue indicate positive and negative correlations, respectively. The correlation value is depicted as a size of the circle.

degraded faster than cyanidins (*k* of 0.0055) in BC. The highest *k* value of malvidins showed the highest degradation rate, indicating the substitution of hydroxyl groups of the B ring by the methoxy groups decreased the stability of anthocyanins during storage at 40 °C. This result was consisting with the study of Fleschhut et al., in which the stability of commercial standards of malvidin, cyanidin, delphinidin, pelargonidin, peonidin and their glycosides were monitored up to 5 h at 37 °C (Fleschhut et al., 2006). However, in another research of the stability of anthocyanins in red wine (pH was adjusted to 1.5), malvidin 3-*O*-glucoside was more stable than the 3-*O*-glucosides of delphinidin

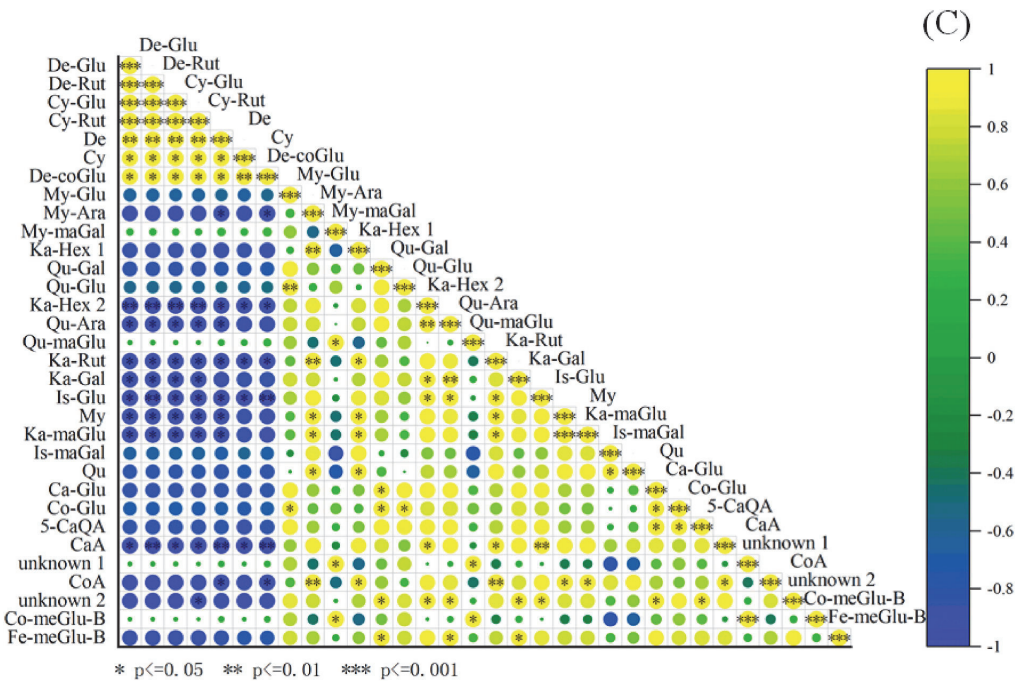

Fig. 4. (*continued*).

and petunidin during simulated digestion process (Liu et al., 2018). Since digestive enzymes were excluded in that research, the reason of different degradation rates of malvidins might be attributed to the food matrix effect and environment pH (Hanuka Katz et al., 2020). Besides, the faster degradation rate of delphinidin derivatives than cyanidin derivatives was explained as more hydroxyl groups in the B ring of delphinidins decreasing their stability (Dobson et al., 2017). In addition to different types of aglycones, the rate of degradation is highly dependent on the attached position and number of sugar moiety and acylated glycosyl groups on the anthocyanidins. In BB, the k values of delphinidins, cyanidins, and malvidins followed the increasing order of glucoside > galactoside > arabinoside from the most to the least stable. The results were in accordance with the findings of previous research, in which the storage stability of 15 anthocyanins in a BB product was compared (Trošt et al., 2008). Anthocyanins with hexose as sugar moiety (*e.g.*, glucose and galactose) exhibited higher stability than those attached with pentose (*e.g.*, arabinose). It is likely due to an increased steric hindrance caused by the larger structures of sugars (Fracassetti et al., 2013). In SB, pelargonidin 3-*O*-rutinoside (k of 0.0041) showed better stability than pelargonidin 3-*O*-glucoside (k of 0.0267). On the contrary, in BC, delphinidin 3-*O*-rutinoside and cyanidin 3-*O*-rutinoside had higher k values than their glucosides, respectively.

Acylation increased the k values of glycosylated anthocyanins in all our studied berries, indicating that acylation enhanced the resistance of anthocyanins to storage degradation. The stability of acylated anthocyanins is increased due to the intramolecular folding and creation of a steric hindrance by acyl groups (Zhao et al., 2017). Additionally, the stability of anthocyanins may also be influenced by the nature of acylated groups (Zhao et al., 2017). For example, in SB, pelargonidin 3-*O*-(6″-succinyl)-glucoside showed lower k value (0.0018) than pelargonidin 3-*O*-(6″-malonyl)-glucoside (k of 0.0066), indicating that the succinyl group might possess a stronger ability to stabilize pelargonidin than the malonyl group.

Moreover, the first-order kinetic model was used to describe the temperature-dependent degradation of anthocyanins in different berry samples (Table 2). The values of the determination coefficient (R^2) showed the fit between experimental values and first-order reaction. In the ASLT, most of the anthocyanins in BB had high R^2 values, ranging from 0.9064 to 0.9829. Lower values of R^2 were found among the anthocyanins in SB (0.4913–0.7146) and BC (0.8025–0.8190). As a result, compared to SB and BC, the ASLT model might be more suitable to assess the degradation rate of anthocyanins in BB.

3.6. Estimation of ASLT storage time based on Q_{10} factor

To conduct an ASLT test on berry-rich mueslis, an acceleration factor Q_{10} of 3 (a common setting for almost all food products) was selected (Choi et al., 2017). However, the comparison of test results at 23 °C and 40 °C in our study showed that the concentrations of anthocyanins declined significantly faster at higher temperatures, with equivalent changes to those observed occurring within just 8–18 days (Table 2). Therefore, to accurately reflect the changes in anthocyanin contents of berry-rich mueslis at room temperature, the acceleration factor Q_{10} must be significantly higher. Knowing the estimated storage time at 40 °C reflecting the changes at 23 °C for 365 days, corresponding Q_{10} values for total and dominant anthocyanins in each berry muesli were calculated (Table 3). Since SB showed the largest decline in anthocyanin content in RT (32.8 %) but also required the longest time for accelerated degradation (18 days), the Q_{10} value used to accelerate total anthocyanin degradation in SB was the lowest among the berries ($Q_{10} = 6$). In contrast, as BC had the smallest decline in anthocyanin content yet required the shortest time to reach equivalent degradation under accelerated conditions, the acceleration factor for conducting ASLT on BC is the highest ($Q_{10} = 9$). When assessing the quality of berry products under accelerated conditions based on the decline in specific anthocyanin concentrations, it is important to consider that different acceleration factors apply to them. For example, the accelerated degradation of total anthocyanin content in BB was described by $Q_{10} = 8$, but for

Table 2
Modelling and estimating the degradation of total and individual anthocyanins during storage at 40 °C using the first order kinetics.

Compound	k (day^{-1}) ± standard deviation	R^2	$t_{1/2}$ (days)	Estimated storage time (days) in ASLT[a]
SB				
Total anthocyanins	0.0139 ± 0.0044	0.7035	50	18
Total cyanidins (aglycones and glycosides)	0.0020 ± 0.0004	0.4913	350	–
Total pelargonidins (aglycones and glycosides)	0.0147 ± 0.0046	0.7146	47	18
Cyanidin 3-*O*-glucoside	0.0020 ± 0.0008	0.4913	350	–
Pelargonidin 3-*O*-glucoside	0.0267 ± 0.0067	0.8641	26	13
Pelargonidin 3-*O*-rutinoside	0.0041 ± 0.0018	0.4754	170	–
Pelargonidin 3-*O*-(6″-malonyl)-glucoside	0.0066 ± 0.0027	0.5220	105	112
Pelargonidin (the aglycone)	0.0001 ± 0.0000	0.4665	4951	–
Pelargonidin 3-*O*-(6″-succinyl)-glucoside	0.0018 ± 0.0007	0.5086	385	–
BB				
Total anthocyanins	0.0142 ± 0.0014	0.9732	49	10
Total delphinidins (aglycones and glycosides)	0.0123 ± 0.0011	0.9790	56	3
Total cyanidins (aglycones and glycosides)	0.0117 ± 0.0013	0.9602	59	13
Total petunidins (aglycones and glycosides)	0.0115 ± 0.0009	0.9829	60	7
Total peonidins (aglycones and glycosides)	0.0115 ± 0.0020	0.9064	60	16
Total malvidins (aglycones and glycosides)	0.0167 ± 0.0018	0.9705	41	12
Delphinidin 3-*O*-galactoside	0.0124 ± 0.0009	0.9844	56	–
Delphinidin 3-*O*-glucoside	0.0106 ± 0.0011	0.9690	65	1
Cyanidin 3-*O*-galactoside	0.0127 ± 0.0012	0.9741	55	12
Delphinidin 3-*O*-arabinoside	0.0142 ± 0.0010	0.9881	49	9
Cyanidin 3-*O*-glucoside	0.0095 ± 0.0013	0.9374	73	5
Petunidin 3-*O*-galactoside	0.0132 ± 0.0010	0.9837	52	5
Cyanidin 3-*O*-arabinoside	0.0133 ± 0.0014	0.9675	52	17
Petunidin 3-*O*-glucoside	0.0120 ± 0.0012	0.9740	58	7
Peonidin 3-*O*-galactoside	0.0115 ± 0.0020	0.9064	60	16
Petunidin 3-*O*-arabinoside	0.0099 ± 0.0006	0.9884	70	10
Delphinidin (the aglycone)	0.0130 ± 0.0020	0.9281	53	2
Malvidin 3-*O*-galactoside	0.0176 ± 0.0020	0.9706	39	8
Malvidin 3-*O*-glucoside	0.0166 ± 0.0020	0.9633	42	16
Malvidin 3-*O*-arabinoside	0.0195 ± 0.0017	0.9834	36	14
Cyanidin (the aglycone)	0.0081 ± 0.0014	0.8863	86	17
Delphinidin 3-*O*-(6″-acetyl)-glucoside	0.0044 ± 0.0010	0.8206	157	78
Petunidin (the aglycone)	0.0046 ± 0.0007	0.8994	150	–
Petunidin 3-*O*-(6″-acetyl)-glucoside	0.0087 ± 0.0018	0.8681	80	51
Malvidin 3-*O*-(6″-acetyl)-galactoside	0.0102 ± 0.0017	0.9129	68	–
Malvidin 3-*O*-(6″-acetyl)-glucoside	0.0089 ± 0.0010	0.9639	78	65
Malvidin (the aglycone)	0.0103 ± 0.0018	0.9039	67	8
BC				
Total anthocyanins	0.0056 ± 0.0013	0.8115	125	8
Total delphinidins (aglycones and glycosides)	0.0056 ± 0.0013	0.8190	124	7
Total cyanidins (aglycones and glycosides)	0.0055 ± 0.0013	0.8025	126	8
Delphinidin 3-*O*-glucoside	0.0057 ± 0.0014	0.8025	121	10
Delphinidin 3-*O*-rutinoside	0.0063 ± 0.0013	0.8402	111	7
Cyanidin 3-*O*-glucoside	0.0056 ± 0.0013	0.8142	123	21
Cyanidin 3-*O*-rutinoside	0.0060 ± 0.0014	0.8118	116	6
Delphinidin (the aglycone)	0.0006 ± 0.0003	0.3451	1155	166
Cyanidin (the aglycone)	0.0006 ± 0.0004	0.3934	1155	223
Delphinidin 3-*O*-(6″-coumaroyl)-glucoside	0.0011 ± 0.0004	0.6395	619	39

[a] The estimated time in ASLT for 1 year storage at room temperature was calculated by fitting the anthocyanin contents of 12-month in RT using $C_t = C_0 \times e^{(-kt)}$, where C_t is anthocyanin contents at t days, C_0 is anthocyanin contents at 0 day and t is the storage time.

Table 3
The acceleration factor Q_{10} values of total and dominant anthocyanins in strawberry (SB), blueberry (BB) and blackcurrant (BC) mueslis [a].

Berry compounds	Q_{10}
SB	
Total anthocyanins	6
Pelargonidin 3-*O*-glucoside	7
BB	
Total anthocyanins	8
Malvidin 3-*O*-galactoside	9
Malvidin 3-*O*-glucoside	6
Malvidin 3-*O*-arabinoside	7
BC	
Total anthocyanins	9
Delphinidin 3-*O*-rutinoside	10
Cyanidin 3-*O*-rutinoside	11

[a] Q_{10} value is the number of times that the reaction rate changes with a 10 °C change in temperature.

different dominant malvidins, this value could vary between 6 and 9. The same consideration should be applied to the quantitatively dominant anthocyanins in BC. To the author's knowledge, no comparable scientific literature exists on the anthocyanin kinetic reactions of whole freeze-dried SB, BB or BC, or on berry-rich mueslis in general. However, some comparisons can be drawn from the limited available literature of

similar berries in different matrices. For example, Moldovan and co-authors studied the effect of storage temperature on the total phenolic content of Cornelian cherry fruits extracts (Moldovan et al., 2016). In contrast to our findings, the Q_{10} value was 1.87 in their study, representing storage temperature rise from 22 to 55 °C. Similarly, Fracassetti et al. studied the effect of time and storage temperature on anthocyanin degradation in wild BB powder (Fracassetti et al., 2013). They concluded that the Q_{10} value for the degradation of anthocyanins in wild BB powder stored at 42–52 °C was 1.98. These remarkably lower indicators may be due to shorter testing times in RT, showing little changes in the content of polyphenols and anthocyanins. In more detail, as the degradation of phenolic compounds is exponential, Q_{10} value depends on the storage duration. Besides, the half-life ($t_{1/2}$) values were also compared with the results in our study and previous studies. In the research of Moldovan et al., the half-life of polyphenols at 55 °C in cherry extracts was 17.8 days (Moldovan et al., 2016), whereas the half-life of total anthocyanins for SB and BB at 40 °C in our study was 50 and 49, respectively. Comparing to the half-time of freeze-dried BB powders in the study conducted by Fracassetti et al. (39 days), our study showed higher half-time of BB (49 days) (Fracassetti et al., 2013). The difference might have been due to the slight difference of temperatures in our study (40 °C) and previous study (42 °C). Beside the temperature, the type of tested products can also affect the half-time, suggesting that anthocyanins in the freeze-dried berry powders are more susceptible to temperature than that in the freeze-dried whole berries (Fracassetti et al., 2013).

Our study offers several notable strengths that contribute to practical application in food development. Employing LC-MS allows systematic analysis of phenolic compounds in commercial food products and reveals changes in the composition of these bioactive and sensory-relevant compounds. By linking degradation dynamics with structural features of phenolics (including sugar moiety and acylation patterns), our research provides mechanistic insights into degradation behavior, which is often overlooked in food stability studies. The degradation behavior of phenolic compounds underscores the importance of molecular structure in determining the shelf-life of bioactive compounds in complex food matrices. A comprehensive evaluation of phenolic compound stability in a real food matrix will offer food industries with the guidance of product development and shelf-life prediction.

While our findings provide valuable insights, some limitations should be acknowledged. The ASLT was conducted at a single elevated temperature (40 °C) in this study, although certain phenolic compounds (*e.g.*, anthocyanins) are known to be temperature-sensitive. This study aimed to accelerate the degradation sufficiently to observe meaningful changes within a practical timeframe, while avoiding excessive thermal stress that could lead to non-specific degradation or complete breakdown. Additionally, 40 °C can reflect the storage conditions in regions with higher ambient temperatures, which impact product storage during transportation or warehousing. The complexity of the muesli matrix may also influence the changes of phenolic compounds during storage. The interactions between berry phenolics and other components (*e.g.*, proteins, fibers, lipids and phenolics from grains) should be analyzed in future research.

4. Conclusions

In summary, this study systematically revealed phenolic profiles of three berry-rich food products and their changes during both ASLT and RT. Based on 90 phenolic compounds identified by LC-MS, our results suggested that the variation in phenolic profiles was highly dependent on their molecular structures and storage temperature. The degradation rates of anthocyanins were significantly higher at 40 °C than at 23 °C. The contents of other phenolic compounds fluctuated during ASLT with either increased (in BB and BC) or decreased (in SB) total contents at 365-day storage. Although anthocyanin degradation of BB fitted better in first-order kinetics, some compound contents had significant differences between ASLT storage time points and the corresponding room-temperature storage time points. This indicates that this accelerated storage model is compound-specific. The findings provide important guidance and serve as a useful reference for designing the shelf-life and assessing the quality of berry products during storage.

CRediT authorship contribution statement

Ying Zhou: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Kärt Saarniit:** Writing – review & editing, Writing – original draft, Visualization, Resources, Funding acquisition, Formal analysis, Conceptualization. **Mahsa Sadat Jafari:** Visualization, Formal analysis, Data curation. **Sirli Rosenvald:** Writing – original draft, Supervision. **Oskar Laaksonen:** Writing – review & editing, Supervision, Project administration, Formal analysis, Conceptualization. **Ye Tian:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis. **Baoru Yang:** Writing – review & editing, Supervision, Resources, Funding acquisition.

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Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Kart Saarniit reports financial support was provided by European Commission, European Union. Baoru Yang reports equipment, drugs, or supplies was provided by Research Council of Finland, Finland. Ying Zhou reports financial support was provided by Turku University Foundation, Finland. Ye Tian reports financial support was provided by Niemi Foundation, Finland. Ye Tian reports financial support was provided by Finnish Cultural Foundation, Finnish Cultural Founda. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Abbreviation used

Abbreviation used in the article are: **De**, Delphinidin; **Cy**, Cyanidin; **Pl**, Pelargonidin; **Pt**, Petunidin; **Po**, Peonidin; **Ma**, Malvidin; **My**, Myricetin; **Ka**, Kaempferol, **Qu**, Quercetin; **Is**, Isorhamnetin; **La**, Laricitrin; **Sy**, Syringetin; **Cat**, (+)-Catechin; **ECat**, (−)-Epicatechin; **CaA**, Caffeic acid; **Ca der**, Caffeic acid derivative; **CaQA**, Caffeoylquinic acid; **CoA**, Coumaric acid; **CaCoQA,** Caffeoyl-coumaroylquinic acid; **Co-meGlu-B**, Coumaroyloxymethylene-glucopyranosyloxy-butenenitrile; **Fe-meGlu-B**, Feruloyloxymethylene-glucopyranosyloxy-butenenitrile; **Ci**, Cinnamoyl; **ElA**, Ellagic acid; **Rut**, rutinoside; **Gal**, galactoside; **Glu**,

glucoside; **Co-Glu**, coumaroyl-glucoside; **Ca-Glu**, caffeoyl-glucoside; **acGlu**, acetyl-glucoside; **maGlu**, malonyl-glucoside; **suGlu**, succinyl-glucoside; **Ara**, arabinoside; **Gluc**, glucuronide; **Hex**, hexoside; **maHex**, malonyl-hexoside; **acHex**, aceyl-hexoside; **Deox**, deoxyhexose; and **Pent**, pentoside.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2025.118119.

Data availability

Data will be made available on request.

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Five key references (indicated by an * in front of the reference in the reference section)

1 Fleschhut, J., Kratzer, F., Rechkemmer, G., & Kulling, S. E. (2006). Stability and biotransformation of various dietary anthocyanins in vitro. *European Journal of Nutrition, 45*(1), 7–18. https://doi.org/10.1007/s00394-005-0557-8This research provided possible explanations for that malvidins showed the highest degradation rate, comparing to the other anthocyanins. The reason is probably because the substitution of hydroxyl groups of the B ring by the methoxy groups decreases the stability of anthocyanins.

2 Fracassetti, D., Del Bo', C., Simonetti, P., Gardana, C., Klimis-Zacas, D., & Ciappellano, S. (2013). Effect of time and storage temperature on anthocyanin decay and antioxidant activity in wild blueberry (*Vaccinium angustifolium*) powder. *Journal of Agricultural and Food Chemistry, 61*(12), 2999–3005. https://doi.org/10.1021/jf3048884This research provided possible explanations for the different degradation rates of glucoside, galactoside, arabinoside of delphinidins, cyanidins, and malvidins.

3 Piljac-Žegarac, J., & Šamec, D. (2011). Antioxidant stability of small fruits in postharvest storage at room and refrigerator temperatures. *Food Research International, 44*(1), 345–350. https://doi.org/10.1016/j.foodres.2010.09.039In this study, total anthocyanin content decreased fast at 25 °C and no anthocyanin was detected after 4-day storage. The compared results in our study indicated that the modified atmosphere package retarded anthocyanin degradation at 23 °C.

4 Saarniit, K., Lang, H., Kuldjärv, R., Laaksonen, O., & Rosenvald, S. (2023). The stability of phenolic compounds in fruit, berry, and vegetable purees based on accelerated shelf-life testing methodology. *Foods, 12*(9). https://doi.org/10.3390/foods12091777In this study, the stability of phenolic compounds in blueberries and combinations of blueberries with other fruits were studied in RT and ASLT. The degradation of total phenolics was monitored for 14 months. The results of phenolic degradation and Q10 in this study can be compared with our results.

5 Tian, Y., Liimatainen, J., Alanne, A. L., Lindstedt, A., Liu, P., Sinkkonen, J., Kallio, H., & Yang, B. (2017). Phenolic compounds extracted by acidic aqueous ethanol from berries and leaves of different berry plants. *Food Chemistry, 220*, 266–281. https://doi.org/10.1016/j.foodchem.2016.09.145This research provides the fragmentation pattern and the retention time of phenolic compounds in MS and MS2. The findings in our study were compared to this research for phenolic compound annotation.

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Juhendatud väitekirjad

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Lang, H., magistrikraad, 2022, (juh) **Saarniit, K.**, Kuhtinskaja, M.; Kiirendatud säilivuskatse metoodika arendus päevalilleõliga valmistatud kartulikrõpsudele; Tallinna Tehnikaülikool, Loodusteaduskond, Keemia ja biotehnoloogia instituut; AS TFTAK

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