

MINERAL CONTENTS IN THE WHOLE FRUIT, FLESH AND PEEL OF FIVE ROMANIAN APPLE CULTIVARS

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Abstract. The minerals content (Ca, Cu, Fe, Mn, Mg, Na, K and Zn) was determined in five Romanian apple cultivars (Ardelean, Auriu de Cluj, Feleac, Productiv de Cluj and Rosu de Cluj). The apples were collected from an orchard located in Cluj County, North-West region Romania, during 2014. The analytical method for the determination of selected elements in whole apple, flesh and peel consists in microwave acid digestion followed by inductively coupled plasma optical emission spectrometry measurement. The concentrations of the elements found in whole fruit/flesh + peel (a) flesh (b) and peel (c) were found to be comparable for most of the elements of interest, namely in mg/kg (d.w.): 28290, 28434 and 30350 K; 8.14, 7.66 and 8.31 Na; 241, 231 and 280 Ca; 244, 226 and 347 Mg; 3.18, 1.65 and 3.08 Cu; 2.82, 2.50 and 2.94 Fe; 1.30, 0.35 and 2.29 Mn and 1.57, 1.71 and 2.51 Zn, respectively.

Keywords: Romanian apple cultivar, microwave digestion, ICP-OES, minerals content

INTRODUCTION

Apples are the second most produced tree fruit (apple production is estimated at 75 million metric tons/2011) in the world after bananas (FAO, 2013). In 2011 in the European Union, in terms of apple production, Romania ranked sixth (620.000 tones), close to Spain, Italy, France and Greece. Apples are a good source of monosaccharides, dietary fiber, minerals, vitamin C, vitamin A and some phenolic compounds known for their action as natural antioxidants [1-4]. Generally, the content of total phenolic compounds and the oxidants activity is particularly higher in the apple peel than in the flesh and the whole fruit [6]. Interesting is the real proportion of apple peel to the whole apple quantity, based on its weight, especially as this part of fruit is often discarded as a waste product before eating or during apple processing [7, 8]. In Romania, the renewal process of apple cultivar seems to be slow and difficult due both high costs of a new apple orchard and the mentality of farmers/consumers. For many of these ones, especially in Transylvania, the best apple cultivars are still considered *Jonathan*, *Golden Delicious*, *Starkrimson*, *Gustav*, etc. The most well-known and spread apple cultivars created in Central Transylvania (*Aromat de vara*, *Ardelean*, *Ancuta*, *Feleac*, *Rosu de Cluj*, *Auriu de Cluj*, *Estival* and *Productiv de Cluj*) are producing good yields and highly appreciated fruit quality [9, 10].

The aim of this study was to determine the minerals content (Ca, Cu, Fe, Mn, Mg, Na, K and Zn) of 5 Romanian apple cultivars, under the climatic conditions of Cluj County, Romania.

MATERIALS AND METHODS

Materials and chemicals. Five apple cultivars (*Ardelean*, *Auriu de Cluj*, *Feleac*, *Productiv de Cluj* and *Rosu de Cluj*), were harvested from an experimental orchard located

in Iara (latitude 46°33'21" N, longitude 23°31'58" E and altitude 465 m), Cluj county, Romania, at harvest maturity, during 2014.

HNO₃ 65% and H₂O₂ 30% were of analytical grade and purchased from Merck (Darmstadt, Germany). Multi-element working standard solutions were prepared by appropriate dilution of the stock ICP multi-element standard IV Merck (Darmstadt, Germany) 1000 mg/L of Ca, Cu, Fe, Mn, Mg, Na, K and Zn in 0.2% (v/v) HNO₃. The certified reference material (NIST-SRM 1515 apple leaves) was obtained from LGC Standards GmbH (Wessel, Germany). All dilutions were prepared using ultrapure water (18.2 MΩ/cm) obtained from a Millipore Direct-Q3 UV system (Millipore, France) was used. All glassware was previously cleaned with nitric acid 10% prior to use.

Instruments. For the digestion of samples, a Berghof MWS-3+ closed-vessel microwave system with temperature control mode (Eningen, Germany) was used. The minerals content was determined by OPTIMA 5300 DV (Perkin Elmer, USA), inductively coupled plasma optical emission spectrometer (ICP-OES). The operating conditions for ICP-OES determination were 1300W RF power, 15 L/min plasma flow, 2.0 L/min auxiliary flow, 0.8 L/min nebulizer flow and 1.5 mL/min sample uptake rate. The axial view was used for metal determination, while a 2-point background correction and three replicates were used to measure the analytical signal. The emission intensities were obtained for the most sensitive lines free of spectral interference. Working wavelengths (nm) were: Ca 396.847, Cu 327.393, Fe 238.204, K 766.490, Mg 285.213, Mn 257.610, Na 588.995 and Zn 213.856. Argon (5.0 quality) from Linde Gas SRL Cluj-Napoca, Romania was used to sustain plasma and as plasma support gas.

Sample preparation. The fruit samples were washed several times with distilled water and dried before analysis. The flesh + peel (a), flesh (b) and peel (c) were obtained from 5 randomly selected apples in each trial to reduce variation. The flesh + peel (a) was considered the edible portion of the apple with the quantity of flesh and peel maintained in the same proportions as in the whole apple. The apples were peeled with a ceramic knife and the peel was separated from the flesh for analysis. The flesh was considered the edible portion of the apple without the peel.

The samples were dried at 105 °C and the dried samples were ground and homogenized using a metal-free mortar. Amounts of 0.2 g samples were weighted in Teflon reaction vessel for microwave assisted digestion. A volume of 7.5 mL of HNO₃ 65% and 3 mL of H₂O₂ 30% were added to each sample and the vessels were allowed to stand open until the initial reaction subsided. The samples were digested using a 5 step heating program (Table 1). After mineralization, the samples were quantitatively transferred to 25 mL volumetric flasks and diluted to the mark with deionized water.

Certified reference material NIST 1515 apple leaves and blank, consisting of deionized water and reagents, were prepared in the same way as the sample. All determinations were carried out in triplicate.

Table 1

Operating conditions for the microwave digestion system

Parameter	Stage				
	1	2	3	4	5
Temperature (°C)	170	200	120	100	100
Pressure (bar)	30	30	20	20	20
Time (min)	10	15	10	10	1
Slope (min)	5	1	1	1	1
Power* (%)	80	80	10	10	10

* 100 % power refers to 1450 W

RESULTS AND DISCUSSIONS

Quality of the analytical procedure was assured using NIST SRM 1515-Apple Leaves standard reference material. The obtained values (Cd, Cr, Cu, Fe, Pb, Zn, Ca, K, Mg and Na) of CRM compared with the certified values indicate that the measured values correlate well with certified values. The recoveries degrees of minor and major elements in the standard material were in the range 87-101%.

The obtained results, as given in Table 1 and 2, of the tested apple cultivars showed higher amounts of potassium followed by calcium, magnesium and sodium. The concentrations of these elements were determined in edible part of this fruits (whole fruit, flesh and peel).

The order of magnitude of the concentration for the elements found in whole fruit/flesh + peel (a) flesh (b) and peel (c) were found to be comparable for most of element of interest: 28290, 28434 and 30350 mg/kg K; 8.14, 7.66 and 8.31 mg/kg Na; 241, 231 and 280 mg/kg for Ca, 244, 226 and 347 mg/kg Mg, 3.18, 1.65 and 3.08 mg/kg Cu, 2.82, 2.50 and 2.94 mg/kg Fe; 1.30, 0.35 and 2.29 mg/kg Mn and 1.57, 1.71 and 2.51 mg/kg Zn, respectively ($K > Ca > Mg > Na > Cu > Fe > Mn > Zn$).

Some differences between cultivars were noticed in K and Ca concentrations. These differences could be probably the result of apple cultivar/plant nutrition given that the samples were collected from a single orchard during the same year (the same variety soil, local climate, production area, farming practices, quality of irrigation water).

The studied apples contain appropriate amounts of K, given that a low content of this element could determine some problems in terms of apple quality during long-term storage time [11].

The content of major elements (K, Na, Ca and Mg) in whole fruit (a) was found to be lower than those reported by Cindrić [3] for apple flesh and peel (39-47 mg/g K, 9-14 mg/g Na, 3-7 mg/g Mg), Hamurcu [12] (Na - 39.9 mg/kg) and higher than those determined by Horsley [13] for Ca - 0 mg/kg; K -11942 mg/kg, Hamurcu [12] for K - 921 mg/kg, Mg - 14.8 mg/kg.

The mean concentrations of minor elements obtained for apple were generally lower than those reported by Cindrić et al., 2012 (Zn - 3-7 mg/kg). Similar results were obtained by Nour [10] who reported K as the most abundant nutrient in different apple cultivars, followed by Mg, Ca, Na and Fe.

The recommended dietary allowances (RDA) for investigated elements are: 4700 mg K, 1500 mg Na, 1000 mg Ca, 400 mg Mg, 1.2 mg Cu, 8.0 mg Fe, 2.3 mg Mn and 11.0 mg Zn, respectively [14].

Therefore, one apple (~300 g fresh weight or 40 g dry matter) can offer up to 1132 mg K (24.1% RDA), 0.326 mg Na (0.02% of RDA), 9.64 mg Ca (0.96% of RDA), 9.76 mg Mg (2.44% of RDA), 0.143 mg Cu (11.9% of RDA), 0.147 mg Fe (1.84% of RDA), 0.073 mg Mn (3.17% of RDA) and 0.077 mg Zn (0.70% of RDA).

Thus, the investigated minor and major elements were found to have good nutritional contribution in accordance to RDA. The high amounts of K (35263 mg/kg), Mg (272 mg/kg) and Ca (413 mg/kg) and low Na level (9.12 mg/kg) in whole fruit (a) make *Productiv de Cluj*, of interest for the human diet.

Table 2

Mean concentration of investigated major elements in different cultivars: flesh + peel (a), flesh (b) and peel (c)

Apple cultivar	Mean concentration (mg/kg d.w.)			
	K	Na	Ca	Mg
<i>Ardelean</i>				
Flesh + peel (a)	22236 ± 252	7.56 ± 1.10	126 ± 26	266 ± 36
Flesh (b)	22216 ± 243	7.65 ± 0.96	112 ± 39	212 ± 28
Peel (c)	23566 ± 182	8.12 ± 1.45	212 ± 21	423 ± 45
<i>Auriu de Cluj</i>				
Flesh + peel (a)	21236 ± 145	7.23 ± 1.12	210 ± 23	245 ± 26
Flesh (b)	21565 ± 201	6.56 ± 1.56	220 ± 12	225 ± 12
Peel (c)	22879 ± 123	7.34 ± 1.25	234 ± 35	389 ± 39
<i>Feleac</i>				
Flesh + peel (a)	32125 ± 235	8.56 ± 1.00	199 ± 23	223 ± 12
Flesh (b)	31254 ± 128	7.23 ± 0.78	189 ± 17	202 ± 26
Peel (c)	33158 ± 189	8.65 ± 1.13	222 ± 35	369 ± 32
<i>Productiv de Cluj</i>				
Flesh + peel (a)	35263 ± 235	9.12 ± 1.12	413 ± 34	272 ± 32
Flesh (b)	34568 ± 345	8.95 ± 0.99	410 ± 36	256 ± 23
Peel (c)	37562 ± 232	9.14 ± 0.89	456 ± 53	298 ± 19
<i>Rosu de Cluj</i>				
Flesh + peel (a)	33265 ± 356	8.23 ± 0.72	256 ± 35	212 ± 20
Flesh (b)	32565 ± 324	7.89 ± 0.56	223 ± 42	234 ± 19
Peel (c)	34585 ± 235	8.30 ± 0.89	278 ± 36	255 ± 21

Table 3

Mean concentration of investigated minor elements in different cultivars: flesh + peel (a), flesh (b) and peel (c)

Apple cultivar	Mean concentration (mg/kg d.w.)			
	Cu	Fe	Mn	Zn
<i>Ardelean</i>				
Flesh + peel (a)	4.02 ± 0.18	3.21 ± 0.28	1.69 ± 0.21	1.23 ± 0.25
Flesh (b)	2.23 ± 0.23	2.36 ± 0.29	0.34 ± 0.05	1.65 ± 0.22
Peel (c)	4.23 ± 0.23	3.01 ± 0.17	3.01 ± 0.12	2.23 ± 0.17
<i>Auriu de Cluj</i>				
Flesh + peel (a)	3.98 ± 0.11	2.29 ± 0.18	1.23 ± 0.12	1.89 ± 0.12
Flesh (b)	2.01 ± 0.19	2.01 ± 0.15	0.35 ± 0.06	1.93 ± 0.22
Peel (c)	2.75 ± 0.15	2.45 ± 0.23	2.99 ± 0.23	2.78 ± 0.32
<i>Feleac</i>				
Flesh + peel (a)	3.26 ± 0.26	2.01 ± 0.23	1.23 ± 0.14	1.23 ± 0.24
Flesh (b)	1.23 ± 0.20	2.03 ± 0.12	0.45 ± 0.05	1.09 ± 0.32
Peel (c)	3.45 ± 0.17	2.34 ± 0.24	1.34 ± 0.11	2.20 ± 0.32
<i>Productiv de Cluj</i>				
Flesh + peel (a)	2.56 ± 0.28	3.56 ± 0.28	1.01 ± 0.20	2.28 ± 0.45
Flesh (b)	1.23 ± 0.19	3.23 ± 0.17	0.39 ± 0.09	2.56 ± 0.32
Peel (c)	2.75 ± 0.23	3.64 ± 0.14	1.89 ± 0.23	3.12 ± 0.42
<i>Rosu de Cluj</i>				
Flesh + peel (a)	2.10 ± 0.12	3.01 ± 0.21	1.35 ± 0.23	1.24 ± 0.26
Flesh (b)	1.56 ± 0.14	2.89 ± 0.23	0.23 ± 0.08	1.32 ± 0.12
Peel (c)	2.23 ± 0.20	3.27 ± 0.17	2.23 ± 0.11	2.20 ± 0.19

CONCLUSIONS

The results of this study provide valuable data regarding the minerals content in five Romanian apple cultivars, under climatic conditions of Cluj County, Romania. The

investigated Romanian apple cultivars (*Ardelean*, *Auriu de Cluj*, *Feleac*, *Productiv de Cluj* and *Rosu de Cluj*) have high content of K, Ca and Mg, but low in Na, as well as other essential minerals (Cu, Mn, Fe and Zn) in low concentrations, their consumption representing a good and healthy contribution to the nutrition.

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