

MINOR AND MAJOR ELEMENT LEVELS IN DIFFERENT VARIETIES OF APPLE GROWN IN CLUJ COUNTY, ROMANIA

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ABSTRACT. The concentrations of minor and major (Cd, Cr, Cu, Fe, Mn, Pb, Zn, Ca, K, Na and Mg) elements were determined in six apple varieties (*Florina*, *Golden Delicious*, *Idared*, *Jonathan*, *Prima* and *Starkrimson*). The apple samples were collected from an orchard located in the North-West region of Romania, Cluj County, during September 2011. The analytical method for the determination of selected elements in apple consists in microwave acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) measurement. In all samples, of all the investigated minor elements, iron was found to be the dominant element (4.64 mg/kg).

The increasing order was: Mn<Zn<Cu<Fe; Cd, Cr and Pb were below detection limit. The increasing order of investigated major element concentration was: Na<Ca<Mg<K, potassium being the dominant element (6921 mg/kg).

Key words: *apple, microwave digestion, ICP-OES, ICP-MS, minor and major elements*

INTRODUCTION

Apples are the second most produced tree fruit (apple crop is estimated at 69 million metric tons/year) in the world after bananas (<http://faostat.fao.org>). Despite competition from tropical and exotic fruits, world apple production has grown by about two per cent per year during the last period (<http://www.e-belrose.com/2013WorldAppleReview.html>). They are a good source of fiber, including the soluble fiber pectin, vitamin C, vitamin A and potassium (Wu et al., 2007). Besides 75–95% water, the edible portion of apples contains an important quantity of phenolic compounds, which contribute to flavor and can protect the human body from free radicals and reactive oxygen species (Cindrić et al., 2012; Hyson, 2011; Pandey et al., 2009).

Therefore numerous studies of different types of fruits, including apples, have been carried out because of the nutritional importance of these fruits, mainly regarding their acid, amino acid, mineral and vitamin contents (Auclair et al., 2008; Vieira et al., 2009; Ko et al., 2005).

Sample preparation is an important step in elemental analysis; microwave digestion has many advantages in comparison with open vessel digestion: short experimental time, low reagent consumption, good recoveries and enhanced operator safety (Krushevskaja et al., 1993; Bocca et al., 2007). Inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are rapid and accurate techniques for the simultaneous determination of the minor and major element contents in apples and apple juice. ICP-OES is useful for measuring higher concentrations, such as nutritional elements or high levels of contamination, while ICP-MS is suitable for determination of trace level elements or low levels of contamination Cindrić et al., 2012; Barnes, 1999; Froes et al., 2009; Zeiner et al., 2010; Davidowski et al., 2009).

The chemical composition of apples can be a good indicator of their quality and the health status of consumers. There are many variables that may influence the chemical composition and the nutritional value of apples, such as: the variety, soil, local climate, production area, farming practices, quality of the irrigation water, storage and commercialization conditions. To avoid the influence of these factors, the samples were collected from only one farm during only one harvest and not representative of the market.

The present work aimed to determine the content of minor and major element (Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Pb and Zn) in apples collected from a home orchard by using microwave assisted digestion followed by ICP-MS and ICP-AES measurement.

MATERIALS AND METHODS

Chemicals

All reagents used for this research work were of p.a. grade and purchase from Merck, Darmstadt. The certified reference material (NIST-SRM 1515 apple leaves) was obtained from LGC Standards GmbH, Wessel, Germany. All glassware was cleaned with nitric acid prior to use. For all dilutions ultrapure water (18.2 MΩ/cm) obtained from a Millipore Direct-Q3 UV system (Millipore, France) was used.

Instruments

For the microwave digestion of samples, a closed-vessel microwave system Berghof MWS-3+ with temperature control mode (Eningen, Germany) was used. The contents of major elements (Ca, Fe, K, Mg, Na) were determined by ICP-OES (OPTIMA 5300 DV, Perkin Elmer, USA), while those of minor elements (Cd, Cr, Cu, Mn, Pb, Zn) by ICP-MS (ELAN DRC II, SCIEX, Perkin Elmer, Canada).

Sampling and sample preparation

The fruit samples, six varieties of apple (*Florina*, *Golden Delicious*, *Idared*, *Jonathan*, *Prima* and *Starkrimson*), were collected from a home orchard located in the North-West region of Romania, in Cluj County, Cacova-Ierii village which is part of Iara commune, during September 2011. All trees were grafted on M106 apple tree rootstock.

Fruits were picked at the harvest maturity which is recommended for fruit destined for storage. The fruit samples consisted of five individual apple fruits picked from the same tree of the investigated orchard. The fruit samples were first cleaned and washed with water and then washed several times with double-distilled water. The edible portion of the fruit was sliced to small pieces with a ceramic knife and dried at 105°C. The water content was about 85%. The dried samples were ground and homogenized using a metal-free mortar. 0.5 g samples were weighted in a Teflon reaction vessel for microwave assisted digestion. 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 heating program in 5 steps (Table 1). After mineralization, the samples were quantitatively transferred to 25 mL volumetric flasks and diluted to the mark with deionized water. All digestions were made in triplicate. Certified reference material NIST 1515 apple leaves and blank, consisting of deionized water and reagents, were prepared in the same way as the sample. Three replicate measurements were made for each sample.

Table 1. Operating conditions for the microwave digestion system

Parameter	Stage				
	1	2	3	4	5
Temperature (°C)	170	200	100	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 Standard reference material (NIST-SRM 1515-Apple Leaves). The obtained values (Cd, Cr, Cu, Fe, Pb, Zn, Ca, K, Mg and Na) of CRM draw against 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% (Table 2).

Six apple varieties cultivated in Romania (*Florina*, *Golden Delicious*, *Idared*, *Jonathan*, *Prima* and *Starkrimson*) were analyzed for their minor and major element contents. The obtained results, as given in Table 3, of the tested apple varieties showed that all the analyzed samples contained higher amounts of potassium followed by calcium, magnesium and sodium. The concentrations of these elements were determined in edible part of this fruits. The content of major elements ranged from 5523-6921 mg/kg for K, 2634-3368 mg/kg for Ca, 2665-3502 mg/kg for Mg and 45.2-119 mg/kg for Na, respectively. The concentration of K was the highest in *Golden Delicious* while lowest in *Florina*. *Idared* exhibited the highest contents of Ca, whereas, lowest in *Prima*, respectively. *Jonathan* and *Starkrimson* showed the maximum and minimum values of Mg. The concentration of Na was highest in *Golden Delicious* while lowest in *Jonathan*.

Table 2. Certified and measured values of elemental concentrations in the standard reference material NIST 1515 apple leaves)

Element	Certified Value ^a (mg/kg)	Obtained value (mg/kg)	Recovery (%)
Cd	0.013 ± 0.002	0.012 ± 0.002	92.3
Cr	(0.3)	0.28 ± 0.02	93.3
Cu	5.64 ± 0.24	5.41 ± 0.07	95.9
Fe	83 ± 5	81.5 ± 1.1	98.2
Pb	0.470 ± 0.024	0.442 ± 0.024	94.0
Zn	12.5 ± 0.3	10.9 ± 1.0	87.2
Ca(%)	1.526 ± 0.015	1.432 ± 0.102	93.8
K(%)	1.61 ± 0.02	1.42 ± 0.07	88.2
Mg(%)	0.271 ± 0.008	0.272 ± 0.081	101

^a information values in brackets

With regard to the amount of minor elements, the content of Fe (2.44-4.44 mg/kg) was higher compared to Zn (0.77-1.65 mg/kg) in all tested apple varieties. The highest values of both of these elements were found in *Jonathan*, while the lowest in *Prima*. Similar results were obtained by Nour et al., 2010 who reported K as the most abundant nutrient in different apple varieties, followed by Mg, Ca, Na and Fe. In all apple samples the contents of heavy metals (Cd, Cr and Pb) were below the limit of detection (0.01, 0.10 and 0.01 mg/kg, respectively).

The content of major elements (K and Na) as determined in our present investigation was found to be lower than those reported by Cindrić et al., 2012 for apple flesh and peel (38600 and 9920 mg/kg d.w.), while the amount of Ca and Mg were comparable with our presented data. The concentrations of minor elements obtained for apple were generally lower than those reported by Cindrić et al., 2012.

European legislation (1881/2006/EC setting maximum levels for certain contaminants in foodstuffs) regulates the maximum admitted concentration of Pb (0.10 mg/kg wet weight) and Cd (0.05 mg/kg wet weight) in fruits. The obtained concentrations of Pb and Cd in all apple samples were lower than the values set by European regulations, indicating no harmful impact to human health by the consumption

of the apples grown at this part of Romania. The high amounts of K, Mg and Ca and low Na levels make these fruits, especially *Golden Delicious*, of interest for the human diet.

Table 3. Mean concentration of minor and major elements in different varieties of apple fruits

Variety	Mean concentration (mg/kg d.w.)			
	Cu	Zn	Mn	Fe
<i>Florina</i>	1.25	1.65	0.290	2.64
<i>Golden Delicious</i>	3.60	1.73	0.220	4.64
<i>Idared</i>	2.20	1.13	0.231	2.61
<i>Jonathan</i>	2.25	1.48	0.452	4.33
<i>Prima</i>	2.43	0.77	0.322	2.54
<i>Starkrimson</i>	2.21	1.53	0.139	2.87
	Ca	Na	Mg	K
<i>Florina</i>	2634	78.5	3400	5523
<i>Golden Delicious</i>	3107	119	2861	6921
<i>Idared</i>	3368	63.0	2951	6653
<i>Jonathan</i>	3154	45.2	3502	6678
<i>Prima</i>	2562	56.4	2853	5914
<i>Starkrimson</i>	2751	72.9	2665	6188

CONCLUSIONS

The total concentrations of minor and major elements were measured in six apple varieties cultivated in Romania (*Florina*, *Golden Delicious*, *Idared*, *Jonathan*, *Prima* and *Starkrimson*). The investigated apple samples contain significant amounts of several essential elements such as Ca, Cr, Fe, K, Mg, Mn, Na and Zn, their consumption representing a good and healthy contribution to the nutrition.

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