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Mineral concentration in citrus peel flours

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Abstract

Citrus fruits are known for their health benefits but managing processing waste is a challenge. Extracting bioactive compounds from these residues to create new products is promising, but mineral analysis is essential for food safety. The objective of this study was to analyze how the methodology for obtaining flour from sweet passion fruit peel, Tahiti lime, Murcott tangerine, and pearl pineapple influences the amounts of minerals Fe, Zn, Mn, Cu, Cr, and to determine the presence of these minerals in flours according to the defined limits. Maceration demonstrated a significant reduction in mineral content, such as iron, zinc, manganese, copper, and chromium, in the flours of lime and tangerine peels and passion fruit albedo. There was an increase in mineral levels after this process, such as zinc in passion fruit flavedo flour and manganese in tangerine and pineapple peels. Fe, Zn, Mn, Cu, Cr were respectively determined in 100g^{-1} in flours, from lime peel: 3,696mg; 1,273mg; 22,834mg, 0.422mg; 1104.945 µg; tangerine peel: 1,322mg; 2,560mg; 13,571mg; 0.236mg; passion fruit albedo: 8,596mg; 6,480mg; 76,003mg; 1,031mg; passion fruit flavedo 8,609mg; 3,363mg; 86,167mg; 2,317mg; in pineapple skin: 12,181mg; 0.704mg; 71,018mg; *mg; 2224.215 µg. Cr was not determined in the flours: albedo and flavedo from passion fruit, and tangerine and Cu from pineapple peel. Flours are sources of minerals but must be consumed with caution due to high quantities that can exceed the maximum tolerable intake limits.

Keywords: atomic absorption spectrometry, fruit growing, waste products

Introduction

Citrus fruits are one of the largest fruit crops globally, having been enjoyed by humans for thousands of years due to their health benefits (Mahato et al., 2019; Ariwaodo & Olaniyan, 2024).

Around 30% of the production of these fruits is destined for the juice industry, generating approximately 60 million tons of waste such as peels, seeds, and membrane waste (Mahato et al., 2019). Although a fraction of agricultural and industrial waste can be reused, whether as animal feed or fertilizer, the majority is discarded, posing an adversity for the food and agriculture sectors. (Güzel & Akpınar, 2019), for representing an environmental threat, and stimulating the growth of pests in plantations (Ariwaodo & Olaniyan, 2024; Fouda-Mbanga & Tywabi-Ngeva, 2022).

The valorization of food by-products presents a variety of challenges, such as the instability of the raw material during processing, technological difficulties in large-scale production, high production costs, the use of non-food solvents for extraction, in addition to the importance of compliance with legislation, there is still a need for more regulations and scientific research. Ensuring the assessment of the safety and quality of valued by-products is essential, following the same standards required for products intended for human or animal consumption (Socas-Rodríguez et al, 2021; Mazzutt et al., 2021; Herrero &Ibañez, 2018).

Citrus fruit residues are rich in sugars, fiber, organic acids, amino acids, proteins, minerals, and essential oils. Currently, there are several technologies for conventional and emerging applications, which aim to isolate these bioactive compounds, or even transform waste into new by-products, that are safe for incorporation in the manufacture of new foods or products, in addition to being environmentally sustainable (Rifna et al., 2023;

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Ganesha et al., 2022).

The use of flour derived from fruit-growing residues in the production of bakery products has been increasingly explored in sensory and acceptance research studies (Sampaio et al., 2022; Oliveira et al., 2019; Micheletti et al., 2018). However, there is little evaluation of the mineral composition of these flours.

Therefore, the objective of this study was to analyze how the methodology for obtaining flour from sweet passion fruit peel, Tahiti lime, Murcott tangerine, and pearl pineapple influences the amount of minerals, Fe, Zn, Mn, Cu, Cr, and determine the presence of these minerals in flour according to defined limits.

Material and methods

Raw material

The sweet passion fruit (*Passiflora alata Curtis*), the Tahiti lime (*Citrus latifolia Tanaka*), and the pearl pineapple (*Ananas comosus L. Merril*) were purchased from CEASA suppliers in Londrina-PR and the Murcott tangerine (*Citrus Sinensis* x *Citrus Reculata*) from CEASA of Mogi Mirim-SP.

Maceration of the peels and production of flour

The fruits were sanitized with 100 ppm chlorinated solution for 15 min and then rinsed. The peels were separated and chopped manually with the aid of a stainless-steel knife, with the sweet passion fruit peel separated into a spongy white part (albedo) and a yellow part (flavedo), and the remaining peels were used entirely. (Sampaio et al., 2022).

Aiming to reduce the bitter taste and astringency, caused by the various compound characteristics of citrus fruit peels, the peels were subjected to a maceration process in water, with the passion fruit flavedo, the passion fruit albedo, and the lime peel immersed in water at a temperature of 25°C for 24, 5 and 13 hours, respectively, changing the water every hour. The tangerine peel was immersed in water at 180°C for fifteen minutes, repeating the process three times, and then immersed in water at 25°C for 3 hours, changing the water every hour (Sampaio et al., 2022; Correia et al., 2021; Silva et al., 2016).

For mineral analysis, samples were collected from all shells that had only been washed in running water, and sanitized samples, which were immersed in water. These samples were dried in a vacuum oven for 48 hours, at 45°C, except for the passion fruit albedo samples, which remained for 68 hours.

To obtain the flours, the peels were dehydrated in an oven with air circulation until constant weight was obtained, lasting 19 hours for pineapple, 20 hours for lime, tangerine and passion fruit flavedo, and 29 hours for passion fruit albedo, all dried at 60°C, and subsequently crushed with the aid of a domestic blender and sieved with a 28 mesh particle size mesh (Sampaio et al., 2022; Correia et al., 2021).

Determination of metals.

The determination of Cu, Mn, Fe, Zn and Cr was carried out in an AA 240FS flame atomic absorption spectrometer (Agilent Technologies®, Santa Clara, CA, USA) equipped with mono elementary hollow cathode lamps (LCO), using the instrumental conditions wavelength, slit width, gas mixture for each element (air-acetylene or nitrous oxide-acetylene) and linear calibration interval to obtain the greatest sensitivity in the element determination method. Digestion of samples of washed, sanitized peels and albedo and flavedo flours of sweet passion fruit, and of Tahiti lime, Murcott tangerine, and pearl pineapple peels were carried out using a wet method in an open system with conventional heating in a digester block and with the aid of concentrated mineral acids (nitric acid and sulfuric acid) and an oxidizing agent (hydrogen peroxide) according to the procedure described below.

Sample decomposition: Around 0.5000g (±0.0001g) of the samples were subjected to acid mineralization in a digester block with the aid of 5.0 mL of HNO3 + 3.0 mL of H2SO4 at 200°C for 150 min. Then, three additions of 3.0 mL of H2O2 were made to the reaction mixture at 30-minute intervals for complete digestion. The final digests were volume to 50 mL with deionized water. The entire digestion procedure was done in triplicate (Peronico, 2014).

The results obtained were evaluated using programs such as Microsoft® Office Excel 2010, and analysis of variance and comparison of means using the Tukey test ($p \leq 0.05$) using Microcal OriginPro® 6.0.

Results and discussion

The mineral content present in fruits or their respective peels is very dependent on the way they are cultivated, fertilization, climate, soil type, and added fertilizers (Rotili et al., 2022), or also on the determination technique. The values obtained from the mineral analysis of the samples washed and sanitized after their drying process in a vacuum oven are found in **(Table 1)**, a process that concentrates the metals present for better evaluation between the samples.

The minerals that did not differ with the maceration process carried out on the peels were iron from tangerine, passion fruit and pineapple peels; zinc from pineapple peel; manganese in lime peel; copper

Table 1. Mineral content of citrus fruit peels before and after immersion in water (mean ± standard deviation)

Samples	Fe, mg g-1	Zn, mg g-1	Mn, mg g-1	Cu, µg g-1	Cr, µg g-1
Lime peel A	0.053±0.001a	0.013±0.000a	0.256±0.014a	4.142± 0.007a	11.495±0.574ª
Lime peel P	0,028±0,001b	0.011±0.000b	0.230±0.008a	3.351±0.001a	ND*b
Tangerine peel A	0.018±0.001a	0,007±0.000a	0.112±0.004a	3.412± 0.123a	10.493± 0.474a
Tangerine peel P	0.015±0.003a	0.024±0.000b	0.137±0.003b	4.234±0.413a	9.821±0.578a
Passion fruit albedo A	0.0910±0.0035a	0.0176±0.0011a	0.8103±0.0447a	12.8251±0.7066a	9.6426± 0.0346a
Passion fruit albedo P	0.0793±0.0046a	0.0101±0.0004b	0.3361±0.0046b	11.3414±0.3044a	*b
Passion fruit flavedo A	0.0889±0.0015a	0.0208±0.0009a	1.3991±0.0531a	33,3757±1.3930a	* a
Passion fruit flavedo P	0.0943±0.0090a	0.0353±0.0004b	0.8368±0.0199b	19.8162±0.3185b	* a
Pineapple peel A	0.1318±0.0100a	0.0057±0.0002a	0.5803±0.0071a	* a	24.8130±1.1259a
Pineapple peel P	0.1362±0.0040a	0.0058±0.0009a	0.6520±0.0043b	* a	26.5540±0.9310a

The same letters in the same column indicate that there was no significant difference between washed and macerated samples of the same fruit, according to the Tukey test ($p \leq 0.05$). A: washed sample. P: sanitized samples after the maceration process. *Values not found above the detection limit of 8 µg L^{-1} for Cu and 50 µg L^{-1} for Cr.

in lime and tangerine peels and in passion fruit albedo, not being quantified in pineapple peel; chromium in tangerine and pineapple peels, with no quantification in passion fruit flavedo.

However, for some minerals in certain samples, the maceration process reduced significant amounts, such as iron in lime peel; zinc in lime peels, tangerines, and passion fruit albedo; manganese in passion fruit albedo and flavedo, copper in passion fruit flavedo; chromium in lime and passion fruit albedo. Furthermore, there was a significant increase in some minerals after the process, such as zinc in passion fruit flavedo; and manganese in tangerine and pineapple, which can be justified by the possible presence of these minerals in the water used during the maceration process, permitted by ordinance GM/MS nº 888, DE 2021, and the characteristics of the peels themselves (Brazil, 2021). Studies that evaluate the types of washing in plant parts, about amounts of transition metals, consider that there is an influence on the control or increase of minerals, and contamination of the parts with the environment may occur (Venson et al., 2015).

Study on the effect of the accumulation of heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) in soils treated in the long term with elements that could be contaminants, observed that in this case there was no increase that reached the pollution levels, nor the presence of elements found in recalcitrant forms. However, when applying waste to the soil, the amount of contaminants that are applied and the respective residence time of each element must be considered, with the aim of not promoting their accumulation in quantities greater than those established by the National Environmental Council (Rocha et al., 2013).

Flour acquired from local food waste has been added to preparations and products that are part of everyday life, to improve nutritional quality, as current lifestyle eating habits are increasingly poor in micronutrients (Cavalcante et al., 2016). But care must be taken with the amount of minerals present in these flours because in some cases, there is a mistaken understanding that if a nutrient is good in a small amount, a large amount would bring greater benefits. The European Food Safety Agency's Micronutrient Guidelines in 2022 brought international recommendations, available in the form of Recommended Dietary Allowance (RDA), or, Dietary Reference Intake (DRI), constitute the most recent revision in terms of nutrient and energy recommendations adopted by the European Union, and bring the highest tolerable levels of intake, and if consumed values above this recommendation, which is defined as the maximum safe limit for consumption (UL), can become harmful (Berger et al., 2022)

In **(Table 2.)**, you can find the values of minerals present in a portion of flour, which is 100g, according to the resolution - RDC nº. 429, (Brazil, 2020).

The peel flours with the highest concentration of copper are the albedo and flavedo of sweet passion fruit, and pineapple did not present detection limit values. The presence of copper in citrus fruit flours can be explained by the fact that it is necessary for the synthesis of chlorophyll and acts by activating photosynthetic enzymes, indirectly influencing the formation of organic acids through respiration and sugars through photosynthesis.

Table 2. Values of minerals present in 100 grams-1 of citrus peel flour (mean standard deviation)

Samples	Fe, mg 100g-1	Zn, mg 100g-1	Mn, mg 100g-1	Cu µg 100 g-1	Cr µg 100 g-1
Lime peel flour	3.696±0,334	1.273±0.0637	22.834±0.368	433.237±20.275	1104.945±5.965
Tangerine peel flour	1.322±0.347	2.560±0.026	13.571±0.631	242.511±10.760	*
Passion fruit albedo flour	8.596±0.341	6.480±0.168	76.003±0.861	1031.161±28.553	*
Passion fruit flavedo flour	8.609±0.497	3.363±0.320	86.167±1.051	2317.183±95.118	*
Pineapple peel flour	12.181±0.349	0.704±0.017	71.018±0.896	*	2224.215±48.689

*values not found above the detection limit of 8µg L^{-1} for Cu and 50µg L^{-1} for Cr.

The copper content in vegetables is related to the soil in which they grow, and long-term dietary consumption of this mineral can cause liver damage (Guedes, et al., 2013). Its recommendation is between 1.1 and 2 mg/day in adults, but absorption is highly variable, ranging between 20 and 50%. Its deficiency appears in some specific clinical conditions, such as severe burns, after gastric and bariatric surgery, and in patients who require continuous renal replacement therapy, or the use of enteral and parenteral diets. Poisoning is rare but can occur in an industrial context. May be caused by dietary supplements or drinking contaminated water (Berger et al., 2022).

Albedo and flavedo flours from sweet passion fruit and pineapple peel had higher iron concentrations. Iron is necessary in lesser amounts to maintain normal physiological processes, being necessary for most, if not all, pathways for energy and substrate metabolism, its recommendation varies according to life cycles (Berger et al., 2022). Iron consumption above the UL, which is 45 mg per day, can cause gastrointestinal zinc to be present in lower concentrations in pineapple peel flour. Recommendations vary according to the life cycle and guidelines from different organizations: WHO recommends 3.0 to 9.8 mg/d for women and 4.2 to 14.0 mg/d for men; The Institute of Medicine suggests 8 mg/d for women and 11 mg/d for men; The European Food Safety Agency recommends 7.5 to 12.7 mg/d for women and 9.4 to 16.3 mg/d for men. Zinc plays roles in the body divided into three general functional classes: structural, catalytic, and regulatory. Zinc toxicity depends on the route and dose of exposure, varying between acute and chronic exposure (Berger et al., 2022).

Chromium is a transition element that exists in several valence states. Although Cr IV, V, and VI are carcinogenic, trivalent chromium is an essential trace element that is a component of metalloenzymes (Berger et al., 2022). We need more studies to know in what form it was found in Lime and pineapple peel flours. Studies are showing that chromium enhances the effect of insulin in vivo and in vitro, and regulates circulating lipids, but there is not much progress regarding harmful effects on the body as it is not a mineral that causes deficiencies in humans. Chromium is widely distributed in foods, but its distribution in fruits can vary (Institute of Medicine, 2002). Adequate oral intake of chromium is 35 µg/day and 25 µg/day for young men and women, respectively. Oral poisoning is rare due to poor absorption (Berger et al., 2022).

Manganese is present in several foods and the recommended intake for adults is 2.3 mg for men and 1.8 mg for women. It is a crucial mineral in bone formation, but excessive consumption can lead to neurotoxicity and worsen conditions in people prone to liver damage. (Institute Of Medicine, 2002; Berger et al., 2022).

The main route for ingesting metals is through food, however, there are few studies on their presence in foods, and in specific plant parts, there is no monitoring. According to Brazilian regulations, introduced by RDC No. 269 (Brazil, 2005), the mineral recommendation for the adult population is 14mg of Fe; 7mg of Zn; 900 µg of Cu; 35µg of Cr; and 2.3mg of Mn. These values must be consumed daily in the recommended amount to meet the nutritional needs of most healthy individuals, and food consumption below these amounts can cause various nutritional deficiencies. In general, lime, pineapple, tangerine, flavedo, and passion fruit albedo flours are sources of minerals, requiring attention with the portion size offered of these flours, as the metals Cu and Mn are found in abundant in fruit peels and can easily reach maximum intake limits, going from essential to harmful.

Conclusion

The technique for obtaining flour from fruit peels can influence the amount of minerals present, and the change in minerals present in the peel will depend on the characteristics of each fruit and the nature of the minerals present. The peels are excellent sources of minerals, in addition to contributing to the full use of food, but their use in the production of flour and the elaboration of new products must be carried out cautiously, considering the levels of minerals, especially contaminating metals, as the number of studies on metals in plant parts is still small, and these may have harmful effects on human health.

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