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Effect of Temperature Extraction on the Potassium and Calcium Content in the Lemon and Orange Water Peel Extracts

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Abstract

The aim of this study is to examine the effect of temperature extraction on the potassium (K) and calcium (Ca) contents in orange and lemon peel extracts. The extractions were done at 62 °C and 92 °C for 15 minutes and atmospheric pressure in distilled water. The fruit peel content in the extraction mixture was 5 % (w/v) in all samples. Calcium (Ca) and potassium (K) concentrations have been determined by flame photometric method. This research has revealed that by increasing the temperature of extraction, in particular, the concentration of Ca and K concentrations increased as applied extraction temperatures increased.

The concentration of potassium is higher than the concentration of calcium in orange and lemon extracts, respectively. The concentration of K was 308 mg/l at 62 °C and 361 mg/l at 92 °C in lemon extracts, while in orange extracts the concentration of K was 476 mg/l at 62 °C and 483 mg/l at 92 °C. The concentration of Ca was 70.8 mg/l at 62 °C and 71.9 mg/l at 92 °C in lemon extracts, while in orange extracts the concentration of Ca was 91 mg/l at 62 °C and 93.6 mg/l at 92 °C. These results confirm that both citrus could be a very valuable source of potassium and calcium which are needed micronutrients to ensure the water and electrolyte balance and to build and maintain strong bones, proper function of muscles and nerves.

Keywords: Orange And Lemon Peel, Water Extracts, Potassium, Calcium.

Introduction

The European circular economy package (European Commission, Closing loop—An EU action plan Circular Economy, 2015) explicitly aligns to the Sustainable Development Goal 12.3 and made food waste one of its priority areas. Any approach tackling food waste needs to align with sustainable development, making environmental, social and economic sense. Unger and Razza in 2018 suggesting that industry and society should move to circular economy models. Sweet orange (*Citrus aurantium*) is a very well known fruit, widely available in countries around the world. Although, sweet orange is the major fruit in this group constituting ~ 70% of the total citrus production and consumption.

Other citrus fruits, such as tangerine or mandarin (*Citrus Reticulata*), grapefruit (*Citrus Vitis*), lime (*Citrus Aurantifulia*), and lemon (*Citrus Limonum*) are also grown and consumed extensively (Okwi & Emenike, 2006; Sharma et al., 2017). The citrus processing industry yearly generates tons of residues, and orange peel is the primary waste fraction, from the extraction of citrus juice in industrial plants. The amount of world industrial waste of citrus is estimated at 15×10^6 tons (Marin et al., 2007). The management of these wastes, which produce odor and soil pollution, represents a major problem for the food industry (Ma et al., 1993). However, numerous studies have shown that orange peel can be further used to produce citric acid (Torrado et al., 2011) or even pyrolyzed orange peels as solid biofuels and biosorption of heavy metals (Santos et al., 2015).

This waste is rich in sugars, fibers, organic acids, amino acids and proteins, minerals calcium and magnesium, oils, lipids, and large amounts of flavonoids and vitamin A, vitamin B, vitamin C (Braddock , 1999) which are a



powerful antioxidant and may help to protect cell damage (Bratovcic, 2020). Therefore, citrus wastes are of immense economic value as it contains abundant amounts of various essential compounds. The composition of citrus fruits is affected by several factors, such as variety, growth, maturity stage and climatic conditions of that particular region (Salunkhe & Kadam, 1995). Calcium and potassium are minerals micronutrients that the body needs in smaller amounts. The fruit peel extracts may be further encapsulated, as recently has been reported by Bratovcic and Suljagic in 2019. The ratio of calcium to potassium is called the thyroid ratio and when it is not good, the thyroid gland does not work properly.

Four major minerals help regulate thyroid and adrenal function. These are calcium, magnesium, sodium and potassium. The normal level for each of these minerals is expressed in milligrams or percentages - for calcium it is 40, magnesium 6, sodium 25 and potassium 10. Potassium is involved in the regulation of the water and electrolyte balance and the acid-base balance in the body (Pohl et al., 2013; Stone et al., 2016). Calcium is an essential nutrient that is necessary for many functions in human health. Calcium is the most abundant mineral in the body with 99% found in teeth and bone. Only 1% is found in the serum. Calcium is involved in vascular contraction, vasodilation, muscle functions, nerve transmission, intracellular signaling and hormonal secretion (Beto, 2015). Lactose intolerance may determinate calcium malabsorption or may decrease calcium intake by the elimination of milk and dairy products.

The diet is characterized by food containing a high amount of calcium, potassium, magnesium and low amount of sodium. If it is impossible to reach the requirement with only diet, it is needed the supplement of calcium and vitamin D. Some drugs may interfere with calcium and other nutrients and produce an unfavorable effect on bone health (Miggiano & Gagliardi, 2005). The white inner part between the skin and the fruit can be consumed. It is sour or bitter but it contains more vitamin C than the fruit itself with a good deal of fiber. The bitter taste is the result of many flavonoids that orange peel contains. Flavonoids in orange peels have several anti-cancer effects. Global production of citrus fruit has significantly increased during the past three years. According to the Food and Agriculture Organization of the United States (FAO), the world orange production in 2017 was 17 218 173, while lemons and limes were 73 313 089 tonnes.

Recent research carried out by Czech et al., 2020 have revealed the greatest difference between pulp and peel was observed in pomelo and orange, as the peel of these two fruits was nearly seven and five times richer in this macronutrient than the pulp. Nutrients found in lemon (*Citrus limon*) peel specifically polyphenols, can help to manage blood glucose levels and improve insulin resistance. Health benefits of orange peel include: improves digestion, speeds up metabolism, helps in weight loss, strengthens the immune system, helps prevent cancer, improves oral health, beneficial for skin, good for diabetes. Based on all of the above, orange is a great source of nutrients, essential for overall health, as well as their peels, are equally important to include in everyday diet.

Research has shown that adequate calcium intake can reduce the risk of fractures, osteoporosis, and diabetes in some populations. The study aimed to investigate the influence of temperature on calcium and potassium contents in orange and lemon peel extracts, as well as to compare the mineral content between the citrus peel extracts and to determine which citrus fruit, among orange and lemon is the richest in examined minerals.

Materials and Methods

About 10 kg of fresh oranges and 5 kg of fresh lemons were collected in February 2018. The fruits were purchased at the same supermarket in Tuzla in Bosnia and Herzegovina. The origin of citrus fruits were from Spain. The goal of the author was to determine the concentrations of calcium and potassium and the information about cultivar is missing. Fruit peel extracts were collected after consuming a certain type of fruit. The fruit was washed with the tap water before consumption. Each fresh fruit peel after consumption was weight and then cut in small pieces and dried in the air for seven days. After air drying, the samples were ground in a grinder AD 443, Adler Europe, 150 W, then the same sample was weight and the free water percentage was determined.



Determination of free water

Free water is a part of total water, which evaporates at room temperature. The amount of each sample taken for air drying was 100 g. The previously weighed wet samples were left for drying at room temperature about 25 °C. Experimental data confirm that seven days of drying of the samples at room temperature were enough that the mass of the samples no longer change and remain constant.

From the mass data obtained before and after drying was possible to estimate the percentage of free water by using the following equation:

% free water = $\frac{a-b}{a}x100$

where:

a - mass of the sample in gram before drying

b - mass of the sample in gram after drying.

The drying of the sample has been done because of the stability of the samples in the dried state. During drying process, each piece of the sample were separated, because the formation of moist were observed when the pieces of fruit peels were overlapped. The final goal is to use air-dried fruit peels as the source of Ca and K.

pH and conductivity measurements

pH measurements were done by pH Meter Mettler Toledo MP220 and glass pH electrode Hanna Instruments HI 1053, 0-12 pH, temperature -5 to 70 °C in prepared fruit peel extracts, while conductivity measurements were done by conductometer Mettler Toledo MPC 227 pH/conductivity meter equipped with the electrode for conductivity measurements – Metler Toledo InLab 730 NTC, 0....1000 mS, 0 ... 100 °C.

Determination of potassium and calcium

Potassium analysis was performed by the plant-available phosphorus (P) and potassium (K) extracted by ammonium lactate (AL) solution (Egner-Riehm-Domingo method) (Egnér et al., 1960). The principle of the method is based on the extraction of potassium by an AL solution, which in chemical composition is 0.1 mol/l ammonium -lactate (CH₃CHOHCOONH₄) and 0.4 mol/l ethanoic acid (CH₃COOH). This AL solution desorb K⁺ ions from the sorption complex from the orange or lemon peel filtrate extracts.

In the extract filtrate, potassium is determined directly by flame photometry. Prepared standards are used to determine the potassium concentration. The standards are read on a flame photometer and a calibration curve is made, followed by plant extract filters. The potassium and calcium were determined by a flame photometric method with Microprocessor flame photometer, Labtronics AN ISO 9001:2008 certified company model LT-671.

Chemicals

Calcium carbonate (CaCO₃) was purchased from PanReac Quimica SLU (Barcelona, Spain) and potassium chloride (KCl) was procured from Lachner (Neratovice, Czech Republik). All chemicals and solvents used were of analytical grade.

Preparation of basic standard solution for potassium

0.5 g of potassium chloride was previously dried for 2 hours at 105 °C and then dissolved in 1 liter of distilled water. Five standard solutions for the potassium calibration curve were prepared in the concentration range



from 0-20 mg/l. The standard solutions consist of basic standard solution 0.5 g/l and 10 ml of AL working solution.

Preparation of AL working solution

275.48 ml of lactic acid with 0.66 l of distilled water were put in volumetric flask of 1 liter and left in the oven at 96 °C. After 48 hours, the distilled water was added on it. Then, 837.43 ml of this prepared solution were mixed with 577 ml of 99 % acetic acid. In this solution were added 256.6 g of ammonium acetate and then were diluted up to 3.3 liter with distilled water.

Basic standard solution for calcium

1000 mg/l: 0.624 g CaCO₃ was dissolved in a mixture of HCl and distilled water in a ratio, 1:1 and diluted to 250 ml. From basic standard solution, 1000 mg/l, was prepared 100 mg Ca/l, and then a series of standard solutions. The total number of standard solutions was 10 and they were prepared in 100 ml in the concentration range from 10-100 mg/l.

Preparation of orange and lemon peel extracts

In 100 ml of distilled water 5 g of air-dried orange/lemon peel was added and was heated to 62 °C and 92 °C and stirred at 500 rpm and kept for 15 min to make an extraction. Then, the samples were filtered through Whatman filter paper LGG-Plain disc filter, qualitative, very slow. The extracts prepared in this way were stored at 4 °C until further use. The names were given to samples by following weight percent w%, the initial letter of fruit and temperature: 5% N62C and 5% N92C; and 5% L62C; and % L92C, respectively.

Results and Discussion

In Fig. 1 is shown the appearance of the air dried orange and lemon peel samples. In a previous section under materials and methods the explanation of the procedure of preparation of samples are in detail described. These solid orange and lemon peels were used for the preparation of water peel extracts.



Figure 1. Air-dried orange and lemon peel samples.

In **Table 1** are shown the experimental results of mass % of free water in orange and lemon peels. The procedure of determination of the mass % of free water in orange and lemon peels were previously described in detail.



Number of samples	Mass % free water in orange peel	Mass % free water in lemon peel
1	73.1	76.3
2	73.5	75.9
3	74.2	74.5
4	72.8	76.3
5	70.7	77.5
Average mass % of free water	72.86	76.1

Table 1. Mass % of free water in orange and lemon peels.

From Table 1 is noticeable that fruit peel contain about 70 mass % of free water and 30 % of solid material. The solid part of orange and lemon were used for the preparation of water peel extracts.

In **Table 2** the experimental results of the pH and electrical conductivity are shown.

Table 2. Values of pH and conductivity of lemon and orange extracts.

Sample	рН	Electrical conductivity (µS/cm)
lemon	3.50	1938
orange	3.92	1023

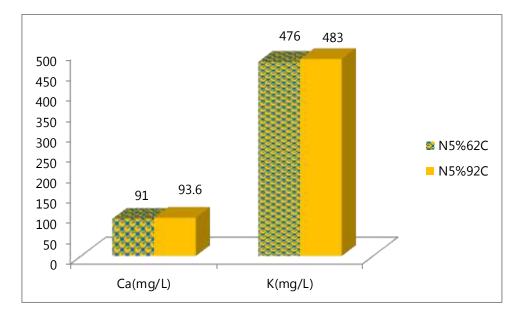
The results of pH (**Table 2**) indicate that both extracts are weakly acid. The pH value of lemon extract is 3.5 and the pH value of orange extract is 3.92. In recent research carried out by Bratovcic et al., 2018 were studied the physical-chemical properties and stability of orange juice at room temperature. The results have shown that the pH of squeezed orange juices with and without pulp was 3.2. This result indicates that the 5% orange peel extracts give more alkaline pH which is 3.92 compared to squeeze orange juice. This result may be explained by the different chemical composition of the pulp and peel fruits.

The conductivity values of the orange and lemon peel extracts were lower (1.023 and 1.938 mS/cm) than in squeeze orange juice (3.37 mS/cm). It is possible to assume that the presence of distilled which is not a good conductor of electricity and consequently gives lower conductivity values.

Determination of potassium and calcium

In Figs. 2-3 are presented the concentrations of calcium and potassium in 5 w/v of orange and lemon water peel extracts determined by the previously described method.





In Fig. 2 are shown the concentration of calcium and potassium in 5% w/v of orange water peel extracts.

Figure 2. The concentration of calcium and potassium in 5%w/v of orange water peel extracts at 62 and 92 °C.

From Fig. 2 is possible to note that the concentration of potassium in orange peel extracts is higher than the concentration of calcium. These results are in line with the raw nutrition facts of orange peel, where the concentration of calcium is 161 mg/100 g and potassium 212 mg/100g (NutritionValue.Org. available on: https://www.nutritionvalue.org/Orange_peel%2C_raw_nutritional_value.html). By increasing the temperature of extraction, the concentration of calcium and potassium slightly increases.

In Fig. 3 are shown the concentration of calcium and potassium in 5%w/v lemon water peel extract.

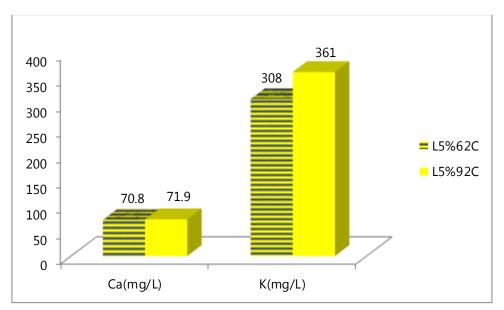


Figure 3. The concentration of calcium and potassium in 5%w/v of lemon water peel extracts at 62 and 92 °C.

From Fig. 3 is clear that the concentration of potassium in lemon peel extracts is higher than the concentration of calcium. These results are in line with the raw nutrition facts of lemon peel, where the concentration of calcium is 134 mg/100 g and potassium 160 mg/100g.



It is evident that by increasing the temperature of extraction the concentration of calcium slightly increase, while the higher concentration of potassium is more pronounced at higher temperature.

From Figs. 2 and 3 is possible to note that the concentration of potassium and calcium is higher in orange peel extracts, then in lemon peel extracts. This research reveals higher potassium and calcium content in oranges, which is in accordance with studies carried out by two different research groups (Baghurst et al., 2003; Liu et al., 2001). By increasing the temperature, the concentration of potassium is increased for 7 mg/l in orange peel extract, while in lemon peel extract is increased for 53 mg/l, while the concentration of calcium does not change significantly. Therefore, the influence of temperature extraction on potassium concentration is more evident than for calcium content. The results can help establish dietary guidelines for people suffering from potassium deficiency, as well as for lactating women, whose potassium requirement is higher, at about 5.1 g/d (Otten et al., 2006). The recommended daily intake (RDI) of calcium is 1000 mg per day for most adults, though women over 50 and everyone over 70 should get 1200 mg per day, while children aged 4–18 are advised to consume 1300 mg (Jennings, 2018).

Conclusions

In this paper, the assessment of temperature extraction on potassium and calcium contents in orange and lemon water peel extracts were done. Generally, the results indicate that by increasing the temperature of extraction from 62 to 92 °C the concentration of potassium is increased, while the concentration of calcium was almost constant. There is a small influence of temperature extraction on the concentration of both elements, but not significant. The results suggest that is better to make an extraction of citrus peel extracts at lower temperature considering that there are no significant changes in the concentration of examined minerals as well as from the point of saving energy and cost. The results have shown that orange peel extracts contain higher concentrations of potassium and calcium than lemon peel extracts. However, by increasing the temperature of extraction, increasing the concentration of potassium in lemon extracts is much more evident. According to the experimental results, the quantities of calcium and potassium indicate that lemon and orange peel extracts could be valuable sources of examined minerals. Lemon and orange peel could be employed as a functional food and become a significant source of micronutrients in the pharmaceutical industry for the production of mineral preparations in the form of tea or tablets with a high content of calcium and potassium. In future, this research is going to be extended to the study of the antioxidant capacity of the orange and lemon peel extracts. This may be one of the ways of the move towards a circular economy model relating to sustainable development, making environmental, social and economic sense.

Conflicts of Interest

The author declares no conflict of interest.

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References

- 1. Baghurst, Katrine & CSIRO. Health Sciences and Nutrition & Horticulture Australia (2003). *Update of citrus health benefits literature review*. Horticulture Australia, Sydney
- 2. Beto, J.A. (2015). The role of calcium in human aging. *Clinical Nutrition Research*. 4, 1-8. https://doi.org/10.7762/cnr.2015.4.1.1
- 3. Braddock R.J., Handbook of citrus by-products and processing technology (1999). Inc New York; John Wiley & Sons: 1-247



- 4. Bratovcic, A. (2020). Antioxidant Enzymes and their Role in Preventing Cell Damage. *Acta Scientifci Nutritional Health*, 4(3), 01–07. https://doi.org/10.31080/asnh.2020.04.0659
- 5. Bratovcic, A., & Suljagic, J. (2019). Micro- and nano-encapsulation in food industry. *Croatian Journal of Food Science and Technology*, *11*(1), 113–121. https://doi.org/10.17508/cjfst.2019.11.1.17
- 6. Bratovcic, A., Odobasic, A., Sestan, I., Tucic, E., Hasanbasic, A. & Saric, E. (2018). Determination of physicalchemical properties and stability of orange juice at room temperature, *Sixth international scientific conference "June 5th – World environment day*", 76-88.
- 7. Czech, A., Zarycka, E., Yanovych, D., Zasadna, Z., Grzegorczyk, I., & Kłys, S. (2020). Mineral Content of the Pulp and Peel of Various Citrus Fruit Cultivars. *Biological Trace Element Research*. https://doi.org/10.1007/s12011-019-01727-1
- 8. Egnér, H., Riehm, H., & Domingo, W. R. (1960). Untersuchungen über die chemische Bodenanalyse als Grundlage für die Beurteilung des Nährstoffzustandes der Böden. II. Chemische Extraktionsmethoden zur Phosphor- und Kaliumbestimmung. *Kungliga Lantbrukshögskolans Annaler*.
- 9. European Commission, Closing loop—An EU action plan Circular Economy, *Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions*, C.O.M. 0614, 2015.; available on: <u>https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52015DC0614</u>
- 10. Food and Agriculture Organization of the United Nations, available on 27.12.2019. http://www.fao.org/faostat/en/#data/QC
- 11. Jennings, K. A. (2018) Top 15 Calcium-Rich Foods (Many Are Non-Dairy). *Healthline*, available on 27.12.2019. https://www.healthline.com/nutrition/15-calcium-rich-foods
- 12. Liu, Y., Ahmad, H., Luo, Y., Gardiner, D.T., Gunasekera, R.S., McKeehan, W.L., & Patil, B.S. (2001). Citrus pectin: characterization and inhibitory effect on fibroblast growth factor-receptor interaction. *Journal of Agricultural and Food Chemistry*, *49*, 3051–3057; <u>https://doi.org/10.1021/jf001020n</u>
- 13. Ma, E., Cervera, Q., & Mejía Sánchez, G. M. (1993). Integrated utilization of orange peel. *Bioresource Technology*. 44, 61-63. <u>https://doi.org/10.1016/0960-8524(93)90209-T</u>
- 14. Marín, F. R., Soler-Rivas, C., Benavente-García, O., Castillo, J., & Pérez-Alvarez, J. A. (2007). By-products from different citrus processes as a source of customized functional fibres. *Food Chemistry*. 100, 736-741. https://doi.org/10.1016/j.foodchem.2005.04.040
- 15. Miggiano G.A., & Gagliardi L., (2005) Diet, nutrition and bone health. *La Clinica Terapeutica*. *156*, 47-56. Available on: <u>https://www.ncbi.nlm.nih.gov/pubmed/16080661</u>
- 16. NutritionValue.Org, Nutrition facts Product: Orange peel raw, available on 27.12.2019. https://www.nutritionvalue.org/Orange peel%2C raw nutritional value.html
- 17. Okwi, D.E & Emenike, I.N. (2006). Evaluation of the phytonutrients and vitamins contents of citrus fruits. *Int. J. Mol. Med. Adv. Sci. 2*, 1-6; available on: <u>https://medwelljournals.com/abstract/?doi=ijmmas.2006.1.6</u>
- Otten, J. J., Hellwig, J. P., & Meyers, L. D. (2006). Part III: Vitamins and Minerals: Thiamin Dietary Reference Intakes. In *Dietary Reference Intakes: The Essential Guide to Nutrient Requirements*. <u>https://doi.org/10.17226/11537</u>



- 19. Pohl, H. R., Wheeler, J. S., & Murray, H. E. (2013). *Sodium and Potassium in Health and Disease*. https://doi.org/10.1007/978-94-007-7500-8 2
- 20. Salunkhe D.K., & Kadam S.S. (1995). Handbook of fruit science and technology. Production, composition, storage and processing. CRC press; 1-632. Available on: <u>https://www.routledge.com/Handbook-of-Fruit-Science-and-Technology-Production-Composition-Storage/Salunkhe-Kadam/p/book/9780824796433</u>
- 21. Santos, C. M., Dweck, J., Viotto, R. S., Rosa, A. H., & de Morais, L. C. (2015). Application of orange peel waste in the production of solid biofuels and biosorbents. *Bioresource Technology*. 196, 469-479. https://doi.org/10.1016/j.biortech.2015.07.114
- 22. Sharma, K., Mahato, N., Cho, M. H., & Lee, Y. R. (2017). Converting citrus wastes into value -added products: Economic and environmently friendly approaches. *Nutrition*. 34, 29-46. <u>https://doi.org/10.1016/j.nut.2016.09.006</u>
- 23. Stone, M. S., Martyn, L., & Weaver, C. M. (2016). Potassium intake, bioavailability, hypertension, and glucose control. *Nutrients*. 8, 444. <u>https://doi.org/10.3390/nu8070444</u>
- Torrado, A. M., Cortés, S., Salgado, J. M., Max, B., Rodríguez, N., Bibbins, B. P., ... Domínguez, J. M. (2011). Citric acid production from orange peel wastes by solid-state fermentation. *Brazilian Journal of Microbiology*. 42, 394-409. <u>https://doi.org/10.1590/S1517-83822011000100049</u>
- 25. Unger N., & Razza F. (2018) *Food Waste Management (Sector) in a Circular Economy*. In Benetto, E., Gericke K., Guiton M. (eds.), Designing Sustainable Technologies, Products and Policies. Springer, Cham. 127-132, https://doi.org/10.1007/978-3-319-66981-6 15

