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An analytical approach to determine the health benefits and health risks of

consuming berry juices

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ABSTRACT

 Food products composition analysis is a prerequisite for verification of product quality, fulfillment of regulatory enforcements, checking compliance with national and international food standards, contracting specifications, and nutrient labeling requirements and providing quality assurance for use of the product for the supplementation of other foods. These aspects also apply to the berry fruit and berry juice. It also must be noted that even though fruit juices are generally considered healthy, there are many risks associated with mishandling both fruits and juices themselves. The review gathers information related with the health benefits and risk associated with the consumption of berry fruit juices. Moreover, the focus was paid to the 27 quality assurance of berry fruit juice. Thus, the analytical methods used for determination of compounds influencing the sensory and nutritional characteristics of fruit juice as well as potential contaminants or adulterations.

 Keywords: berry juice; antioxidants; adulteration; health benefits; health risks; green analytical chemistry.

1. Introduction

 Human nutrition science has developed in the last decades, turning from looking at foods as a simple source of energy to the appreciation of their role in maintaining health and in reducing disease risks. Nowadays, berry plants have become very attractive to the food industry, as it is a trend to prompt their application as replacements for synthetic nutraceuticals. In addition, the berry itself is often used to produce juice (Li et al., 2017). Due to the high content of polyphenols, antioxidants, and other bioactive compounds, berry fruit juices are often seen as one of the healthiest and the most nutritious beverages (Skrovankova et al., 2015). The mentioned groups of compounds are responsible for various health benefits, including cardiovascular diseases, prevention of inflammation disorders, or protective effects to lower the risk of various cancers (Figure 1) (de Souza et al., 2014). Because of that general assumption, it is important to evaluate whether the amount of numerous bioactive ingredients is sufficient for them to be beneficial to human health. Moreover, it is important to assess the content of substances such as polyphenols, antioxidants, and vitamins in different juices, since their levels may differ depending not only on the type of fruit but also on its origin, processing, or storage

(Arfaoui, 2021).

Figure 1. Health benefits and risks related to the consumption of berry fruit juices.

 Even though berry fruit juices are generally considered healthy, there are many risks associated with mishandling both fruits and juices themselves (Abisso et al., 2018). It is important to collect information on the negative effects that microbial contamination, inappropriate storing condition, or the use of stale fruits may have on juices composition and safety of their consumption. While some of the risks are minimized in the case of commercially available berry juices, quality assessment is of particular importance in the case of homemade juices, since consumers are not bound to obey the same sanitary standards as food producers (Li et al., 2017).

 One of the most overlooked problems associated with fruit juices, including berry fruit juices consumption is the possibility of their adulteration (Dasenaki & Thomaidis, 2019). To decrease the cost of juices production, the producer may mix in fruits that are not only cheaper but also might not have as many health benefits, as well as resorting to the addition of water. Moreover, since juices that are the richest in bioactive compounds are not always seen as the most palatable, additives are used to improve their sensory qualities leading to a further decrease of wholesomeness. Another important adulteration is the application of artificial flavors to mimic the natural aroma (Hrubá et al., 2021).

 This work aims to assess the current status of analytical approaches to fruit juices analysis and quality assessment to identify both the current limitations and future trends. In the article, we critically review the up-to-date literature on fruit juices analysis, in particular on their quality assessment. The information is provided in a concise and approachable form, focusing on practical aspects and examples of implementation rather than on detailed technical aspects and principles of operation of the described methods. The focus is mainly placed on novel methods for fruit juices quality assessment in the context of green analytical chemistry, but diverse and interesting examples of studies that showcase the possibilities of future developments are presented. In addition, the practicality of the reviewed methods for end-users in and outside of analytical laboratories are given. Current trends and lines of future research are also discussed.

2. Health benefits related to consumption of berry juice fruit

 The consumption of berry juice has been widely associated with a decreased risk of certain chronic diseases (Giampieri et al., 2015; Habanova et al., 2019). Several studies report that berry juice have different biological activities *in vitro* and *in vivo* systems, which are related to their bioactive composition (Bakuradze et al., 2019; Giampieri et al., 2015; Toaldo et al., 2015). These juices are excellent sources of vitamins, minerals, and phenolic compounds, especially 82 phenolic acids and anthocyanins (Geraldi et al., 2021). The chemical composition of fruit juices depends especially on the fruit species, maturation, climate, and the treatments to which the fruit and the juices themselves are submitted. In addition, during cultivation, climatic conditions have a direct influence on the chemical quality and the polyphenolic complexity of the fruits (Coelho et al., 2021). The technology employed in juice production can provide different levels of extraction of bioactive compounds. The crushing step contributes to the extraction of phenolic compounds present in berries. It is interesting to note that during the fruit processing, some steps, such as freezing and thawing, can affect the extraction of some valuable components in the grinding and pressing steps, changing the phytochemical composition of the 91 fruit juices (Weber & Larsen, 2017).

 In addition, other processing steps affect the bioactive composition of juices, such as enzymatic treatment, filtration, clarification, and pasteurization. In enzymatic treatment, pectinolytic enzymes are used to increase productivity of juice. The use of the pectinase enzyme causes pectin degradation, which results in reduced juice viscosity and changes in physicochemical properties, such as total soluble solids, pH, and turbidity (Marsol-Vall et al., 2019). Filtering or clarification is carried out before or after pasteurization. The heat treatment (pasteurization) to which the fruit juices are subjected can also cause reductions in the content of vitamins and polyphenols (Stübler et al., 2020), however, pasteurization is still conventionally used as a procedure to preserve juices from microbial contamination (Marsol-Vall et al., 2019). Martino et al. (2013) report that polyphenol retention and antioxidant activity were significantly higher

 in grape juice clarified after thermal processing (pasteurization) compared to grape juice clarified before pasteurization. In the same way as pasteurization due to the use of high processing temperatures, the evaporation technique used to concentrate fruit juices can reduce the nutritional value and bioactive properties of the product (Amran & Jusoh, 2016). In contrast, low temperatures are employed in the membrane separation technique used to concentrate fruit juices preserving the most thermosensitive compounds, especially vitamins and polyphenols (Bhattacharjee et al., 2017). In addition to the reported steps, storage conditions such as exposure to heat and light have an important influence on polyphenol retention. During storage, the content of monomeric anthocyanins decreases leading to the polymerization of 111 anthocyanins into more stable compounds (Marsol-Vall et al., 2019)...

 Knowledge about the processes mentioned above is of paramount importance for the elucidation of the chemical composition of wild fruit juices and the correct correlation with the health benefits promoted by the regular consumption of these bevereges, since the concentration of vitamins, minerals and bioactive compounds directly depends on the processes to which the fruits and juices are submitted. Clinical and pre-clinical studies have shown that berry fruits and their juices can act as potential therapeutic agents in the prevention of various pathologies, such as diabetes, neurodegenerative and cardiovascular diseases, and cancer (Wang et al., 2021; B. Yang and Kortesniemi, 2015). The literature studies showed that berry fruits and their juices, alone or in combination with other functional foods or dietary interventions, can improve glycemic and lipid profiles, blood pressure, and surrogate markers of atherosclerosis (Calvano et al., 2019).

 Berry fruits contain large amounts of essential and physiologically important macroelements such as P, Mg, K, and Na (Szymczycha-Madeja et al., 2014). As well as some microelements such as Ca and Fe (Toaldo et al., 2015). Both macro and microelements play an important role in the regulation of osmotic homeostasis, blood pressure control, nerve impulse transmission, muscle contraction, and blood pressure balance (Gharibzahedi & Jafari, 2017). The daily consumption of fruit juices can be a part of the recommended daily doses of some nutritionally important elements, such as Co, Cr, Cu, Fe, Mn, Ni, Zn, and Se (Szymczycha-Madeja et al., 2014).

 The berry fruit juices are also rich in vitamins A, C, and E, and vitamins of the B complex, which are essential for health, as their consumption stimulates the immune system and reduces inflammation (Skrovankova et al., 2015). Since inflammation plays a key role in the development of diabetes, asthma, cardiovascular disease, and cancer, the consumption of appropriate amounts of the above-mentioned vitamins reduces the risk of those diseases (Maleki et al., 2019). Trych et al. (2020) reported that black currant contains approximately 160–285 mg/100 g of vitamin C. Zheng et al. (2009) reported vitamin C contents of 60–190 mg/100 mL in blackcurrant juices. Sapei et al. (2014) reported that the ascorbic acid content of fresh strawberry juices ranged from 20 to 40 mg/100 mL. The consumption of vitamin C is associated with several health benefits, as it has anti-inflammatory, antibacterial, and neuroprotective action.

 We also highlight that in addition to the composition of minerals and vitamins, wild fruit juices are excellent sources of phenolic compounds, especially anthocyanins and phenolic acids (Bakuradze et al., 2019). It is known that polyphenols present in fruits and vegetables exert beneficial biological activities to the human body when consumed regularly due to their antioxidant, cardioprotective, anti-inflammatory, and neuroprotective activities. It is known that food matrix in which given compounds are present is important factor determining its release and stability while digested in a human body. To become bioavailable and subsequently bioaccessible polyphenols must be removed from the digested matrix and solubilized in the gastrointestinal fluids. Therefore, it is important to say that phenolic compounds exert their health-related properties when they reach the target tissue of the human body in biologically active concentrations (da Silva Haas et al., 2019). Anthocyanins are the most important flavonoids present in berry fruits and contribute to their high antioxidant capacity. These compounds are responsible for the flavor and the red color of the fruits (Cortez et al., 2017).

 The small and aromatic berries of blackcurrant (*Ribes nigrum*) are rich in anthocyanins (delphinidin 3-glucoside, delphinidin 3-rutinoside, cyanidin 3-glucoside, and cyanidin 3- rutinoside) (Tian et al, 2023), and its consumption inhibits the activities of the dipeptidyl peptidase-enzymes IV, α-amylase, α-glucosidase, nitric oxide synthase, and cyclooxygenase-2 which are biochemical markers of type 2 diabetes and inflammation (Kowalski & Gonzalez de Mejia, 2021). Other health benefits were reported by Cortez and Gonzalez De Mejia (2019), such as improved cardiovascular, nervous, ocular, skeletal, skin, and renal systems (Cortez & Gonzalez de Mejia, 2019).

 The blueberry juice (*Vaccinium ashei*) also has high concentrations of anthocyanins, such as cyanidin-3-glycoside, peonidin-3-glycoside, malvidin-3-glycoside, malvidin-3-galactoside, and malvidin-3-arabinoside (Wu et al., 2021). Yang and Kortesniemi (2015), reported an inverse association between anthocyanin intake and the incidence of chronic disease. Recent research shows that flavonoids can inhibit regulatory enzymes or transcription factors important for the control of mediators involved in inflammation, in addition to attenuating tissue damage and fibrosis (Maleki et al., 2019).

 Strawberry juice (*Fragaria X ananassa, Duch*.) is one of the berry juices that has been gaining interest for its positive effect on health due to its polyphenol composition, with emphasis on phenolic acids and anthocyanins. Among the acids, ellagic acid stands out, it is a dimeric condensation product of gallic acid and is found naturally in strawberries, raspberries, and blackberries and has important anticancer, antithrombotic, and anti-inflammatory properties (Muthukumaran et al., 2017). In addition, strawberries are rich in anthocyanins (pelargonidin- 3-glucoside, cyanidin 3-glycoside, and pelargonidin 3-rutinoside) that promote benefits to human health, as they can regulate gene expression and prevent DNA damage (Giampieri et al., 2015). Preclinical and clinical investigations support the role of anthocyanins in ocular health, these polyphenols have been associated with several benefits pertinent to neurodegeneration. The anthocyanins allow the reduction of induced oxidative stress, decreasing the levels of reactive oxygen species, and malondialdehyde and increasing the levels of superoxide dismutase, catalase, and glutathione peroxidase in the pigment epithelium of the human retina (Huang et al., 2018). According to McNamara et al. (2018) supplementation with blueberry powder generated an improvement in the cognitive function of elderly people with subjective cognitive impairment, supposedly derived from a vaso-modulatory effect.

 On the other hand, the acute consumption of grape juice (*Vitis labrusca* L.) rich in catechin, epicatechin, *trans*-resveratrol, and anthocyanins (cyanidin 3,5-diglucoside and malvidin 3,5- diglucoside) increases the levels of antioxidants in plasma and erythrocytes in healthy individuals, reducing the lipid peroxidation (Toaldo et al., 2016). Grape juice consumption may render additional benefits for healthy adults who exercise regularly. Grape juice had great potential as an antioxidant source in improving the antioxidant status and cardiometabolic profile of healthy adults. Catechin, isoquercetin, and procyanidin B1 were the major compounds in grape juice from cultivars Isabel, Bordô, and Concord. The plasma antioxidant activity and HDL-cholesterol increased after grape juice intake, and LDL-cholesterol and systolic blood pressure decreased after grape juice consumption (Toscano et al, 2017). Renaud and De Lorgeril proposed in 1992 the French paradox which states that the consumption of polyphenols is associated with a low incidence of heart and coronary disease, despite a high-fat diet. It is noteworthy that the understanding of the "French Paradox" has stimulated the interest of further research to investigate whether polyphenols may offer protective effects beyond the cardiovascular system and whether different botanical sources may also offer beneficial effects on human health (Sun et al., 2002).

 With regards to the stability of phenolic compounds, they are susceptible to several structural changes during gastrointestinal digestion, and among polyphenols, phenolic acids seem to be the most resistant compounds, being the most relevant to explain the biological activity of foods (Corrêa et al., 2017; Lingua et al., 2019). Chlorogenic and protocatechuic acids are the major phenolic acids in blueberry juice (*Vaccinium ashei*) (Wu et al., 2020) and blackberry juice (*Rubus americanus*) (Wu et al., 2021). It is known that polyphenols act in the prevention of oxidative stress, inhibiting inflammation and improving vascular health (Sinopoli et al., 2019). According to Yang and Kortesniemi (2015), regular consumption of polyphenol-rich fruit juices improves the postprandial glycemic response and the profile of circulating inflammatory markers, in addition to increasing plasma antioxidant capacity and delaying the loss of related cognitive functions the age.

 Growing evidence suggests that wild fruit consumption has significant potential in preventing and treating most risks associated with a metabolic syndrome like diabetes mellitus (Hameed et al. 2020, Vendrame et al. 2016). This is probably due to the presence of polyphenols with known antioxidant and anti-inflammatory effects, such as phenolic acids and anthocyanins. In offering efficient and secure dietary therapies for diabetes mellitus prevention and control, tailored berries nutrition is compared to an individual pharmaceutical strategy (Hameed et al., 2020). In this context, the use of analytical methods to determine the bioactive composition of wild fruit juices is extremely important for the beverage industry, as this way, it is possible to report their nutritional potential and possible health benefits. We emphasize that to elucidate different perspectives on the nutritional potential of food, it is necessary to consider the effect of digestion, absorption, and metabolization of the bioactive compounds in the human body (Attri et al., 2017; Velderrain-Rodríguez et al., 2014).

3. Risks associated with consumption of fruit juice

 The insightful evaluation of the quality of berry fruit juices is of great importance for consumer safety. Although the consumption of fruit juices generally has several positive health effects, it is notorious to emphasize the possible risks associated with microbiological contaminations, characterized by the presence of pathogenic microorganisms, such as bacteria, viruses, and fungi, and chemical contaminations, which mainly include the presence of pesticides, mycotoxins, illegal additives, metals, bisphenols, and organic pollutants (Mostafidi et al., 2020).

- Quality inspection of fruit juices is governed by different bodies in their respective countries and regions. The European Fruit Juice Association Code of Practice (AIJN COP) brings together a collection of reference guidelines for fruits and vegetables. The AIJN COP contains parameters that a fruit or vegetable juice needs to meet in the European market, establishing criteria for evaluating juices with respect to quality, authenticity, and identity. In addition to the AIJN COP, other bodies establish drink quality criteria, such as the Polish Association of Juice Producers (KUPS) in Poland and the Food and Drug Administration (FDA) in the United States. It should be noted that the SDS requires the application of Hazard Analysis Critical Control Point (HACCP) principles that aim to ensure the safe and sanitary processing of fruit and vegetable juices.
- 3.1. Microbiological Contaminations
- 3.1.1. Bacteria

 The contamination of fruit juices by bacteria, these occur in places with inadequate facilities and a lack of hygienic-sanitary standards, mainly due to the lack of care when handling the fruits used during juice preparation (Nawawee et al., 2019). The bacteria *Escherichia coli, Salmonella typhi, Pseudomonas spp, Staphylococcus aureus,* and *Vibrio cholerae* are the most common in fruit juices and the consumption of drinks contaminated by these pathogens can lead to diarrhea, typhoid fever, gastroenteritis, and food poisoning (Sharma et al., 2020).

3.1.2. Fungi

 The presence of fungi in fruit juices is an important factor to be considered since fungi are capable of producing mycotoxins, which are toxic secondary metabolites that pose a potential risk to human health (Fliszár-Nyúl et al., 2020). Recent studies have shown that a wide variety of small berries, such as strawberries, blueberries, mulberries, blackcurrants, and raspberries, due to their soft and fragile skin, are susceptible to small lesions that allow the growth of fungi, especially molds. Once present in the fruit, fungi can resist heat treatments used in the processing of fruit juices and persist in the product. In addition, products stored at room 259 temperature are more prone to the occurrence of fungi (Jackson & Al-Taher, 2008). The main fungi found in fruits belong to the genera *Aspergillus, Penicillium,* and *Alternariae* (Guo et al., 2021)*.*

 The norovirus or hepatitis A virus is one of the most common viruses in fruit derivatives, being recognized as the cause of gastroenteritis and hepatitis in humans. Virus contamination of fruit juices is mainly related to the contamination that occurs during the various stages of raw material (fruits) production, including production, harvesting, processing, and distribution (Takahashi et al., 2018). A significant source of viruses can result from water contaminated with the viruses that are used for irrigation during planting, as it is not practical for all fruit farms to use potable water. Furthermore, bacterial indicators employed for water quality control generally cannot predict viral contamination, giving negative results for indicator tests. In addition to water, viral contamination can occur through the hands of fruit handlers without proper hygiene (Maunula et al., 2013).

3.2 Chemical contamination

 Considering the quality and the safety of fruit juices, there is a growing interest in evaluating potential chemical contaminants such as pesticides, bisphenols or metals, as well as the presence of adulterants. Chemical contaminants present in fruit juices are usually derived from the fruit itself, which during crop production, post-harvest, and additional processes are exposed to contaminants like pesticides, metals, etc. In addition, packaging can be a potential source of chemical contaminants (Mostafidi et al., 2020).

3.2.1. Pesticides

 In recent years agriculture has advanced rapidly and intensified the use of a huge amount of chemical inputs, mainly synthetic pesticides that play an important role in the protection of several cultivars, including pest control and disease prevention (Heidari et al., 2020). Pesticides belong to different chemical groups such as carbamates, neonicotinoids, organochlorines, organophosphorus, phenoxyacids, pyrethroids, strobilurins, triazines, triazoles etc.) and have two different modes of action (contact or systemic). Pesticides with contact action accumulate on/in the plant layer, while pesticides with systemic action penetrate deeper into plant tissues, and were definitely more difficult to reduce during juice production (Jankowska et al., 2018). It was proven that after squeezing of blackcurrants, the pesticide residue levels in the juice were lower by more than 50% compared to raw fruits. Moreover, the contact pesticides remained on the peel and minimally penetrated into the juice (18% compared to the raw fruits) (Jankowska et al., 2018). The beverage industry is the fastest-growing food sector worldwide, especially the production of fruit juices (*Food And Beverages Global Market Report 2022- Product Image Food And Beverages Global Market Report 2022*, 2022). On the other side, in the latest sector some problems can be pointed out, especially, the application of enormous doses of pesticides used to increase productivity and product quality. As a result, from the use in agricultural activities, residual pesticides can ultimately be found in the human diet, since if they are not naturally degraded, they can penetrate plant tissues and be found in the fruit pulp and later in the juices. In addition, the use of techniques to concentrate processed juices can promote an increase in the pesticide content in the final product when compared to fruits (Jin et al., 2012).

 Prolonged exposure to pesticides can generate several negative health effects, from acute effects such as headaches and nausea to chronic effects such as endocrine disruption, infertility, neurotoxicity, and carcinogenesis (de-Assis et al., 2020). Within this context, it is important to emphasize that pesticides are regulated to ensure that pesticide residues in food do not pose a risk to human health. Thus, commercialized pesticides are authorized after an intensive assessment of possible health and environmental risks (Torović et al., 2021). The maximum legally permitted concentrations of pesticide residues in specific foods, including fruit juices, are regulated by the European Union (CE/nº299/2008), but also the United States Environmental Protection Agency sets such limits. Furthermore, efforts to minimize the impact of pesticide residues can be adopted through the implementation of practices such as the rational use of pesticides, exploitation of natural pesticides, promotion of organic agriculture, and adequate application intervals (Mostafidi et al., 2020).

3.2.2. Metals

 Fruit juices are an important source of minerals, which are essential for maintaining health (Caswell, 2009). However, in addition to the presence of elements beneficial to health, juices can contain harmful metals such as Hg, Sn, As, and Cd that can trigger serious problems for human health, even at low concentration levels. The consumption of metals through fruit juices can cause chronic diseases or mutagenesis and carcinogenesis (Bhattacharya et al., 2016). In addition to the risk of these elements to human health, the presence of some metals in excess, like Fe and Cu can reduce the shelf life of foods or possibly decrease the nutritional value of juices, since these metals are responsible for catalyzing oxidative processes, through free radicals oxidative deterioration (Mohamed et al., 2020).

 The presence of unwanted metals in juices can come from the packaging or from the fruit itself. Juices stored in aluminium containers can be contaminated by the metal through leaching processes. Al (III) is highly toxic to humans due to the potential accumulation in the brain that can trigger Parkinson's and Alzheimer's disease (Hafez et al., 2019). The metals derived from fruits are commonly related to the mineral composition of the planting soil, agricultural practices with abusive use of pesticides or contaminants transported by air or water, in this sense, it is extremely important to regularly monitor the dietary intake of food sources to ensure safe food. In addition to ensuring the nutritional value of food (Anastácio et al., 2018).

3.2.3. Biogenic amines

 Biogenic amines (BAs) are aliphatic or aromatic organic compounds of low molecular weights. They are generated during cellular metabolism in bacteria, plants, and animals due to microbial decarboxylation of the corresponding amino acids. The amount and kind of BAs produced are influenced significantly by the food composition, and factors that allow bacteria to flourish during food processing and storage (Gomez-Gomez et al., 2018). Low quantities of BAs in food are not thought to be dangerous, but they may have toxic effects when eaten in large doses. Their analysis in food samples is of tremendous interest not just because of their potential toxicity, but also because they can be utilized as indications of food freshness or rotting (Saaid et al., 2009). Many works have been published according to the determination of BAs in berry 341 juice samples (Sub-section 4.2.2).

3.2.4. Adulteration

 The adulteration of beverages is commonly related to dilution practices, the addition of artificial flavors to mimic the natural aroma, and the addition of flavor masking to alter specific characteristics, such as reducing or eliminating unpleasant flavors such, as bitterness. In addition, the addition of different chemical mixtures capable of masking themselves so that adulteration is not perceived also constitutes adulteration. As a result of adulterations, a lower nutritional value is expected of beverages (Xu et al., 2019).

 Some examples found in the literature on fruit juice adulteration include the adulteration of grape juice with the addition of fruit juices of lesser commercial value. A good example is the addition of apple juice to whole grape juice. Apples are rich in pectin, which acts as a gelling and natural thickening agent that prevents the separation of the juice phases. Moreover, the addition of apple juice masks other adulterations, including the addition of water and other additives (Oliveira et al., 2019). Similarly, orange juice (*Citrus sinensis*), consumed worldwide, can suffer adulteration by the addition of *Citrus reticulata* (mandarins and tangerines), *Citrus aurantium* (sour orange), tangors or hybrids of sweet orange, and tangerine (Jandrić et al., 2017).

 Beyond the addition of other fruit juices, one of the artificial ingredients often added is glucose- fructose syrup (Europe) or high fructose corn syrup (United States). These syrups are added as an alternative to sucrose due to their viscosity, which contributes to preventing crystallization and having a lower cost than sucrose (Wójcik & Jakubowska, 2021). Both components are associated with obesity risks when consumed in excess (Yu et al., 2013, Süli et al., 2017). Besides that, corn syrup may have levels of trace mercury resulting from syrup production technology (Wójcik & Jakubowska, 2021).

 The authenticity of juices is verified by basic analytical information, such as Brix or total acidity, besides biomolecular approaches, and isotopic analysis. Also important is the application of analytical methods that assess the chemical profile of fruit juices including the quantification of sugars, anthocyanins, organic acids, carotenoids, and amino acids. Although these options are usually applied, there is a need for fast and accurate analysis methods to determine the presence of possible adulterants in fruit juices (Wójcik & Jakubowska, 2021).

3.2.5. Mycotoxins

 The mycotoxins are secondary metabolites of mold and fungi, which even in low concentrations are harmful to humans. The main fungi in fruits belong to the genera *Aspergillus, Penicillium* and *Alternariae* and give rise to a wide range of mycotoxins, including aflatoxins, produced by *Aspergillus*, ochratoxins produced by *Aspergillus* and *Penicillium*, while citrinin and patulin are mycotoxins produced by *Penicillium*. And finally, *Alternaria* toxins are produced by *Alternariae* fungi (Guo et al., 2021).

 Mycotoxins can be transferred from the fruit to the juice if the spoiled fruit is not discarded during the beverage making process. Therefore, quality control of the raw material (fruits) is essential to prevent mycotoxin contamination in fruit juices (Gil-Serna & Patiño, 2020). Prevention strategies, both during agricultural production and in beverage production, have proven to be good alternatives to inhibit mycotoxin biosynthesis, including care during the

 harvest, such as field management, use of biological and chemical agents, types of residence, and post-harvest care, which include improved drying, decontamination processes and care with storage conditions (Mostafidi et al., 2020). It is important to emphasize that, the occurrence of mycotoxins depends on several factors, including, the composition of the food matrix, moisture content, temperature, pH, relative humidity, and physical damage (Pallarés et al., 2021).

 The great concern with mycotoxin contamination is related to adverse health effects since chronic exposure to these substances can result in neurotoxic, immunological, mutagenic, genotoxic, carcinogenic, and teratogenic problems (Guo et al., 2021, Marin et al., 2013). The Codex Alimentarius, the European Union, and countries such as the United States, Canada, and China established maximum levels for some mycotoxins in fruit juices, with a maximum of 50 μ g kg⁻¹ for patulin and 2 μ g kg⁻¹ for ochratoxin A (Guo et al., 2021).

3.2.6. Bisphenols

 Bisphenols are a class of anthropogenic chemical substances widely used as modifier monomers in plastic production to improve material properties, including greater flexibility and strength (Hafez et al., 2019). A total of seventeen bisphenols have been documented for industrial applications, including bisphenol A, bisphenol B, bisphenol F, bisphenol AF and tetrabromobisphenol A. Among them, bisphenol A (BPA) is the most widely applied in plastic production, including the production of food packaging and beverage packaging. Due to its low production cost, high thermal and chemical stability, BPA is widely applied as a raw material (Khan et al., 2021).

 Incomplete polymerization processes or polymer degradation can easily result in the migration of bisphenols from packaging to food and beverages during prolonged storage and at elevated temperatures (D. Yang et al., 2018). Exposure to these compounds poses a potential risk to human health since bisphenols are classified as endocrine disruptors, with a negative effect on the hormonal system. Furthermore, studies indicate that BPA can cause diseases related to the cardiovascular, metabolic, and immune systems, as well as diabetes (Hafez et al., 2019).

3.2.7. Pollutants

 Fruit juices can contain trace-level contaminants belonging to different classes of organic pollutants, including polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). The PCBs are a group of synthetic organic compounds considered to be persistent organic pollutants in the environment. They are highly lipophilic compounds and for this 414 reason, they are found in concentrations in the range of $ng \text{ mL}^{-1}$ in aqueous samples, such as fruit juices (Abujaber et al., 2019). Exposure to PCBs is associated with adverse neurobehavioral problems, endocrine disturbances, and immunological effects (Darvishnejad & Ebrahimzadeh, 2019).

 The PAHs, in turn, constitute one of the largest groups of contaminants present in different matrices, including food. These compounds are derived from the incomplete combustion of organic matter and can come from natural and anthropogenic processes such as pollution, food processing, packaging, and thermal procedures such as cooking. PAHs are often found in different beverages, including fruit juices. The great concern for the scientific community and

 the food industry is related to harmful health properties, including carcinogenic and mutagenic activities (Rascón et al., 2018).

4. Application of analytical techniques

 Food is a complex heterogeneous mixture of a wide range of chemical constituents as well as a wide array of additives and contaminants. Product composition analysis is a prerequisite for verification of product quality, fulfilment of regulatory enforcements, checking compliance with national and international food standards, contracting specifications and nutrient labelling requirements and providing quality assurance for the use of the product for the supplementation of other foods (Kumar & Gowda, 2014). These aspects also apply to the berry fruit which intends to be the sub-product for the production of juice. It also must be noted that even though fruit juices are generally considered healthy, there are many risks associated with mishandling both fruits and juices themselves (Abisso et al., 2018).

 As was previously mentioned, it is important to collect information on both, the positive and negative effects connected with berry fruits and juices. While some of risks are minimized in the case of commercially available juices, quality assessment is of particular importance in the case of homemade juices, since consumers are not bound to obey the same sanitary standards as food producers (Li et al., 2017). And here, analytical chemists are coming with the specific practical knowledge of how to use analytical techniques for quality control of berry fruit juice. In this chapter, the specific techniques are described with examples of their application in the analysis of berry fruit juice. The focus is mainly placed on the novel methods for fruit juices quality assessment in the context of green analytical chemistry, but also we give diverse and interesting examples of studies that show the possibilities of future developments.

- 4.1. Benefits assessment
- 4.1. 1. Spectroscopic techniques

 Spectroscopic techniques are a useful analytical platform for any food screening because their application is rapid, mobile, and, in the case of some techniques, non-destructive. Spectroscopy is a popular technique commonly used at the stage of preliminary research to determine the summary parameters (Boqué & Giussani, 2021).

 The spectrophotometric technique was applied for the evaluation of the effect of total phenolic concentration on the flavor of blue berry juice. The total phenolic content of blueberry juices from different cultivars was determined using the Folin-Ciocalteu method. The method showed good sensitivity (0.05-0.5g/L) (Bett-Garber et al., 2015). The Folin-Ciocalteu method is widely applied for the analysis of total phenolic compounds, however, this method has limitations, as the Folin-Ciocalteu reagent is not specific for phenolic compounds and may also react with other oxidizable compounds present in the sample, including ascorbic acid, amino acids, sugars, ferrous ions, among others, thus, the total polyphenol content can be overestimated (Granato et al., 2016). Furthermore, the Folin-Ciocalteu method does not allow the quantification of individual phenolic compounds. Therefore, it is not possible to correlate specific compounds and their individual properties (Martins et al., 2022). Bett-Garber et al. (2015) related sensory

- analyzes together with physical-chemical analyzes and concluded that berries from different cultivars showed variability in their aroma and flavor. However, it was noticed that polyphenols had no significant effect on the bitter and astringent taste of berries but higher polyphenols concentrations contributed to more intense sweet taste (Bett-Garber et al., 2015). This work presents that the impact of juice composition on flavor is very complicated, and in fact, the estimating flavor with physicochemical parameters is a difficult task due to the composition of the juice. In addition to the phenolic composition, other factors can affect the flavor of fruits and juices, including natural sugars and organic acids. Furthermore, bitterness can be especially influenced by the presence of iridoids. Iridoids are monoterpenoids synthesized naturally in different plants and are characterized by a very bitter taste. However, it should be noted that iridoids present in plants have diverse biological activities, such as anti-inflammatory, antioxidative, anti-cancer, etc (Oszmiański & Kucharska, 2018).
- In the work presented by Tolić et al. (2017), effects of weather conditions on fruit quality attributes, phenolic compounds and antioxidant capacity of selected chokeberry juice over three consecutive years were investigated. Total phenols were determined by Folin-Ciocalteu method, while the pH differential spectroscopic method was used for total anthocyanins determination. Although quality parameters and phenolic composition vary over growing seasons, chokeberry juices from all three seasons have very high contents of phenolic substances and high values of antioxidant properties. This allows to state that weather conditions affect the concentration of antioxidative compounds. In addition, the results presented in this study showed that chokeberry juices characterized by high phenolic compound values had also high antioxidant activity. This is why it can be deduced that due to the high proportion of natural antioxidants their consumption could bring health benefits.

 As the measurement of total anthocyanin value along with polymeric colour can be very useful to assess the quality of colour of anthocyanin-containing juices during heating, the knowledge on kinetic of anthocyanins degradation in specific temperature is required. Such research was performed by Danışman et al. (2016). The kinetic degradation of anthocyanins in grape juices was studied in the temperature range of 70-90˚C. The absorbance of diluted grape juice samples in buffers at pH 1.0 and 4.5 were measured at 520 nm (λmax) and 700 nm using an UV-Vis spectrophotometer. The method had simple sample preparation steps and an acceptable LOD value. In addition, the formation kinetics of percent polymeric colour (%PC) was also studied by application of the bisulphite bleaching method. High correlations were found between anthocyanin degradation and % PC formation during heating. The obtained results allow to state that due to the fact that the heat treatment had a significant effect on monomeric anthocyanins and polymeric colour, it should be carefully optimised to decrease the anthocyanin losses and polymeric colour formation in the commercial processing of grapes into juice.

4.1.2. Chromatographic techniques

 Many properties as well as content of specific important compounds can be determine by application of different chromatographic methods. Such analysis allow to estimate and evaluate the quality of different berries. Furthermore, the application of chromatographic analyses is

 recommended for identification and quantification of specific compounds, allowing the correct correlation of such compounds and their properties. In this chapter, the specific examples of such applications are presented.

 As was previously mentioned berries are commonly consumed as juice, however, the juice- processing conditions could affect their bioactive compounds. This is why many researches are published to present the impact of pasteurization conditions on the bioactive compounds content. The effect of thermal treatment on the phenolic compounds, anthocyanins and ellagitannins content as well as the antioxidant capacity of black berry was evaluated by the HPLC-PAD method (Azofeifa et al., 2015). With the use of the described method, it was possible to follow the concentration of phenolic compounds, anthocyanins and ellagitannins content. Neither of the two pasteurization conditions that were examined in this study significantly altered the concentrations of the total polyphenols or total/individual ellagitannins compared to those in the non-pasteurized juice. On the other hand, the concentration of anthocyanins significantly decreased. Over and above, the pasteurized juice was found to inhibit the peroxidation as well as non-pasteurized juice.

 Another chromatographic method was used for analysis and comparison of the phenolic composition, anthocyanins, and antioxidant capacity in blackcurrant juice from ten different cultivars (Kowalski & Gonzalez de Mejia, 2021). In this work, the ultra-high performance liquid chromatography (UHPLC) method was used after sample extraction from freeze-dried black currant juice with methanol acidified with acetic acid. This method has the main advantage over the HPLC method of having shorter analysis time and hence, less solvents consumption (Azofeifa et al., 2015). It was found that anthocyanins content varied in the collected samples, moreover, anthocyanins were found predominantly in the skins of the fruit. In general, the findings of this study clearly indicate that the juices obtained from different blackcurrant cultivars differ with respect to a number of characteristics of interest.

 In another work, folate vitamers and total folate in different berries were estimated using UHPLC-MS/MS (Zou et al., 2019). In addition, the changes in their concentration during handling of berries into juice were examined. In this method, a simple extraction method (boiling and centrifugation) was used followed by solid-phase extraction for further purification. According to the obtained results, the overall folate yield in the juicing fractions differed amongst berries (strawberries and blackberries had the highest total folate values (93– 118 g/100g), whereas blueberries had the lowest total folate contents). The total folates in all tested were raised by 7 to 12 % after juicing which may be due to excessive release of folates from the fruit matrix during processing. In general, it can be concluded, that most of the investigated berries are good to excellent folate sources.

 In case of red fruit juices, a selected method for quality and authentication is International Federation of Fruit-Juice Producers (IFU) Method No. 71 (1998), which allows to determine anthocyanin profiles by HPLC with visible detection. Despite the fact that the principle of the method is simple and the specific compounds of red fruit juice matrices or adulterations can be detected, correct interpretations of chromatograms are not as easy as expected (Obón et al., 2011), this is why the method is many often modified. Such modification was applied in the

 research performed in order to determine the composition of selected red fruit and vegetable juices and to evaluate their quality and authenticity. Profiles of anthocyanins, betacyanins, synthetic red pigments, hydroxycinnamic acids, hydroxybenzoic acids and catechins in these fruits were studied with the use of the HPLC-UV-VIS or HPLC-fluorescence detector methods (Obón et al., 2011). The method succeeded to separate all the studied components in 46 min analysis time, hence it can be considered as a useful technique for quality and authenticity control of fruit based products and for the detection of fraudulent mixtures with synthetic or natural red food pigments. On the other hand, as health claims of the red drinks can be related to their polyphenol contents, this method could be applied within the juice industry to label the content of components with potential health benefits.

 The outcome of enzymatic processing on blackcurrant juices was studied through analysis of anthocyanins, flavonol glycosides, hydroxycinnamic acids, sugars, and acids content (Laaksonen et al., 2014). Analysis of anthocyanins, flavonol glycosides, hydroxycinnamic acids was done through developing an HPLC/DAD method, while sugars and acids were evaluated by GC/FID after derivatization with trimethylsilyl (TMS) derivatizing agent. The results show that the enzyme-aided juices were more astringent and bitter than the non-enzymatic juices. The reason was connected with lower contents of sugars, higher contents of phenolic compounds, and lower pH and sugar/acid ratio. In general, the non-enzyme-aided juices obtained higher ranking in flavour, while the enzyme-aided juices received more points in odour parameter.

 In addition to evaluate the content of specific bioactive compounds in berry juices, their stability in higher temperatures is also of high importance, and thus, researchers also are focused on this aspects. The stability of polyphenols (anthocyanins, flavanols and phenolic compounds) in chokeberry and blue berried honeysuckle juices previously subjected to one of two sterilization methods (traditional thermal method and sterilization using Enbiojet® Microwave Flow Pesterizer) was tested and compared. (Piasek et al., 2011). The chemical properties verified included determinations of anthocyanins and other polyphenols by HPLC-DAD-MS, however the profiles of antioxidants were obtained by application post-column derivatization. The concentration of phenolic acids and flavonoids (except anthocyanins) did not change significantly under the influence of microwave-assisted sterilization. Moreover, it was observed that using the EnbioJet device, the decrease in anthocyanin content was lower compared to the conventional thermal method, especially in the case of blue berried honeysuckle juice. The 576 present results allow to state that sterilization with $\text{EnbioJet}^{\circledR}$ Microwave Flow Pasteurizer is highly conservative as regards bioactive phytochemicals found in examined berry juices. This conclusion could be true for other plant preparations rich in bioactive phytochemicals.

 Another aspect of the application of chromatographic techniques in the context of determining compounds that have beneficial effect on human health, is their use to assess authenticity or possible adulteration of selected berry juices. In the work (Zhang et al., 2018), a metabolomic approach for authentication of berry fruit juices by liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) was established. In the untargeted metabolomics analysis, obtained data were subjected to chemometric analysis such as principal component analysis-discriminant analysis. In the targeted metabolomics analysis,

 the 41 juice biomarkers, such as flavonoids and anthocyanins provided to separate adulterated juices from berry fruit juices. In addition, adulterants have different flavonoid glycosylation patterns as well as noteworthy differences in phenolic acids. One can conclude that the introduced LC-QTOF-MS-based metabolomic method can be used as a powerful tool to verify the quality of berry fruit juices.

 In addition, the use of HPLC system in determination of specific parameters, ion chromatography (IC) is also an option while speaking about cations and anions of selected compounds. Such technique coupled to suppressed conductivity detection was applied for simultaneous analysis of organic acids and inorganic anions in different fruit juices including blueberry and grape juices (Uzhel et al., 2021). In contrast to HPLC, a simple sample pre- treatment method was applied (only filtration through 0.45 Mm membrane filter and dilution). In this method, a novel hyperbranched anion exchanger was synthetized and successfully applied to provide the baseline separation of glycolic, acetic, formic, and lactic acids, which are not resolved to baseline with modern commercially available columns when purely aqueous eluents are used. The most important factor used to improve selectivity of stationary phase was the introduction of dicarboxylic aspartic acid into the internal part of positively charged hyperbranched phase. This solution allowed to separate the selected organic acids applying KOH as an eluent without adding traditional, organic solvents. The study show, that the main organic acid present in blueberry juice was found to be citric acid (77-87% of total acids content), which improves ketosis and prevents diabetes, followed by malic acid (protects from ischemic lesions and has a positive effect on myocardium) and quinic acids (4-11% of total acids), which can be metabolized to hippuric acid, which is a strong antibacterial agent. This novel ion exchanger can be used for the estimation of organic acid profiles in food quality control to detect its deterioration during storage or authenticity assessment.

- 4.2. Risk assessment
- 4.2.1. Spectroscopic techniques

 In most of the published articles dedicated to the issue of metal content in fruit juices, an atomic absorption spectroscopy (AAS) (Abbasi et al., 2020; Anastácio et al., 2018; Okhravi et al., 2020; Sorouraddin et al., 2020) and atomic emission spectroscopy (AES) (Demir et al., 2020) were applied with different sample extraction methods.

 Some researchers performed, a microwave-assisted digestion with either the combination of nitric acid and hydrogen peroxide (Anastácio et al., 2018) or nitric acid and perchloric acid (Abbasi et al., 2020) followed by analysis using AAS. Microwave-assisted digestion results in shorter digestion time and avoids loss of metals by volatilization. However, the latter showed lower sensitivity.

 Moreover, Co and Ni were analysed in pomegranate juice with the application of a graphite furnace atomic absorption spectrometer after complexation with 8-hydroxyquinoline and liquid-liquid microextraction (Okhravi et al., 2020). The most outstanding advantage of a given technique was the use of nitrogen instead of toxic chlorinated solvents. The extraction was 625 performed within seconds and LODs on the level of 0.36 μ g/L for Ni(II) and 0.20 μ g/L for

 Co(II) were achieved. Another study shows, a green deep eutectic solvent dispersive liquid liquid extraction method (DLLE) used to extract and preconcentrate metals from the grape juice samples (Sorouraddin et al., 2020) followed by their analysis using FAAS. The most important factor in the DLLE technique is the choice of a relevant extraction and dispersion solvent. Hence, extraction solvent must have a high affinity for analytes, low solubility, high sample stability, be a liquid under standard conditions and have low vapor pressure (Makoś et al., 2020). In the study, the deep eutectic solvent acted as both a complexing agent and an extraction solvent. Application of deep eutectic solvents instead of hazardous chlorinated organic solvents is more and more popular. It may be due to their physicochemical properties: viscosity, density, acidity, basicity, polarity and good extractability. They can be designed according to the needs. Moreover, they are biodegradable, non-flammable. Thus, their use is in line with the requirements of green analytical chemistry (Makoś et al., 2020).

 Several researches intended to assess the quality of fruit juices, indicated the presence of some metals like Cr, Ni, Mn above their permissible limits established by Decree-Law 306/2007 from $27th$ August of Portuguese Legislation for drinking water, WHO (World Health Organization) and USEPA (United States Environmental Protection Agency)(Abbasi et al., 2020; Anastácio et al., 2018; Sorouraddin et al., 2020). Moreover, the health risks index (HRI) for some metals was evaluated. HRI was calculated as a proportion between the estimated daily intake of the metal and reference oral dose for each metal and the body weight. When HRI is below 1, the exposure to metal is considered as safe. However, the results showed HRI for Cd, Cr and Pb over 1, what signalize a danger for human health. Thus, the data confirms the importance of monitoring of metal ions in fruit juices. (Abbasi et al., 2020)

 Another approach of metal determination in fruit juices and nectars were done by inductively coupled plasma optical emission spectrometry (ICP-OES) method after microwave-assisted digestion (Demir et al., 2020). This method is characterized by fast extraction without the need of using organic solvents. Additionally, it showed a high sensitivity for all analyzed metals.

4.2.2. Chromatographic techniques

 Chromatographic techniques including GC and HPLC are widely applied techniques when it comes to monitor varietal organic contaminations in juice samples, as shown in Table 1. *Alternaria* mycotoxins in pomegranate fruit and juice samples were determined with the use of HPLC-DAD method (Myresiotis et al., 2015). In this method, samples were subjected to the QuEChERS-based extraction method using acetonitrile (ACN) as organic solvent. Moreover, ACN was also used as the organic modifier in the applied mobile phase what is a big drawback. Hence the single analysis lasts 35 min the ACN is consumed in large quantities per each sample. On the other hand, high sensitivity being able to detect at targeted analysis even trace amount 661 of toxins (LODs $\leq 0.02 \mu$ g/mL) was achieved. PAHs is another group of compounds being a subject of the study when quality of berry fruit juices was discussed. Analysis of a given group of compounds is very challenging, because they are present in very low concentration, so they need a pre-concentration step as well as a very sensitive analytical method of analysis (Zhao et al., 2009). Analysis of eight PAHs in grape juice samples was performed by using dispersive liquid liquid microextraction coupled with high performance liquid chromatography with

 fluorescence detection (DLLME-HPLC-FLD). DLLME was based on ACN (as a dispersive solvent) and methylene chloride (as an extraction solvent). Despite using toxic organic solvents in sample extraction, this method of extraction had a high enrichment factor (enrichment factors ranged from 296 to 462) leading to a wide linear range and high sensitivity as well as low detection limit.

 Another method was published for extraction and pre-concentration of twelve PAHs depending on using a vortex-assisted dispersive solid-phase microextraction (VA-d-μ-SPME) using ionic liquid-modified metal-organic frameworks (ILMIL-100(Fe)) followed by GC/FID (Nasrollahpour et al., 2017). This method has some advantages over the DLLME (Zhao et al., 2009), such as shorter extraction time (only one minute) and higher extraction efficiency (due to the use of ILMIL-100(Fe)). Combination of both (i.e., ionic liquid and MOF) lead to higher sorbent capacity. The developed GC method had high sensitivity (linearity range 0.02-200 ng/mL) and a short analysis time (15 minutes).

 Other researchers proposed GC/FID method for determination of six organic esters. In this method, sample pretreatment and pre-concentration were performed using polycarbazole/ionic liquid fiber for HS-PME. The synthesized fiber was cheap and had a long lifetime. Moreover, the extraction method showed high efficiency, however the extraction time was equal to 40 minutes. The developed GC method showed a wide linear range, as shown in Table.1. Total time of the analysis was 26 min (Feng et al., 2015).

 Furthermore, a highly sensitive GC-MS/MS method was published for analysis of twelve phthalic acid esters in grape juice (Rodríguez-Ramos et al., 2020). In this method, extraction and pre-concentration of the target esters were carried out by a modified QuEChERS method. Results of the validation of the extraction method showed high extraction recovery (75–115%) and good repeatability. The high sensitivity of the developed method facilitated its application for analysis of the cited analytes in grape juice samples and the results confirmed the presence of some of the studied esters at different concentration levels in some of the tested samples.

 As was previously mentioned, BAs are a group of compounds that are important to be monitored due to many reasons. As the BAs are usually hydrophobic, poor chromophores, and their concentration is usually low in complicated matrices, their determination in food samples and beverages is a challenging analytical task. Chemical derivatization by different reagents like dansyl chloride (for both primary and secondary amines) (Gomez-Gomez et al., 2018; Saaid et al., 2009) and O-phthaldialdehyde (specific for primary amines) is commonly used to improve methods sensitivity (Kelly et al., 2010) .

 BAs in different juice samples were analyzed by HPLC methods after different sample pretreatment and derivatization (Gomez-Gomez et al., 2018; Kelly et al., 2010; Saaid et al., 2009). In the method presented by Gomez-Gomez et al. (2018), BAs and phenolic compounds in grape juice were analysed to evaluate their functional and nutritional quality. Samples were homogenized with perchloric acid followed by derivatization with dansyl chloride. As well as, liquid-liquid extraction with toluene was performed. Analysis of eight BAs by HPLC-UV with a mobile phases (A) 100% ACN and (B) 50% ACN was done within 25 minutes. While, phenolic compounds were analysed with the use of the UPLC-UV method applying mobile phases of aqueous phosphoric acid (0.85%) and ACN (100%). Principle component analysis was then carried out and results showed that a higher phenolic compound content may be linked to a higher BAs content. The discovered association also showed that some bacteria that synthesize BAs are becoming more active at high pH levels. Some microbes' metabolism is inhibited by low pH, which prevents the synthesis of BAs (Gomez-Gomez et al., 2018). HPLC- UV method was also applied to determine BAs in blackcurrant and red grape juices after dilution in 0.1M HCl and aqueous extraction followed by derivatization with dansyl chloride (Saaid et al., 2009). The method had a wide linear range (Table 1), acceptable detection and quantitation limits as well as recoveries in the range between 90.0 and 106.3%. Seven BAs in grape juice was also evaluated after automated in-loop pre-column derivatization with an O- phthaldialdehyde and N-acetyl-l-cysteine, followed by HPLC analysis with fluorescence detection (Kelly et al., 2010). Chromatographic analysis takes 39 minutes. Because of the method's great sensitivity, no sample preparation other than a straightforward dilution was needed prior to derivatization, eliminating the necessity for an internal standard.

 In recent years, the application of lactic acid bacteria (LAB) inoculation to fruit and juices processing has gained popularity in the production of unique non-alcoholic fermented beverages. It is a simple and valuable biotechnological method that allows fruits to be processed into products with a longer shelf life. The effect of LAB inoculation on the chemical composition of bog bilberry juice was studied using an HPLC method (Chen et al., 2019). ACN:methanol in the ratio 4:1 (phase A) and 25 mM acetate buffer mixture were used as a mobile phase and separation of seven BAs within 93 minutes. The study also involved the effect of LAB on reducing sugars, organic acids, anthocyanins, and non-anthocyanins phenolic compounds. Results disclosed that inoculation with LAB resulted in significant changes in the juice composition. Sugars, anthocyanins, total phenolic acids, total flavanols, and amino acids contents decreased in the juices after incubation but no changes in organic acids were noticed. It was also observed, that the content of four biogenic amines as tyramine, cadaverine, putrescine and phenylethylamine decreased after incubation but isoleucine content increased 8 times. The findings of this study should be taken into consideration to design a fermentation process that does not result in significant losses of various health-promoting components and does not result in health risk related with the BAs content (Chen et al., 2019).

 Additionally, a UPLC method was published for testing nine BAs in grape juice to be used as a quality marker for grape-derived products (Gomez et al., 2020). The derivatization process for BAs was done with the use of dansyl chloride, while the mobile phase consisted of a mixture of 100% ACN (phase A) and 50% ACN (phase B). Analysis time was shorter as compared to those obtained using HPLC-based procedures (Chen et al., 2019; Gomez-Gomez et al., 2018; Kelly et al., 2010; Saaid et al., 2009). Additionally, it had a wide linear range and good sensitivity as presented in Table 1.

 Moreover, two GC-MS/MS methods were applied for the determination of BAs in grape juice samples (Cunha et al., 2011; Fernandes & Ferreira, 2000). Methods differs in the extraction techniques used. In the first one (Fernandes & Ferreira, 2000), the back-extraction with 0.1 M HCl was done after the amines have been extracted with the ion-pairing agent bis-2- ethylhexylphosphate dissolved in chloroform. Derivatization of the extracted amines was

- performed by using heptafluorobutyric anhydride reagent. Seven amines (β-phenylethylamine, tyramine, 1,3-diaminopropane, putrescine, cadaverine, spermidine and spermine) were quantified using this method with high sensitivity, accuracy and reproducibility. In the second one (Cunha et al., 2011), liquid-liquid extraction was used with a toluene as an extraction solvent and isobutyl chloroformate as an derivatizing agent. Application of a given method enables quantification of 22 biogenic amines in 25 minutes.
- Pesticides residues are also often present in complex matrices such as berry juice at very small concentrations, hence for detection of these harmful components highly sensitive and selective analytical methods are needed.
- The most widely used chromatographic technique for pesticide determination in fruit juice samples is GC with the application of different extraction techniques and detectors like:
- Liquid-liquid microextraction combined with gas chromatography coupled with time- of-flight mass spectrometry (LLME GC-ToFMS) which was developed for screening 165 contaminants from the group of pesticides and dioxins like PCBs and PAHs. Despite the satisfactory recoveries (76-120%) and simplicity of the extraction method, the use of chloroform and cyclohexane makes it unfavourable from the Green Analytical Chemistry requirements (Dasgupta et al., 2011).
- Multiresidue matrix solid-phase dispersion combined with GC coupled with electron capture detector (ECD) and nitrogen-phosphorus detector (NPD). The method allows to determine 160 pesticides in berry fruits and their products. The disadvantage of the proposed approach is the use of hexane as one of the extraction solvent (Wołejko et al., 2014a).
- Counter current salting-out homogenous liquid-liquid extraction combined with dispersive liquid-liquid microextraction coupled with GC/FID (CCSHLLE-DLLME GC/FID). The approach uses ACN as a coextraction/disperser, 1,2-DBE as an 775 extraction solvent and demonstrates large linear ranges (even $1-10000 \mu g L^{-1}$) for the 776 target analytes under the optimum extraction conditions (Farajzadeh et al., 2015).
- Montmorillonite clay intercalated with ionic liquids co-deposited with polythiophene polymer (PTh IL-Mmt) coated electrochemically on SPME coupled to GC/ECD (PTh IL-Mmt SPME GC/ECD). The method allows determination of 5 analytes in 33 min. The imidazolium group in IL, along with the porous surface structure of the fiber, all 781 contribute to the hybrid material's strong electrostatic contacts, hydrogen bonds, and π -782 π interactions, which results in a high capacity for adsorption of volatile pesticides (Pelit et al., 2015). The method is characterised by high extraction efficiency (88.7- 101.7%), high sensitivity and low detection limit presented in Table 2.
- Dispersive liquid-liquid extraction coupled with GC and nitrogen phosphorus detector (DLLME GC/NPD). The method allows to determine three classes of 787 pesticides (triazine, triazole, and neonicotinoid) at the ng mL^{-1} range. It is based on acid-base reaction, in which the extraction solvent (*p*-chloroaniline) is dispersed (by deionized water) into an aqueous sample. In this study low LODs and LOQs and high extraction recoveries and enrichment factors were attained present in Table 2 (Farajzadeh et al., 2016).
- Continuous sample drop flow microextraction combined with GC-MS (CSDF-ME GC- MS) was used to determine phorate, diazinone, dimethoate, disulfoton, and chlorpyrifos from the fruit juice. The application of narrow-necked conical shaped vessel results in short analysis time, high sensitivity and low total solvent consumption (Moinfar et al., 2020).
- Continuous sample drop flow microextraction combined with GC-MS (CSDF-ME GC- MS) is a similar approach as presented in the year 2020 however, different design of extraction vessel (the extraction vessel was a conical open-end vial set in a little container filled with double-distilled water) and halogen-free organic extraction solvent were applied. Lower limit of LODs and LOQs then in previously published report were achieved and the extraction recoveries in the range between 25.5 and 48.0% (Moinfar et al., 2021).
- Dispersive liquid-liquid microextraction coupled with GC/FID. And D (DLLME GC- FID) was used to determine pesticide residues including penconazole, chlorpyrifos, ametryn, clodinafop-propargyl, diniconazole, oxadiazon, and fenpropathrin from fruit juice. The *iso*-propanol was used as disperser and 1,2-dibromoethane as an extraction solvent. Moreover special shaped vessel (downward vaporization gas orientation) was designed and used for vaporization and ultra-preconcentration of the extract from DLLME step. The innovations of this study were good outcomes (presented in Table 2) using readily available, straightforward equipment. Recoveries from extraction were on the level of 55-89% (Farajzadeh et al., 2021).
- Multi-plug filtration clean-up combined with gas chromatography-electrostatic field orbitrap high resolution mass spectrometry (m-PFC GC-Orbitrap/MS) is a method developed for screening of 350 pesticides in grape and strawberry juice samples. This extraction method was found to be simple and time-effective. Moreover, highly efficient clean-up of all targeted samples was observed due to the fact that the m-PFC column has the advantage of multiwall carbon nanotubes (MWCNTs). MWCNTs have superior adsorption capacities compared to other sorbents because of their extraordinarily high surface area and distinctive structure. The extraction recovery was found to be 72.8–122.4%, revealing the high performance of the used extraction method (Meng et al., 2021).

 Another approach used for pesticides determination utilizes LC. Seven insecticides in grape juice samples were analysed using HPLC (M. Yang et al., 2014) after the ionic liquid-assisted LLME, which was based on the solidification of floating organic droplets utilizing a bell-shaped collection device (BSCD). The modification of the traditional LLME method increased its extraction efficiency since the use of BSCD allowed easier collection of the mixed extraction solvents (1-dodecanol and IL, which replaced commonly applied chlorinated solvents) and quicker separation after solidification. The method resulted in an efficient concentration of the studied components in the tested samples, the enrichment factor was in the range of 160 to 246 with little consumption of organic solvents.

 Picó & Kozmutza (2007) developed a highly sensitive LC-MS/MS for the analysis of four pesticides and their metabolites in different grape juice samples (Picó & Kozmutza, 2007). Solid-phase extraction (SPE) was carried out before the analysis, which yield in good extraction recovery (more than 80%), high sensitivity and low quantitation limit, as shown in Table 1.

- Many of the pesticides are prone to degrade due to oxidative mechanisms, thus authors checked
- the role of antioxidant for the increase of the durability of certain of the pesticide in fruit juice.
- Results indicated that the degradation rate of the targeted pesticides was slower in grape juice
- and quercentine-containing aqueous solutions than in water. These findings suggested that
- natural antioxidants found in fruit juices might decrease pesticide breakdown rates and enhance
- their persistence.

 Timofeeva et al. (2017) developed another fully-automated LC-MS/MS method for the detection of four pesticides in fruits and berry juices. Under the optimized conditions the proposed extraction procedure takes less than 2 min. Apart from that it is simple to perform, inexpensive and does not require complex equipment. However, authors suggest that combination with other pre-concentration method like SPE can improve the sensitivity (Timofeeva et al., 2017).

848 PCBs are another important group of compounds to be monitored in food and beverage samples. 849 Magnetic oleate-coated Fe₃O₄ nanoparticles (Ol-coated MNPs) were used for magnetic solid- phase extraction (mSPE) of selected PCBs from grape juice samples followed by GC-MS/MS analysis (Pérez et al., 2016). Authors compared the developed method with other presented in the literature like DLLE-SFO. It was showed that recovery obtained in this research was between 52-85% which was lower than in DLLE-SFO (73-106%). However, the mSPE GC-854 MS/MS method achieved higher sensitivity (LOD in the range between 1.6-5.4 ng L^{-1}) than in 855 the other work $(3.7-18.5 \text{ ng } L^{-1})$. Although no PCB was detected in real samples, the method validation results confirmed its ability to determine targeted chemicals in different samples.

 Furan and its derivatives are another group of compounds being of high interest of researchers. Furans are heterocyclic compounds, which contribute to the sensory qualities of a wide range of thermally processed foods (Shen et al., 2016). Shen, et al. (2016) proposed to determine furans in the foodstuff including grape, blueberry and pomegranate juice by static headspace GC-MS. Method was characterized by simple sample preparation (only homogenization by manual shaking and sodium chloride addition was needed). Satisfactory validation parameters were achieved for 13 furans determination (Table 1). However, the GC-MS analysis last more than 40 min. Results of this study revealed that furans were detected in trace amounts in the tested fruit juices (Shen et al., 2016).

 On the other hand, the aromatic profile of pomegranate fresh and commercial juices was studied and correlated to their sensory flavors using partial least squares regression (Vázquez-Araújo et al., 2011). In this study, a headspace–SPME combined with the GC-MS method was used. This study showed that there was a significant difference between fresh and commercial juices. Results showed that there were significant changes in their chemical composition with fresh- squeezed juice being distinguished primarily by the presence of terpenes and aldehydes, whereas furans played a key role in commercial juice aroma. Moreover, different juice manufacturing processes were found to alter the aromatic profile of the fresh juice. So,

- companies should search for different processing methods for pomegranate juice to improve its
- quality without affecting its health benefits or increasing its health risks.
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 Varming, et al. (2004) evaluated the effect on the aroma and thus, the content of aromatic compounds including furans, of blackcurrant juice after the thermal treatment's. For the purpose of the study a headspace GC/MS method (Varming et al., 2004). In this study, 881 blackcurrant juice samples were exposed to different temperatures (45-90 °C) for different periods (57, 80, 110, 130 s). Then the aromatic compounds were collected (samples were purged with nitrogen and target compounds were collected into the traps). Collected volatiles were thermally desorbed and determined using GC-MS. The developed analytical method was applied for the determination of 49 aroma compounds involving three furans. Results of the study proved that the concentration of several terpenoids, furans, and phenols have significantly 887 increased after thermal treatment of 90°C for 60 min. However, application of 60°C and less had no influence of the juice aroma compounds composition.

Another method used for furans determination was based on the SPME combined with GC-MS

designed to distinguish between healthy and noble-rotten grape berries (Furdíková et al., 2019).

 The concentration of 7 out of 13 significantly differs between healthy and noble-rotten grapes. It was noticed that the content of furans such as: 2-pentylfuran, dihydrofuran-2(3H)-one, 5-

butyldihydrofuran-2(3H)-one, 5-pentyldihydrofuran-2(3H)-one, 5-acetyldihydrofuran-2(3H)-

one 5-hexyldihydrofuran-2(3H)-one and 5-ethyldihydrofuran-2(3H)-one were higher in noble-

rotten grapes than in healthy fruits.

897 Table 1 Characterization of analytical methods applied for the metals, mycotoxins, PAHs, aromatic esters, pesticides, biogenic amines and furans determination in different fruit juices.

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898 BAs – biogenic amines; CCSHLLE-DLLME - counter current salting-out homogenous liquid-liquid extraction combined to dispersive liquid-liquid micro-extraction; CSDF-ME - continuous sample
899 drop flow micro-extraction; 899 drop flow micro-extraction; DAD – diode array detector; DES – deep eutectic solvent; DHS – dynamic headspace; DLLME – dispersive liquid-liquid microextraction; ECD – electron capture detector;
900 FAAS – flame atomic a 900 FAAS – flame atomic absorption spectrometry; FID – flame ionization detector; FLD – fluorescence detector; GC- gas chromatography; GFAAS – graphite furnace atomic absorption spectrometry;
901 HPLC – high performance li 901 HPLC – high performance liquid chromatography; HRTOF-MS – high resolution time-of-flight mass spectrometry; IC - ion chromatography; ICP-OES – inductively coupled plasma optical emission
902 spectrometry; IL – ionic li 902 spectrometry; IL – ionic liquid; ILSFOD-LLME – ionic liquid-assisted liquid-liquid microextraction based on the solidification of floating organic droplets; IS-SULLE - in-syringe sugaring-out liquid-
903 liquid extract 903 liquid extraction; LC – liquid chromatography; LLE-liquid-liquid extraction; MS – mass spectrometry; MSDP – multiresidue matrix solid-phase dispersion; m-PFC - multi-plug filtration cleanup;
904 mSPE – maanetic solid p 904 mSPE – magnetic solid phase extraction; NPD – nitrogen-phosphorus detector; QuEChERS - Quick Easy Cheap Effective Rugged Safe; PAHs – polyaromatic hydrocarbons; PCBs – polychlorinated
905 biphenyls: PTh IL-Mmt SPE - mo 905 biphenyls; PTh IL-Mmt SPE - montmorillonite clay intercalated with ionic liquids co-deposited with polythiophene polymer coated electrochemically on solid-phase extraction; Va-d-µ-SPE – vortex-
906 assisted dispersive assisted dispersive solid phase extraction; SPE - solid phase extraction; SPME - solid phase microextraction; ToFMS - Time-of-flight mass spectrometry; UV - ultraviolet/visible light detector

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5. Conclusions and future remarks

 From year to year, the demand for fruit juices increases. Particular interest can be observed for juices produced from superfruits, which include berries. This is due to the fact that consumers pay more and more attention to the composition of food products that they include in their daily diet. A very important feature of food has become its health-promoting properties, and thus health benefits.

 The presented literature review focuses on modern analytical methods that enable the determination of analytes contained in fruit juices that may have health-promoting properties, but also those analytes whose presence may be harmful to our health.

 In the case of the determination of bioactive substances, spectrophotometric techniques are used for preliminary studies to determine summary parameters, such as the total polyphenols content or total anthocyanins content. In order to more accurately determine the composition of fruit juices, chromatographic techniques, mainly liquid chromatography, are the most often used. These techniques enable the determination of chemical compounds even at the trace level, and are also characterized by good selectivity, accuracy and precision. The use of high-resolution chromatographic techniques enables the detection of new potential active substances contained in fruit juices. However, analyzes often require high consumption of organic solvents and complicated sample preparation procedures for the isolation of analytes. In accordance with the principles of green organic chemistry, the aim is to replace conventional solvents with greener ones, e.g. DES and solvents of biological origin. During the research, the aim is also to miniaturize modern analytical methodologies while increasing the throughput, thus enabling the determination of as many analytes as possible in a relatively short time. It should be noted that in order to understand the nutritional potential and health-promoting properties of fruit juices, it is necessary not only to determine bioactive substances, but also to study their metabolism in the human body. Increasingly, both targeted and untargeted metabolic approaches are being used in research. When establishing a chemical fingerprint and metabolic profiling, the key element is data analysis, during which bioinformatics tools are used. Metabolomics makes it possible to find new bioactive compounds, as well as new juice biomarkers that allow them to be distinguished.

 In the case of contamination of juices with microbiological and chemical agents, it is very important to find reliable methods to detect them. Due to the increase in the amount of possible food contamination caused by industrialization and globalization, food safety assessment should be at the heart of the food industry.

 Finding fast, reliable and sensitive methods for detecting contaminants in fruit juices is essential for assessing food quality and ensuring consumer safety. Spectroscopic techniques (AAS and ICP-EOS) are mainly used for metal content analysis. For the determination of other pollutants (e.g. pesticides, mycotoxins, phthalates, biogenic amines and others), chromatographic techniques (GC and LC) are most often used. During the research, the aim is to develop modern analytical methodologies enabling the determination of pollutants at lower and lower concentration levels. The ultimate goal of the new methodologies should be selective and sensitive, miniaturized, automated and lab-independent contamination determinations.

 It should also be noted that metabolomics has potential as a screening tool for detecting adulteration of juices, as well as their contamination. It can be a new strategy in the food industry, enabling quick detection of any irregularities in the composition of fruit juices.

- In the future, efforts should also be made to develop new analytical methods enabling the detection of
- impurities and quality control during in-situ juice. Different types of sensors can be used for this purpose,
- such as electronic noses, electronic tongues or electrochemical sensors.
- In accordance with the principles of sustainable development, the industry strives to reduce the amount
- of waste produced. Wastes obtained during the production of juices, such as pomace, seeds, skins, etc.,
- still contain large amounts of bioactive compounds. Future research should therefore aim at developing
- green methodologies for extracting bioactive compounds such as polyphenols, flavonoids or pectins
- from fruit pomace.
- In conclusion, comprehensive specifications for fruit juices should be established in the future. It is to be hoped that modern analytical methods, as well as international cooperation between scientists, will enable the development of such analytical tools that will guarantee that fruit juices entering the market will be healthy and safe for consumers.

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