Multi-element analysis of methanol apple peel extracts by inductively coupled plasma-optical emission spectrometry

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ABSTRACT

Apples are among the most popular fruits in the world. They are rich in phenolic compounds, pectin, sugars, and a vast number of inorganics beneficial for the human health. In this study, variations of macroelements and microelements contents of five different apple cultivars peel's methanol extracts from Serbia were investigated, using inductively coupled plasma-optical emission spectrometry and principal component analysis (PCA). Regarding macro-elements, K, Na, Ca and Mg are with the highest contents. The most abundant essential element is Fe. Among toxic and potentially toxic elements, only the presence of Al and Sr is registered. The analyzed samples are classified into five groups by PCA.

Keywords: macroelements, microelements, methanol extract, apple cultivars

Introduction

Fruit and fruit juices are a highly appreciated, tasty food and usually have exceptional nutritional qualities. However, they can be a potential source of toxic elements, some of them having an accumulative effect or leading to nutritional problems due to the low concentrations of essential elements, justifying the control of mineral composition in fruit and fruit juice (Hague et al., 2008; Tormen et al., 2011).

Trace metals are present in foods in amounts below 50 ppm and have some toxicological or nutritional significance. The elements such as Na, K, Ca, and P are essential for people, while metals like Pb, Cd, Hg, and As, are found to cause deleterious effects even at low levels of 10–50 ppm. However, Fe, Cu, and Zn are found to be necessary in certain quantities in foods, but these elements can cause ill effects when ingested in high amounts. Other non-toxic metals which are not harmful when present in amounts not exceeding 100 ppm include Al, B, Cr, Ni and Sn. The non-nutritive toxic metals which are known to have deleterious effects even in small quantities (below 100 ppm) are As, Sb, Cd, F, Pb, Hg, and Se. For this reason, the determination of both major and trace levels of metal contents in food is important for both food safety and nutritional considerations (Dehelean and Magdas, 2013).

The trace element levels of fruits and fruit juices may be expected to be influenced by the nature of the fruit, the mineral composition of the soil coming from, the composition of the irrigation water, the weather conditions, the agricultural practices such as the types and amounts of fertilizers used, and other factors (Beattie and Quoc, 2000).

The determination of minerals in fruit and their juices has been carried out using several analytical techniques, each with its advantages and disadvantages. Several methods for the determination of trace metals have been commonly conducted by flame atomic absorption spectrometry (FAAS) (Bakkali et al., 2009), graphite furnace atomic absorption spectrometry (GFAAS) (Ekinci and Koklu, 2000), inductively coupled plasma-atomic/optical emission spectroscopy (ICP-AES/OES) (Mitic et al., 2012) or inductively coupled plasma mass spectrometry. Inductively coupled plasma-optical emission spectrometry (ICP-OES) has proved to be a rapid and accurate technique for the determination of minor and major element contents in fruits (Mitić et al., 2019). ICP-OES is attractive for trace analysis, owing to the satisfactory sensitivity coupled with the advantage of simultaneous determinations of several metals at different spectral lines. ICP-OES and exploratory analysis were used for the determination of metals in apple peel, apples and apple juice (Froes et al., 2009; Stojanović et al., 2014).

The extraction of organic compounds is widely studied (Carreraetal., 2012; Kitanovic et al., 2008), while the extraction of minerals is rarely investigated (Milić et al., 2014). Various extraction techniques have been employed for recovering extractive substances from plants. Today, novel extraction techniques such as ultrasound assisted solvent extraction are recommended because they have a greater separation efficiency of bioactive compounds in a shorter time and require a less amount of extracting solvent than the traditional ones (Wang and Weller, 2006).

Therefore, the objectives of this research were: a) to determine the mineral profile of peel of five different apple cultivars, and to examine the efficiency of different HCl concentrations in methanol for the ultrasound-assisted extraction of minerals, and b) to apply principal component analysis (PCA) to obtained results to characterize and differentiate the studied apple's cultivars.

Experimental

Fruit material

Five red apple cultivars (Pink Lady, Red Delicious, Idared, Braeburn and Modi) were purchased from local markets in Niš. All analyzed apple cultivars are frequently consumed in Serbia.

Chemicals

Ultra-scientific ICP multi-standard solutions of about 20.00±0.10 mg/L were used as a stock solution for calibration. Hydrochloric acid and methanol (Merck, Darmstadt, Germany) were both of the analytical grade.

Samples preparation

All apple samples were washed thoroughly and separately. Running tap water was employed to remove the dust and adhered particles and then the fruits were peeled off with a ceramic knife. The samples (apple peel) were later rinsed thrice with deionized water and subsequently dried in the oven at 60-80 ˚C and homogenized in a blender. Prior to ICP-OES analysis, 10 g of homogenized apple peel samples were transferred to an Erlenmeyer flask with 20 ml of solvent. After 1 h in an ultrasound bath (Bandelin SONOREX Digital 10 P, Sigma, USA), the solvent was decanted, fresh solvent added, and the process repeated five times. The extracts were combined, filtered using Whatman Filter Paper 3 Quantitative (pore size 6 μm) and made up to 50 ml with the solvent. Extracts were kept in the fridge until analysis (Stojanović et al., 2017).

The following solvents were used: methanol (%), methanol with 0.1% HCl, methanol with 1.0% HCl and methanol with 2.0% HCl for apple peel.

Instrumentation

The iCAP 6000 inductively coupled plasma-optical emission spectrometer which combines an Echelle optical design, and a change injection device (CID) solid state detector (Thermo Scientific, Cambridge, United Kingdom) was used for the analysis of the mineral contents. The blank sample involving the addition of all used reagents except sample was also processed to make corrections during calculation of elemental concentration. iTEVA operating software series was used to control all functions of the instrument. Under the optimal operating conditions for the instrument (working frequency power – 1150 W; analysis pump rate – 50 rpm; flush pump rate – 100 rpm; nebulizer gas flow – 0.7 L/min; coolant gas flow – 12 L/min and auxiliary gas flow – 0.5 L/min), analytical emission lines for each of the element were selected based on the tables of known interferences, baseline shifts and the background correction (the highest signal-to-background ratio) which was manually selected for the quantitative measurements.

Analyses were made in triplicates and the mean values are reported.

Analytical balance Mettler Toledo (Switzerland) was used to measure the mass. High purity water (conductivity 0.05 μS/cm) was obtained using MicroMed high purity water system, Thermo Electron LED GmbH (Germany).

Statistical analysis

Principal component analysis (PCA) was used as a statistical tool, and it was performed using the statistical application available for Microsoft Excel® (XLSTAT 2014.2.03, Addinsoft SARL, Paris, France).

Results and Discussion

The contents of the 17 minerals were determined in the apple peel extracts. The results, given as mean ± standard deviation, expressed as mg/dm^3 or $\mu g/dm^3$of extract. The determined elements were classified according to the criteria of the World Health Organization into the following groups: essential macroelements (Na, K, Mg, Ca, and P), essential trace elements and trace elements that are probably essential (Cu, Fe, Mn, Ni, Zn, B, V), and toxic and potentially toxic elements - some possibly with essential functions at low levels (Sr, Al, Pb, As, Cd).

The present study confirmed the presence of Na, K, P, Ca and Mg in the extracts obtained from apple peels by methanol solution with different concentrations of HCl. Table 1 shows how the macroelements content change in methanol solution at different acidity. Higher values of macro-elements were detected in the methanol extract with 2% HCl. Content of minerals increased with increasing HCl concentration because of better solubility of the minerals in acidic medium.

The order is as follows: K>P>Ca>Mg>Na. The results of ICP-OES analysis show that the content of K, Mg and P varies depending on the cultivars of apple while the contents Na and Ca show the smallest differences between the different cultivars. The higher Mg, P and Ca content was found in peel of Pink Lady, while higher amounts of K and Na were detected in the peel of Braeburn.

Potassium is the element with a major content in all samples, which average concentration is 22.329 mg/dm^3 in Pink Lady, 18.197 mg/dm^3 in Red Delicious, 8.258 mg/dm^3 in Idared, 23.042 mg/dm^3 in Braeburn and 7.518 mg/dm^3 in Modi, respectively. It plays a role in the maintenance of the balance of the physical fluid system and assisting nerve functions through its role in the transmittance of nerve impulses. It is also related to the heart activity muscle contraction (Ko et al., 2008; Lambert et al., 2008; Martinez-Ballesta et al., 2010). The recommended intake for K is 3500 mg per day (Martinez-Ballesta et al., 2010). Foods of plant origin contain potassium (K) from 20 to 730 mg/100 g fresh weight, although some plants such as 'Idaho' potatoes (*S. tuberosum*), banana (*Musa* spp.) and avocado (*Persea americana*) may all present high K contents (>700 mg/100 g fresh weight) (Martinez-Ballesta et al., 2010).

Mean value of phosphorus of the five cultivars in methanol with 2% HCl is 3.031 mg/dm^3. Phosphorus (P) is present in vegetables in the range of 16.2–437 mg/100 g. The lowest content of P is shown in fruits, which are in the range 9.9–94.3 mg/100 g (Szefer and Grembecka, 2007). Phosphorus is closely related to Ca homeostasis and related to the bone and teeth formation and most of the metabolic actions in the body, including kidney functioning, cell growth and the contraction of the heart muscle (Renkemaet al., 2008; Szefer and Grembecka, 2007). The phosphorus daily recommended intake is 800–1300 mg (Martinez-Ballesta et al., 2010).

Calcium concentration ranged from 1.744 to 2.153 mg/dm^3. The concentration of calcium (Ca) in foods of plant origin shows a wide range of variation. The lower values belong to apples (*Malus domestica*), green pepper (*Capsicum annuum*) and potatoes (*Solanum tuberosum*) (<8.7 mg/100 g) and higher values are present in broccoli (*Brassica oleracea* L. var. italica) (100 mg/100 g) and spinach (*Spinacia oleracea*) (600 mg/100 g) (Martinez-Ballesta et al., 2010). Calcium is an essential mineral for human health, participating in the biological functions of several tissues (musculoskeletal, nervous and cardiac system, bones and teeth, and parathyroid gland). In addition, Ca may act as a cofactor in enzyme reactions (fatty acid oxidation, mitochondrial carrier for ATP, *etc*.) and it is involved in the maintenance of the mineral homeostasis and physiological performance in general (Morgan, 2008; Williams, 2008). Recommended Daily Allowance (RDA) for these nutrients is set out in the wide range of 800–1300 mg/day (Martinez-Ballesta et al., 2010).

The concentration of sodium ranged from 0.813 mg/dm^3 (Idared, solvent-pure methanol) to 1.399 mg/dm^3 (Braeburn, solvent methanol with 1.0 HCl). Raw vegetables and fruit juices contain relatively low levels of sodium (Na) in the range from 2.28 to 94.0 mg/100 g and from 0.04 to 277 mg/100 g, respectively (Szefer and Grembecka, 2007). The role of Na in human physiology is related to the maintenance of the balance of physiological fluids (blood pressure, kidney function, nerve and muscle functions) (Hall, 2003; Sobotka et al., 2008).

It was found that the average contents of Mg found in five varieties of the apple peel samples were 1.860, 1.540, 0.415, 1.072, 0.559 mg/dm^3, respectively. Magnesium (Mg) has a strong presence in vegetable foods and also shows a critical role in the maintenance of human health through the diet. Vegetables and fruits contain, in general, Mg^{2+} in the range of 5.5–191 mg/100 g fresh weight, and the recommended daily intake is 200-400 mg (Martinez-Ballesta et al., 2010). This essential mineral acts as a Ca antagonist on vascular smooth muscle tone and on post-receptor insulin signaling. It has also been related to energy metabolism, release of neurotransmitters and endothelial cell functions (Bo and Pisu, 2008).

There is no literature available for the comparison with the current report as there are no studies on the evaluation of mineral content in methanol extract of apple peels. Nevertheless, several studies have evaluated the mineral composition of apple juice and the methanol extracts of plants. High contributions of K, Mg, and Na were observed in the infusions obtained from *Melissa officinalis* (852.3, 80.0, and 16.2 mg/L, respectively) (Petenatti et al., 2011). Also, high contribution of K, Mg, Ca, Na and P was observed in the methanol extracts of *Semecarpus anacardium* leaf (587.7, 44.5, 8.7, 47.0 and 10.4, respectively) (Pednekar and Raman, 2013). In apple juice the concentration ranges are the following for the major elements: 1.12–196.11 mg/L for Na, 13.07–140.42 mg/L for Mg, 52.52–642.34 mg/L for K and 21.54–338.35 mg/L for Ca (Dehelean and Magdas, 2013). The low contents of mineral in methanol extracts of apple peels are results of the low solubility of minerals in methanol.

Table 1. The content of essential macroelements (mean±SD[a] (mg/dm^3)) in apple peel extracts

Sample/ % HCl	K	Mg	Na	P	Ca
E1, 0.0	6.990±0.062	0.552±0.016	1.124±0.027	1.303±0.020	1.996±0.022
E1, 0.1	26.476±0.221	2.284±0.030	1.150±0.015	3.252±0.047	2.070±0.023
E1, 1.0	27.173±0.077	2.313±0.049	1.129±0.023	3.344±0.039	2.145±0.022
E1, 2.0	28.677±0.188	2.291±0.056	1.132±0.014	4.928±0.075	2.153±0.027
E2, 0.0	16.609±0.108	1.272±0.025	0.973±0.025	1.195±0.028	1.744±0.021
E2, 0.1	18.427±0.140	1.628±0.028	1.075±0.019	1.266±0.018	1.751±0.032
E2, 1.0	18.583±0.153	1.616±0.032	1.147±0.06	2.044±0.039	1.766±0.021
E2, 2.0	19.169±0.100	1.645±0.024	1.219±0.027	2.193±0.036	1.774±0.025
E3, 0.0	5.269±0.076	0.325±0.008	0.813±0.033	1.181±0.003	1.896±0.026
E3, 0.1	6.428±0.063	0.421±0.012	0.863±0.005	2.806±0.003	1.910±0.039
E3, 1.0	10.525±0.093	0.438±0.005	0.851±0.004	2.810±0.008	1.930±0.042
E3, 2.0	10.811±0.106	0.475±0.003	0.863±0.004	3.052±0.013	1.932±0.037
E4, 0,0	20.083±0.144	0.604±0.019	1.257±0.003	1.072±0.002	1.974±0.024
E4, 0.1	20.448±0.376	0.688±0.021	1.214±0.013	1.668±0.006	1.992±0.033
E4, 1.0	23.724±0.305	1.285±0.022	1.399±0.006	1.967±0.009	2.069±0.034
E4, 2,0	27.911±0.426	1.710±0.043	1.393±0.006	2.093±0.035	2.055±0.017
E5, 0.0	4.347±0.065	0.353±0.004	1.049±0.005	2.030±0.010	1.850±0.021
E5, 0.1	7.738±0.094	0.431±0.008	1.232±0.005	1.167±0.010	1.853±0.024
E5, 1.0	9.233±0.057	0.671±0.008	1.231±0.008	2.147±0.018	1.935±0.025
E5, 2.0	8.754±0.081	0.782±0.011	1.255±0.005	2.889±0.010	1.949±0.007

[a]SD-standard deviation for triplicate determination; E1 - Pink Lady; E2 - Red Delicious; E3 - Idared; E4 - Braeburn; E5 – Modi

The results of microelements are shown in Table 2. No significant variations were found for Zn, Ni, B, V and Cu, while Mn and Fe ranged from 3.2 to 43.6 μg/dm^3, 31.6 to 87.6 μg/dm^3 in methanol extracts with different HCl concentrations. In this study it was determined the lower contents for Fe, Mn, Cu, Zn and Ni compared to the apple juice (Dehelean and Magdas, 2013). The literature data showed the low extraction coefficients of these minerals in methanol solution (Micić et al., 2013).

The major microelements found in the methanol extract of apple peel were Fe (Table 2) with mean concentration of 60.8 μg/dm^3 in Pink Lady, 71.3 μg/dm^3 in Red Delicious, 72.5 μg/dm^3 in Idared, 67.5 μg/dm^3 in Braeburn and 83.2 μg/dm^3 in Modi, followed by Mn (34.65, 10.7, 18.4, 22.3, 17.4 μg/dm^3, respectively) and V (6.9, 5.9, 8.9, 7.6, 9.2 μg/dm^3, respectively). The other essential microelements determined (Ni, Zn, B, Cu) exist in much lower concentrations. Iron (Fe) contents in vegetables and fruits are low, varying from 0.13 to 3.01 mg/100 g. The iron in foods of plant origin is mostly present in the form of insoluble complexes of Fe^{3+} with phytic acid, phosphates, oxalates and carbonates. However, the bioavailability of the Fe present in foods is less than 8%. The major function of Fe is related to the synthesis of hemoglobin and myoglobin (Huskisson et al., 2007). The recommended intake of iron is 8–18 mg/day (Martinez-Ballesta et al., 2010). Fruits and vegetables are also characterized by a low content of manganese (Mn). Vegetables contain Mn in the range 0.01–0.078 mg/100 g and fruits 0.01–0.66 mg/100 g (Szefer and Grembecka, 2007). The recommended intake of Mn is 2 mg/day (Martinez-Ballesta et al., 2010), and its main physiological function is being an enzyme cofactor involved in antioxidant reactions related to the glucose metabolism (metabolism of carbohydrates and gluconeogenesis) (Huskisson et al., 2007).

Table 2. The content of essential trace elements (mean±SD[a] (μg/dm^3)) in apple peel extracts

Sample/ % HCl	Mn	Ni	V	Zn	B	Cu	Fe
E1, 0.0	16.8±0.9	0.8±0.0	6.2±0.4	1.6±0.0	0.4±0.0	1.6±0.0	31.6±1.5
E1, 0.1	37.6±2.2	0.4±0.0	7.0±0.4	1.6±0.0	0.4±0.0	1.8±0.0	52.6±1.3
E1, 1.0	40.6±2.0	0.2±0.0	7.2±0.4	1.8±0.0	0.6±0.0	1.8±0.0	79.8±0.8
E1, 2.0	43.6±2.1	2.0±0.0	7.2±0.4	1.8±0.0	0.6±0.0	1.8±0.0	79.2±0.6
E2, 0.0	4.8±0.4	1.6±0.0	5.6±0.4	1.4±0.0	0.4±0.0	1.4±0.0	57.0±1.0
E2, 0.1	8.8±0.6	1.6±0.0	5.8±0.6	1.4±0.0	0.4±0.0	1.4±0.0	57.8±2.0
E2, 1.0	14.6±0.4	1.8±0.0	5.8±0.4	1.6±0.0	0.4±0.0	1.4±0.0	82.8±1.8
E2, 2.0	14.6±0.2	1.4±0.0	6.4±0.6	1.6±0.0	0.4±0.0	1.4±0.0	87.6±1.4
E3, 0.0	3.2±0.2	1.4±0.0	8.6±0.8	1.4±0.0	0.2±0.0	1.2±0.0	63.8±1.6
E3, 0.1	23.4±2.0	1.6±0.0	9.2±0.6	1.4±0.0	0.4±0.0	1.4±0.0	70.8±2.0
E3, 1.0	23.2±2.0	1.6±0.0	9.4±0.6	1.4±0.0	0.4±0.0	1.4±0.0	77.2±2.0
E3, 2.0	24.0±0.6	1.4±0.0	8.4±0.4	1.4±0.0	0.4±0.0	1.4±0.0	78.2±1.6
E4, 0,0	16.2±0.4	1.4±0.0	7.4±0.4	1.4±0.0	0.4±0.0	1.4±0.0	67.2±1.9
E4, 0.1	23.6±0.2	1.4±0.0	7.6±0.6	1.4±0.0	0.6±0.0	1.4±0.0	51.2±1.8
E4, 1.0	24.6±0.4	1.2±0.0	8.0±0.6	1.4±0.0	0.6±0.0	1.6±0.0	77.4±0.6

E4, 2,0	25.0±0.6	1.4±0.0	7.6±0.4	1.4±0.0	0.6±0.0	1.6±0.0	74.4±0.6
E5, 0.0	13.8±0.4	1.0±0.0	8.8±0.8	1.4±0.0	0.4±0.0	1.6±0.0	79.0±0.6
E5, 0.1	15.8±0.6	1.2±0.0	9.6±0.8	1.4±0.0	0.4±0.0	1.6±0.0	75.8±0.6
E5, 1.0	20.0±0.4	1.2±0.0	9.2±0.8	1.4±0.0	0.4±0.0	1.8±0.0	81.0±0.6
E5, 2.0	20.0±0.4	1.0±0.0	9.4±0.6	1.4±0.0	0.4±0.0	1.6±0.0	97.2±0.6

E1 -Pink Lady; E2 -Red Delicious; E3 -Idared; E4 -Braeburn; E5 – Modi

The most toxic heavy metal loadings (Pb, As and Cd) of the samples are not detected, which suggest the absence of these pollutants in the vegetation zone.

According to Lopez et al. (2002) concentration range of Al in fruit juices was 49.3 to 1144 $\mu g/dm^3$. Also, a high level of aluminum was reported by Savić et al. (2015) who detected the aluminum content in the range of 0.29−2.1 mg/L in orange juice. In this study, the recorded amount of aluminum was in the range of 0.8 - 1.2 μ/L (Table 3). Aluminum is known as an extremely pro-inflammatory, pathological and genotoxic element which is particularly deleterious to the normal homeostatic operation of brain cells. But fortunately, aluminum insolubility at biological pH and highly effective epithelial, gastrointestinal and blood–brain barriers prevent this ubiquitous neurotoxin from accessing human biological compartments where it appears to contribute to inflammatory degeneration and pathogenic gene expression programs highly characteristic of the Alzheimer's disease (AD) (Savić et al., 2015; Velimirović et al., 2013).

Strontium belongs to the group of trace minerals and it has a similar biochemical pathway as Ca in the vertebrate body. Strontium has the role in increasing bone deposition, as well as in reducing bone resorption. In our study, the detected amount of strontium was in the range of 6.6 – 9.2 μg/L (Table 3). The obtained concentration of strontium was lower when compared to the results reported by Savić et al. (2015) where the content of strontium in the range of 0.05 – 0.46 mg/L was recorded in orange juices.

Table 3. The content of toxic and potentially toxic elements (mean±SD[a] ($\mu g/dm^3$ w.w.)) in the apple peel

Sample/% HCl	Sr	Al	Pb	As	Cd
E1, 0.0	8.6±0.0	1.0±0.0	nd	nd	nd
E1, 0.1	8.4±0.2	1.0±0.0	nd	nd	nd
E1, 1.0	8.8±0.2	1.0±0.0	nd	nd	nd
E1, 2.0	9.2±0.4	1.0±0.0	nd	nd	nd
E2, 0.0	7.6±0.2	0.8±0.0	nd	nd	nd

E2, 0.1	7.8±0.4	0.8±0.0	nd	nd	nd
E2, 1.0	8.6±0.4	1.0±0.0	nd	nd	nd
E2, 2.0	8.4±0.4	1.0±0.0	nd	nd	nd
E3, 0.0	8.2±0.8	0.8±0.0	nd	nd	nd
E3, 0.1	8.4±0.6	0.8±0.0	nd	nd	nd
E3, 1.0	8.8±0.8	0.8±0.0	nd	nd	nd
E3, 2.0	9.0±0.4	0.8±0.0	nd	nd	nd
E4, 0,0	7.0±0.6	1.0±0.0	nd	nd	nd
E4, 0.1	7.4±0.4	1.2±0.0	nd	nd	nd
E4, 1.0	7.6±0.6	1.2±0.0	nd	nd	nd
E4, 2,0	8.0±0.2	1.2±0.0	nd	nd	nd
E5, 0.0	6.6±0.2	1.2±0.0	nd	nd	nd
E5, 0.1	6.8±0.6	1.2±0.0	nd	nd	nd
E5, 1.0	7.4±0.4	1.2±0.0	nd	nd	nd
E5, 2.0	7.2±0.06	1.2±0.0	nd	nd	nd

E1 -Pink Lady; E2 -Red Delicious; E3 -Idared; E4 -Braeburn; E5 – Modi

For better illustration, PCA was conducted to evaluate the metal content in the extract of apple peel samples.

Based on the data obtained from the determination of the selected elements in the extract of the apple peels (Tables 1, 2 and 3), PCA was used for the possible similarities/differences of apple peel samples. PCA is a useful tool, because one of its advantages is a reduction of the number of variables of the experimental data and extraction of a small number of latent factors (principal components, PCAs) for analyzing relationships among the observed variables (Horel, 1981; Horel, 1984). According to such plot, it is possible to classify samples by their element distribution. The starting point for the PCA calculations was a matrix of data with dimensions n x p, where n is number of cases (rows) and p is the number of variables (columns). In matrix, methanol extracts of apple peel samples (Pink Lady, Red Delicious, Idared, Braeburn and Modi) with different acid concentrations were used as rows. Columns were the results of selected elements analysis of apple samples. As a result of PCA analysis, 14 new variables were obtained which were characterized by Eigenvalues.

Performed statistics with Pearson correlation matrix on apple peel samples based on selected elements content shows that there is a high positive correlation between the quantity of potassium and magnesium (0.868), zinc and magnesium (0.722), phosphorus and manganese (0.755), calcium and manganese (0.733), and aluminum and sodium (0.760); medium positive correlation between the quantity of potassium and manganese (0.648), sodium and potassium (0.552), zinc and potassium (0.523), boron and potassium (0.695), calcium and potassium (0.493), manganese and potassium (0.569), phosphorus and magnesium (0.468), boron and magnesium (0.477), copper and magnesium (0.490), strontium and manganese (0.545), zinc and manganese (0.643), boron and manganese (0.615), copper and manganese (0.480), boron and sodium (0.511), copper and sodium (0.525), strontium and phosphorus (0.568), zinc and phosphorus (0.612), calcium and phosphorus (0.558), copper and phosphorus (0.570), zinc and strontium (0.616), copper and zinc (0.513), aluminum and copper (0.634), calcium and boron (0.696), and copper and calcium (0.631); medium negative correlation between the quantity of vanadium and potassium (-0.525), vanadium and magnesium (-0.600), copper and nickel (-0.533), and aluminum and strontium (-0.528).

The number of factors represents the total number of variables used in the dataset. Eigenvalues for the first five factors are higher (5.451, 2.851, 1.912, 1.360 and 1.066, respectively) compared to values for the rest of factors. So, five factors must be used to explain the obtained variabilities (38.94 %, 20.36 %, 13.66 %, 9.72 % and 7.61 %) (Figure 1).

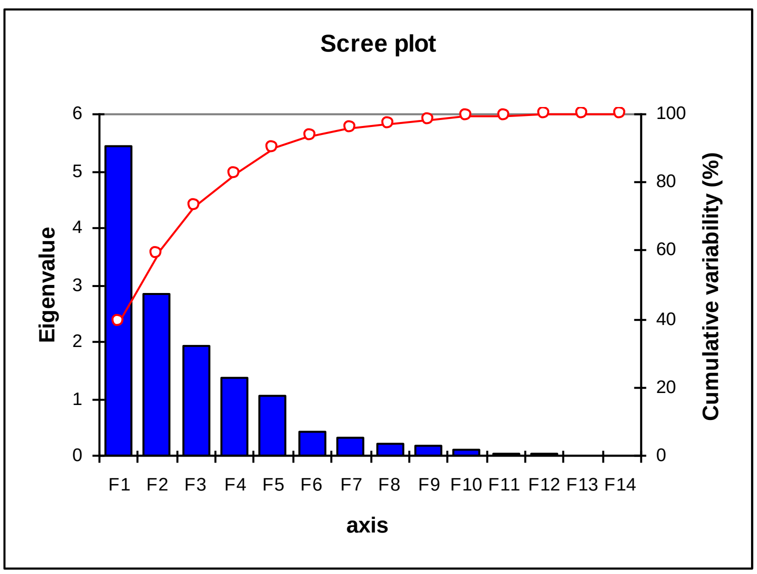
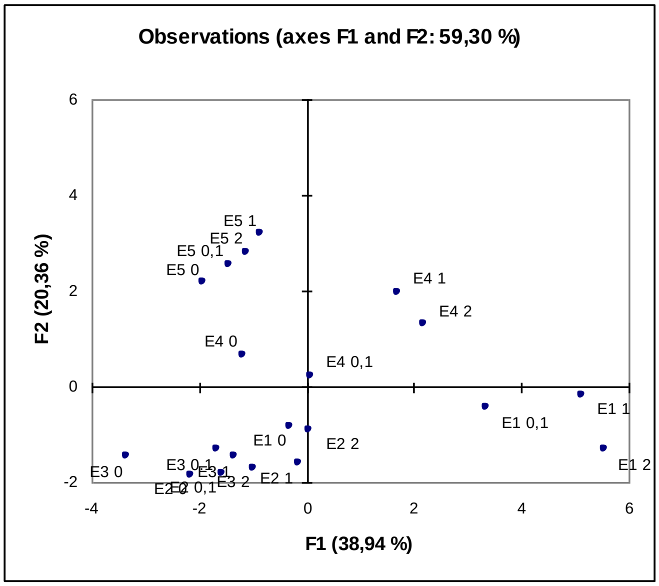
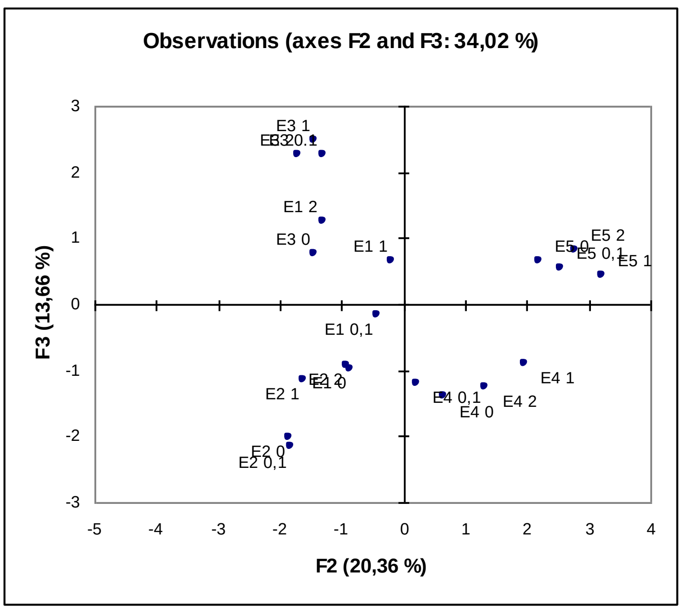


Figure 1. The importance of factors and values of cumulative variabilities

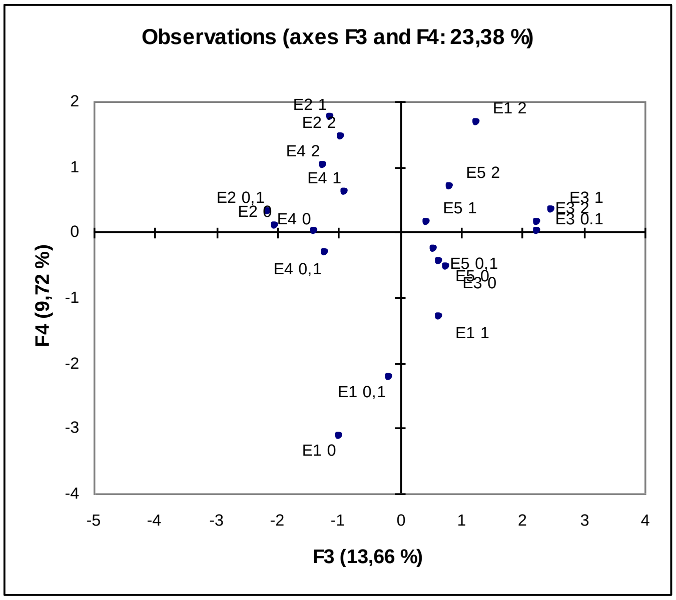
Observation plots based on the content of selected elements are represented in Figure 2.


Observations (axes F1 and F2: 59,30 %)
F2 (20,36 %)
F1 (38,94 %)
E5 1
E5 2
E5 0,1
E5 0
E4 1
E4 2
E4 0
E4 0,1
E1 1
E1 0,1
E1 2
E1 0
E2 2
E3 0
E3 0,1
E3 1
E3 2
E2 1
E2 0
E2 0,1

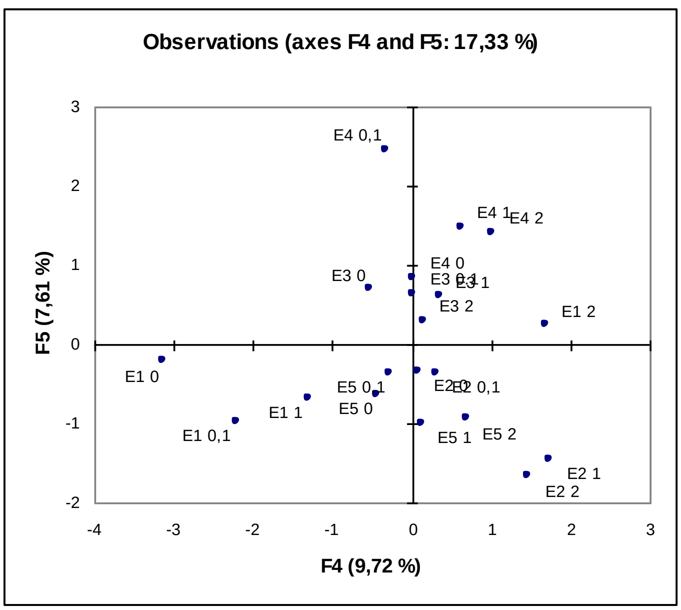
a)


Observations (axes F2 and F3: 34,02 %)
F3 (13,66 %)
F2 (20,36 %)
E3 1
E3 2
E3 0,1
E1 2
E3 0
E1 1
E5 0
E5 2
E5 0,1
E5 1
E1 0,1
E2 2
E1 0
E2 1
E4 1
E4 0,1
E4 0
E4 2
E2 0
E2 0,1

b)



c)



d)

Figure 2. Principal component score plots a) (F1 and F2), b) (F2 and F3), c) (F3 and F4), and d) (F4 and F5) of the studied plant samples based on the content of selected elements

From Figure 2a, it is visible that high content of potassium is present in the extract of apple peel samples on the right side of the plot and low on the left side of the plot. Also, it can be concluded that high content of magnesium is present in extracts of apple peel samples in the upper half of the plot and low on the opposite side of the plot. Similarly, Figure 2b shows high content of magnesium on the right side of the plot, and low on the left side of the plot. High content of manganese is present in the extract of the apple peel samples in the upper half of the plot, and low on the opposite side of the plot. Figure 2c confirms the information of the low and high quantity of manganese, but it also shows the quantity of sodium; high content of sodium is present in the extracts of the apple peel samples in the upper half of the plot and low on the opposite side of the plot. High content of sodium is present in the extract of the apple peel samples on the right side of the plot and low on the left side of the plot (Figure 2d). High content of nickel is present in extract of the apple peel samples in the upper half of the plot and low on the opposite side of the plot (Figure 2d).

Conclusion

The mineral profiles of peel of five different apple cultivars were determined, and the examination of the efficiency of different HCl concentrations in methanol for their ultrasound-assisted extraction was performed. Principal component analysis (PCA) was applied to the results obtained from the ICP-OES analysis to characterize and differentiate the studied cultivars of apple. The contents of the 17 minerals were investigated in the apple peel extracts: macroelements (K, Mg, Na, P, Ca), essential trace elements (Mn, Ni, V, Zn, B, Cu, Fe), and toxic and potentially toxic elements (Sr, Al, Pb, As, Cd). Lead, arsenic, and cadmium were not detected. Reasonable grouping of apple samples was obtained using PCA.

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Conflict-of-Interest Statement

None.

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