

Determination of Trace and Heavy Metals in Fruit Juices in the Romanian Market

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Abstract

The presence of trace, heavy metals in foodstuffs is of intense public interest. The aim of this study was to determine the metal contents in most known commercial fruit juices present on the Romanian market. The multielement analysis was made using the ICP-MS technique, after appropriate dilution, using the external standard calibration method. Multifruit, mango, and kiwi juice have recorded the highest concentration of Cu, while apple and pear juice has recorded the lowest concentration, and in the case of Zn, peach juice has recorded the highest concentration. Concerning Pb, Cd, and As concentration, apple, peach, and multifruit juices recorded the highest levels of concentration. The concentration of Zn, Cu, Co, and As generally, was higher in the juice samples packed in boxes, while Ni, Cr, Pb, and Cd recorded the highest values in the juice packed in plastic bottles.

Keywords: fruit juices, ICP-MS, metal analysis

Introduction

Food is required by all organisms for the sustenance of life, and its associated functions, such as development, growth, and maintenances of the body. Most food are mainly derived from animals and plants (vegetables, fruits, cereals, and grains) and provide the body with essential resources, such as vitamins and minerals (Adepoju-Bello *et al.*, 2012; Magomya *et al.*, 2015; Izah *et al.*, 2017). Some are consumed without further preparation after purchase (i.g. ready-to-eat food) while others require further processing before consumption. Fruit juice is highly appreciated, tasty food and usually has exceptional nutritional qualities, however, it can be a potential source of toxic elements to nutritional problems due to the low concentration of essential elements, justifying the

control of the mineral composition of fruit juice (Dehelean *et al.*, 2013).

The non-alcoholic beverages include many drinks such as carbonated drinks, juices, energy drinks, bottled water, tea, and probiotic drinks, but carbonated drinks and fruit juices represent the largest amount of non-alcoholic beverages, while water and some juices occupy the smallest respectively (Woyessa *et al.*, 2015, Abdel-Rahman *et al.*, 2019). Manufactures of these non-alcoholic beverages should require caution to ensure the purity of constituents used such as raw sources of water and packaging materials which mostly are the sources of contamination in the beverages (Abdel-Rahman *et al.*, 2013, Abdel-Rahman *et al.*, 2019).

In Romania, the consumption of juices have been steadily growing lately, following trends being also in other European Union countries, especially the consumption of fruit juices have been increased (Dehelean *et al.*, 2013). Commercial fruit juices commonly contain nutrients, minerals, trace elements, phytochemicals, and vitamins all of which have many health benefits when consumed moderately as part of a balanced diet, fruit juices have even a positive effect on promoting health and reducing disease risk (Anastácio *et al.*, 2018).

Trace elements are present in food in a concentration below 50 ppm and have some toxicological or nutritional significance. The macroelements, for example, Ca, Mg, K, and P are fundamental for people, while heavy metals like As, Cd, Pb, and Hg may cause injurious impacts even in low levels of 10-50 ppm. However, Zn, Cu, and Fe are found to be necessary in certain quantities in foods, but these elements may be harmful when are ingested in high concentrations. Other nontoxic elements are not unhealthy when present in concentrations beyond 100 ppm (Sn, Cr, B, Al, and Ni). The non-nutritive harmful metals which are known to have deleterious effects even in small levels (below 100 ppm) are Cd, As, Pb, and Hg, consequently, the concentration of both major and trace levels of metals in food is important for both food safety and for nutritional considerations also (Dehelean *et al.*, 2013).

Fruit juice from concentrate is the juice that has been concentrated and returned to its original state by the addition of water. When juice is obtained from a mixture of fruit juices and concentrates, the product label must indicate „partially from concentrates” which must be close to the product name, in the visible text (Rajauria *et al.*, 2018). Concentrate fruit juice is the product obtained from fruit juice by the physical removal of a specific proportion of the water content (normally by evaporation under vacuum). In the production of fruit juice, other than grape, mechanical extraction processes (e.g., pressing) may be combined with the diffusion of pomace (press residue) by water provided that the water extracted soluble solids are added in-line to the primary juice, before the concentration step (Rajauria *et al.*, 2018). Orange and apple juices are the most analyzed types, possibly because they are the most favorite ones and, as a result, the most consumed worldwide. On the other hand, juices

obtained from plum, red fruits, and strawberry were not included in many studies. Indeed, it was not possible to find similar studies analyzing red fruits juice or strawberry juice. Consequently, there are no data available for comparison with the results obtained herein.

The aim of this study was to determine the trace of heavy metals in most well known commercial fruit juices present on Romanian market and to compare these results to the maximum admissible limit set by different international organizations: United States Environmental Protection Agency (USEPA) and World Health Organization (WHO).

Materials and methods

42 commercial fruit juices (packed in box and plastic bottle) (orange, apple, peach, kiwi, pears, multifruit and mango) purchased from the Romanian market were investigated in this study. For the metal determination in juice, 0.5 mL juice was digested with 7 mL of 65% HNO₃ and 1 mL of 35% H₂O₂ using Milestone START D Digestion System, a microwave system (Bora *et al.*, 2018). After the mineralization process, the samples were filtered through a 0.45 µm filter and brought to a volume of 50 ml. The method of microwave digestion was optimized in previous work (Bora *et al.*, 2018). The analysis was made using multielement analysis and ICP-MS (iCAP Q Thermo Scientific) technique, after appropriate dilution, using the external standard calibration method. For each sample analysis replicates were measured in order to assure the quality control of our measurements.

Results and discussions

Cu and Zn are essential metals found in the environment, the biological functions of Cu include cell metabolism, normal iron metabolism, red blood cell (hemoglobin) synthesis, connective tissue metabolism, and bone development (Izah *et al.*, 2017). Multifruit (185.67 µg/L), mango (192.93 µg/L) and kiwi (188.06 µg/L) juice has recorded the highest concentration of Cu, while apple (83.97 µg/L) and pear (67.07 µg/L) juice has recorded the lowest concentration, and in the case of Zn peach juice has recorded the highest concentration. Concerning Ni concentration, peach (66.54 µg/L), kiwi (65.47 µg/L), and mango (67.15 µg/L) juice has recorded the highest concentration, regarding the biological function

Table 1. Concentration of different trace elements in fruit juices (mean ± µg/L)

Element	Samples	Cu	Zn	Ni	Cr	Co	Pb	Cd	As
M.A.L.	(US-EPA, 2018)	1300	5000	100	100	100	15	5	10
M.A.L.	(WHO, 2011)	2000	-	70	50	-	10	3	10
Orange	Box	144.95 ± 10.77 ^b	272.90 ± 12.59 ^c	45.22 ± 6.16 ^c	7.37 ± 0.78 ^d	1.42 ± 0.65 ^c	0.95 ± 0.30 ^e	< LOQ	< LOQ
	Plastic	151.08 ± 13.77 ^b	226.84 ± 9.56 ^d	49.81 ± 5.24 ^c	7.49 ± 2.06 ^d	1.53 ± 0.32 ^c	0.63 ± 0.16 ^e	< LOQ	< LOQ
Apple	Box	83.97 ± 5.28 ^c	322.94 ± 16.78 ^b	28.27 ± 4.00 ^d	34.39 ± 6.04 ^a	0.62 ± 0.11 ^d	10.71 ± 1.35 ^a	0.25 ± 0.08 ^b	< LOQ
	Plastic	84.12 ± 3.96 ^c	319.06 ± 11.61 ^b	27.29 ± 6.87 ^d	38.83 ± 8.54 ^a	< LOQ	11.06 ± 1.92 ^a	0.18 ± 0.05 ^b	0.16 ± 0.06 ^a
Peach	Box	142.71 ± 9.20 ^b	871.73 ± 5.47 ^a	66.99 ± 11.30	19.76 ± 2.35 ^b	< LOQ	3.99 ± 0.45 ^b	0.26 ± 0.15 ^b	< LOQ
	Plastic	144.43 ± 10.49 ^b	870.93 ± 15.86 ^a	66.54 ± 9.75 ^a	21.08 ± 1.30 ^b	< LOQ	3.21 ± 1.01 ^c	0.36 ± 0.01 ^a	< LOQ
Kiwi	Box	188.06 ± 6.22 ^a	32.63 ± 9.04 ^e	65.47 ± 9.47 ^a	13.43 ± 2.52 ^c	2.06 ± 0.15 ^b	1.32 ± 0.08 ^f	< LOQ	< LOQ
	Plastic	182.73 ± 11.24 ^a	36.88 ± 10.38 ^e	72.83 ± 5.63 ^a	17.95 ± 3.85 ^b	2.05 ± 0.14 ^b	1.27 ± 0.08 ^f	< LOQ	< LOQ
Pears	Box	71.43 ± 14.24 ^c	191.54 ± 8.46 ^e	15.30 ± 8.59 ^d	21.02 ± 1.40 ^b	3.76 ± 0.62 ^a	< LOQ	< LOQ	< LOQ
	Plastic	67.07 ± 7.90 ^c	201.56 ± 13.02 ^e	13.85 ± 4.91 ^d	24.07 ± 3.89 ^b	3.68 ± 0.74 ^a	< LOQ	< LOQ	< LOQ
Multifruit	Box	174.82 ± 9.55 ^a	192.13 ± 6.42 ^e	45.83 ± 5.29 ^c	7.71 ± 1.29 ^d	< LOQ	1.99 ± 0.85 ^e	< LOQ	0.19 ± 0.03 ^a
	Plastic	185.67 ± 8.39 ^a	197.39 ± 11.65 ^e	51.67 ± 5.90 ^b	7.19 ± 2.51 ^d	< LOQ	2.43 ± 0.85 ^d	< LOQ	0.17 ± 0.06 ^a
Mango	Box	185.47 ± 6.07 ^a	61.74 ± 11.05 ^f	67.15 ± 9.61 ^a	21.48 ± 1.61 ^b	0.37 ± 0.19 ^d	3.82 ± 0.58 ^b	0.20 ± 0.02 ^b	< LOQ
	Plastic	192.93 ± 16.24 ^a	69.50 ± 9.12 ^f	59.07 ± 14.81 ^b	22.32 ± 2.43 ^b	0.34 ± 0.06 ^d	3.20 ± 0.08 ^c	0.19 ± 0.06 ^b	< LOQ

Note: Average value ± standard deviation (n = 3). Roman letters represent the significance of the difference (Duncan test, p < 0.05). The difference between any two values, followed by at least one common letter, is insignificant. LOQ = lower than the limit of quantification. M.A.L. = maximum admissible limit (µg/L).

of Ni is still somewhat unclear; it is found in the body in highest concentration in the nucleic acids, particularly RNA, and is thought to be somehow involved in protein structure or function (Kumar *et al.*, 2016). Cr is one of the toxic essential heavy metals, it is highly detrimental to humans when its concentration exceeds tolerable limits, it aids in the biosynthesis of glucose tolerance factor, utilization of sugar protein and fats (Izah *et al.*, 2017), apple and pear juices have recorded the highest concentration. The results are agreed to those obtained by Abdel-Rahman *et al.* (2019) who noticed that concentrations of Cu in carbonated drinks range from 170.00 µg/L Cu to 0.560 µg/L Cu. Also, Dehelean *et al.* (2013) and Ofori *et al.* (2013) revealed that Cu, Zn had the highest level in the juice sample as compared to other determined metals. Co is a necessary cofactor for producing the thyroid hormone thyroxin, and also used in anemia treatment causing the red blood cells protection. All the samples studied contained Co concentration below the maximum admissible of USEPA (2008) and WHO (2008) (100 µg/L). In the case of Pb, Cd, and As the highest levels of concentration were recorded in apple (11.06

µg/L plastic bottle, 10.71 µg/L box), peach (0.36 µg/L), and multifruit (0.19 µg/L, 0.17 µg/L) juice. Pb, Cd, and As is highly toxic and responsible for several cases of poisoning through food, a low level of Cd causes adverse changes in the arteries of the human kidney (Bora *et al.*, 2018). The analysis of As content reveals the fact that nine fruit juice samples (apple and multifruit) show traces of these heavy metals, while in the rest of the analyzed samples these heavy metals were below the detection limit. The concentration of the metals found in all fruit juices are comparable with the values reported in the literature (Dehelean *et al.*, 2013). Also, Abdel-Rahman *et al.* (2019) and Abdellseid *et al.* (2013) studied the level of Cu, Cd, and Pb in mango juice from the Libian market, and results were very close to those presented in this study. The concentration of Zn, Cu, Co, and As were higher in the juice samples packed in box, while the highest concentration of Ni, Cr, Pb, and Cd were found in the juice samples packed in plastic bottles, the same conclusions were reached by Ofori *et al.* (2013) and Abdel-Rahman *et al.* (2019). Also, the level of toxic metals in carbonated drinks depends on the efficiency of the purification processes

during the production steps, the migration of metals from packaging materials to packed food or drink (Lahimer *et al.*, 2017). A possible explication for the variation in metals content between our tested samples was the type of water used during the production of carbonated drinks in Romania, and also the raw materials and manufacturing process. The variability of metal content between the different juice samples may result from the raw materials, water used in the juice production, the conditions of plant growth such as the toxic metals level in soil, irrigation water, the environmental contaminations (fertilizers and pesticides), purity of the added sugar, and the industrial processing and contamination of containers (Abdel-Rahman *et al.*, 2019). These results are comparable to those reported by Abdel-Rahman *et al.* (2019) and Hassan *et al.* (2014) who noticed that Pb and Cd were not detected in the most samples of fruit juices.

Conclusion

This study presents data on the levels of trace and heavy metals in commercial fruit juices (orange, apple, peach, kiwi, pears, multifruit, and mango) present on the Romanian market. Multifruit, mango, and kiwi juice have recorded the highest concentration of Cu, while apple and pear juice has recorded the lowest concentration and in the case of Zn, peach juice has recorded the highest concentration. Concerning Pb, Cd, and As concentration, apple, peach, and multifruit juices recorded the highest levels and in case of Cr apple and pears juices have recorded the highest concentration. The concentration of Zn, Cu, Co and As generally, were higher in the juice samples packed in the box, while Ni, Cr, Pb and Cd they recorded the highest values in the juice samples packed in plastic bottles. The variability of metal traces between the different juice samples may result from the raw materials, water used in the juice production, the conditions of plant growth such as the used concentration of toxic metals in soil.

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