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ORIGINAL ARTICLE

The monitoring of mineral elements content in fruit purchased in supermarkets and food markets in Timisoara, Romania

Heghedűş-Mîndru Ramona Cristina[1], Heghedűş-Mîndru Gabriel[1*], Negrea Petru[2], Şumălan Radu[1], Negrea Adina[2], Ştef Ducu[1]

[1] *Banat's University of Agricultural Sciences and Veterinary Medicine „King Michael I of Romania" from Timişoara*
[2] *Polytechnic University of Timisoara, Romania*

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Abstract

This study aimed at evaluating various fruit samples by using the atomic absorption spectrometry method, and the content of mineral elements, macroelements (Na, K, Ca, Mg) and microelements (Cr, Cu, Mn, Fe, Cd, Pb, Zn, Co and Ni). Fruit samples were taken from supermarkets (imported products) and agricultural markets (domestic products) in the city of Timisoara, Romania. The results obtained by chemical analysis were evaluated statistically based on method of main components analyzed. Major influence in the group was evidenced if the macro-elements potassium and sodium, iron and manganese where microelements. The results were compared with results obtained by other researchers worldwide. The results fall within the legal limits set by law.

Key words

Fruits, mineral elements, atomic absorption spectrometry, principal components analysis (PCA), human health

INTRODUCTION

Fruits are an integral part of the human diet as they supply vitamins and minerals, important constituents essential for human health [1].

Plant foods sources of iron include dried fruit, peas, asparagus, leafy greens, strawberries and nuts. On the other hand, with few exceptions, fruits and leafy vegetables are believed to occupy a modest place as a source of trace elements due to their high water content. Consumers look for variety in their diets and are aware of the health benefits of fresh fruits and vegetables. Of special interest are food sources rich in Calcium (Ca), Magnesium (Mg) and Potassium (K). Most of these nutrient requirements can be met by increasing the consumption of fruits and vegetables to 5–13 servings/day In addition to meeting nutrient intake levels, a greater consumption of fruits and vegetables is associated with reduced risk of cardiovascular disease, stroke, and cancers of the mouth, pharynx, esophagus, lungs, stomach, and colon [2].

Numerous studies have shown that fruits and vegetables are rich sources of nutrients as well as non-nutrient molecules with antioxidant or other physiological effects, and it seems likely that given sufficient bioavailability, these compounds may be important constituents of a healthy diet. The health-promoting properties of plant-based foods have largely been attributed to their wide range of phytochemicals, many present at relatively high levels [3].

Trace elements, together with other pollutants, are discharged into the environment through industrial activity, automobile exhausts, heavy-duty electric power generators, refuse burning, and of use pesticides in agriculture, etc. Man, animals and plants take up these metals from the environment through air, water and food [4].

Plants require water, air, light, suitable temperature, and 16 nutrients to grow. Plants absorb carbon, hydrogen and oxygen from air and water. The other 14 nutrients come from the growing medium/soil.

Fruits are generally acceptable as a good source of nutrient and supplement for food in a world faced with the problem of food scarcity. They are known to be excellent source of nutrients, such as minerals and vitamins. Mineral ions are of prime importance in determining the fruit nutritional value, the major ones being potassium, calcium, and magnesium. In the tissue of many fruits, calcium is one of the mineral believed to be an important factor governing fruit storage quality. It has been reported to delay ripening and senescence and to reduce storage disorders. The importance of minerals such as potassium, calcium, sodium, etc. to human health is well known. Required amounts of these elements must be in human diet to pursue a good healthy life [5].

When a trace element is deficient, a characteristic syndrome is produced which reflects the specific functions of the nutrient in the metabolism of the animal. Trace elements are essential components of enzyme systems. Simple or conditioned deficiencies of mineral elements therefore have profound effects on metabolism and tissue structure. To assess the dietary intake and adequacy of minerals, information needs to be collected on the mineral element content of foods, diets and water. There is limited information on the trace element content of water and numerous plant foods consumed in some less developed countries [6].

The importance of mineral elements in maintaining good health is well known. Some elements help to combat infection, but they are also associated with many chronic, epidemic, endemic, and even malignant diseases. Numerous

Adress for correspondence: Heghedűş-Mîndru Gabriel*, Banat's University of Agricultural Sciences and Veterinary Medicine „King Michael I of Romania" from Timişoara
Calea Aradului nr. 119, 300645 Timişoara, jud. Timiş, România
e-mail: ramo75ro@yahoo.com

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epidemiological investigations have pointed out that a lack of essential mineral elements can precipitate an increase in sensitivity to illness, leading to suboptimal health or an enhancement of disease occurrence and development. If the human body is lacking zinc, copper and other trace elements, or if there is an imbalance in the body, it will lead to or aggravate some diseases, including coronary heart disease, diabetes, hyperlipidaemia, hypertension, and childhood zinc deficiency among others. Iodine, selenium, zinc, iron, copper, manganese, and chromium have been recognized as the essential mineral elements indispensable for maintaining normal life activities.

Although mineral elements cannot be synthesized by the human body, they can be obtained from the consumption of certain foods. Through the continuous progression in techniques for the sensitive quantitative analysis of trace elements, it became recognized that green and natural foods are important sources.

Heavy metals are mobile and are easily taken up by plants in the environment, and are commonly found in trace amounts in plants.

Another study showed that the Mn content of the tissue in the central region of the fruit was reduced by NH4 ions, whereas the Cu content of this tissue increased, and the highest concentrations of K were found in the neck and skin tissues, whereas the highest concentrations of Mn and Cu were observed only in the fruit skin [7].

MATERIALS AND METHOD

Chemicals. HCl (Merk), HNO_3 (Merk), C_2H_2 (Linde).

Fruits. 23 vegetables: Plums (Chile), Plums (Periam, Romania), Strawberries (Belgium), Strawberries (Dumbrava, Romania), Apples (Italy), Apples (Bucovat, Romania), Pears (Italy), Pears (Bucovat, Romania), Peaches (Greece), Peaches (Periam, Romania), Apricots (Greece), Apricots (Periam, Romania), Sour cherry (Hungary), Sour cherry (Bucovat, Romania) Cherry (Bulgaria), Cherry (Bucovat, Romania), Raspberry (The Netherlands), Raspberry (Dumbrava, Romania), Watermelon (Greece), Watermelon (Periam, Romania), Melon (Periam, Romania), Melon (Turkey), Grapes (Egypt).

Absorption/flame atomic emission spectrometer. Atomic Absorption Spectrometer – Varian 280 FS SpectrAA. Flame type: air/acetylene. The sodium, potassium, calcium, magnesium, chromium, copper, manganese, iron, cadmium, lead, zinc, elements determination by atomic adsorption spectrometry was performed with the atomic emission method. Analysis by flame atomic absorption spectrometry was performed under the conditions shown in **Table 1 and Table 2.**

In analysis of fruits, particularly importance has taken her test and training environments for analysis because the results should reflect as accurately as the chemical composition of fruit product sample was taken for analysis. In most cases the plant material is not homogeneous.

Conditioning of samples analyzed immediately after harvesting was carried out to remove impurities (ground or vegetation debris, etc.), by washing, followed by removal of adherent water with filter paper to full drying.

Table 1. Analysis by flame atomic absorption spectrometry

Element	Lamp current mA	Wave-length nm	Band width, nm	Air flow L/min	Flow rate C_2H_2, L/min	Standard mg/L
Chromium	7.0	357.9	0.2	13.5	2.9	2/4/6/8/10
Cooper	4.0	324.8	0.5	13.5	2.0	1/2/3/4/5
Manganese	5.0	279.5	0.2	13.5	2.0	1/2/3/4/5
Iron	5.0	248.3	0.2	13.5	2.0	3/6/9/12/15
Cadmium	4.0	228.8	0.5	13.5	2.0	0.5/1/1.5/2/2.5
Lead	9.0	217.0	1.0	13.5	2.0	2/4/6/8/10
Zinc	5.0	213.9	1.0	13.5	2.0	0.5/1/1.5/2/2.5
Calcium	6.0	422.7	0.5	13.5	2.0	5/10/15/20/25
Magnesium	6.0	202.6	1.0	13.5	2.0	5/10/15/20/25

Table 2. Analysis by flame atomic emission spectrometry

Element	Lamp current mA	Wave-length nm	Band width. nm	Air flow L/min	Flow rate C_2H_2. L/min	Standard mg/L
Sodium	6.0	589.0	0.2	13.5	2.9	5/10/15/20/25
Potassium	6.0	766.5	1.0	13.5	2.0	2/4/6/8/10

The primary samples thus obtained were mixed together and from the material obtained medium samples were formed after the quartering method. To determine the dry matter, macro and trace elements content of each variety, 100 ±0.001 g edible parts were selected.

The fruits were divided by cutting into small pieces and removing stones or shells with the use of plastic utensils. Divided fruits were placed in an oven at 105 °C until a constant weight was attained, i.e. when the loss of mass was the same one hour after the last weighing)

The porcelain capsules were cleaned and brought to constant weight by drying at 105 °C, weighing approximately 100 g (with an accuracy of ± 0.001 g) plant product). They were then placed in oven-proof capsules at 50–60 °C where they remained for 6 hours. The temperature was then raised to 105 °C and maintained another for 6 hours. After this time, the samples were removed from the oven capsules and allowed to cool in a desiccator provided with the desiccant agent. After cooling, the capsules were weighed and replaced in the oven. This was repeated until the differences between two successive weighings does not exceed ± 0.001 g.

Dry mineralization. Fruit organic matter was oxidized by oxygen in the air in a calcination furnace, heated gradually to 550 °C, which was maintained for 6–8 hours. The method used was that described in STAS 5954/1–86 (Fruit and vegetable products; mineralization samples for determination of metals – In Romanian), adapted to the specific analysis of plant products.

2 g of plant products obtained after drying were placed in a cold roasting oven. The temperature was gradually raised to 200–250 °C and maintained until complete charring was achieved. The oven temperature was then raised to 550 °C and maintained for 6–8 hours, until a white ash remained.

Wet mineralization. The volume of acid depends on the amount of ash sample. Mineralization of samples was performed as follows: 1–2 g sample with 10 ml HCl and 5 mL HNO_3, or 3–4 g sample with 21 ml HCl and 7 mL HNO_3.

This was boiled until an almost dry sample was obtained, then filtered and the filtrate washed so as to not exceed the volume of 100 mL (volume of the filter flask).

The operation was repeated for all 24 samples analyzed. Filtrates obtained were collected in glass bottles (100 mL) for analysis by atomic absorption of macro- and micro-elements.

Determination of macro and trace elements by atomic absorption spectrometry. The method is based on measurement by atomic absorption spectrometry, the concentration of macro and trace elements in the acid extract obtained from the ashes of the plant product sample. Analytical process includes two steps: digestion, dry route and dosage, by atomic absorption spectrometry.

Macro and trace elements distribute the hydrochloride solution spray mineralization obtained in an air-acetylene flame, and the measured absorbance at a wavelength characteristic of each element was analyzed.

Following the analysis made in terms of load in macro and trace elements (sodium, potassium, calcium, manganese, chromium, cooper, manganese, iron, cadmium. lead, zinc nickel and chromium), samples of primary horticultural products (fruits) bought from supermarkets and food markets were obtained. (**Tab. 3**).

Principal Components Analysis (PCA). In some cases, when the data set contains a large number of dependent variables, it may prove useful to reduce the data set into smaller segments to provide a clearer and more interpretable result. Principal component analysis (PCA) is an ideal tool for such tasks, in that a data set can be described by the principal components according to the degree of variance within the data.

Components with little explained variance can be omitted from the analysis, thus reducing the amount of data while still retaining most of the information. PCA may also be used in exploratory analysis, where plots of the principal component loadings can be used to identify variables that are similar to each other.

PCA is a mathematical tool which performs a reduction in data dimensionality and allows the visualisation of underlying structure in experimental data and relationships between data and samples. PCA was performed using The unscrambler software package (Version 9.7; CAMO, Norway). PCA transforms the original, measured variables into new, uncorrelated variables called principal components

The first principal component covers as much of the variation in the data as possible. The second principal component is orthogonal to the first and covers as much of the remaining variation as possible, etc. [8].

RESULTS

A maximum concentration of the element sodium was recorded for sample Melon (Periam, Romania) (9.35 mg/100g), and the samples: Strawberries (Belgium), Strawberries (Dumbrava, Romania), Apples (Bucovăţ, Romania), Pears (Italy), Melons (Turkey), Watermelons (Periam, Romania),

Table 3. Concentration of macro- and micro-elements (Na. K. Ca. Mg. Cr. Cu. Mn. Fe. Cd. Pb. Zn. Ni. Co) in fruit samples purchased from supermarkets and food markets in Timisoara, Romania

No. Crt.	Sample coding	Fruit samples analyzed	Macro- and micro-elements expressed in mg/100g dry substance										
			Na	K	Ca	Mg	Cu	Mn	Fe	Cd	Pb	Zn	Co
1.	F-1	Plums (Chile)	3.7	154	1.05	3.1	0.28	0.095	0.0475	0.0005	0.03	0.08	< 0.010
2.	F-2	Plums (Periam)*	3.75	151.5	1.2	3.1	0.15	0.105	0.0525	<0.001	0.01	0.02	< 0.010
3.	F-3	Strawberry (Belgium)	6.25	115	1.45	3.6	0.255	0.365	0.1825	0.001	0.035	0.05	< 0.010
4.	F-4	Strawberry (Dumbrava)*	6.2	167	1.05	4.65	0.205	0.215	0.1075	0.0005	0.035	0.07	0.0025
5.	F-5	Apples (Italy)	3.75	156	1.1	2.8	0.17	0.095	0.0475	0.0005	0.05	0.00	< 0.010
6.	F-6	Apples (Bucovat)*	7.2	112.5	1.2	3.5	0.155	0.095	0.0475	0.0005	<0.01	0.015	< 0.010
7.	F-7	Pears (Italy)	5.2	101.5	4.2	3.25	0.005	0.04	0.02	<0.001	<0.01	0.00	0.002
8.	F-8	Pears (Bucovat)*	4.8	83	0.95	2.8	0.27	0.09	0.045	<0.001	0.005	0.035	< 0.010
9.	F-9	Peaches (Greece)	3.75	179.5	0.7	3.6	0.08	0.07	0.035	0.0025	0.04	0.04	0.0055
10.	F-10	Peaches (Periam)*	3.95	186.5	0.9	3.8	0.175	0.115	0.0575	0.0005	0.04	0.06	< 0.010
11.	F-11	Apricots (Greece)	5.6	154	1.7	2.25	0.065	0.055	0.0275	0.004	0.085	0.015	0.019
12.	F-12	Apricots (Periam)*	3.6	210.5	2	4.15	0.125	0.115	0.0575	<0.001	0.01	0.00	0.0195
13.	F-13	Sour cherry (Hungary)	3.65	173	1.25	4.75	0.2	0.08	0.04	<0.001	<0.01	0.00	0.054
14.	F-14	Sour cherry (Bucovat)*	3.8	156	2.5	5.7	0.17	0.13	0.065	<0.001	0.015	0.00	< 0.010
15.	F-15	Cherry (Bulgaria)	3.95	134.5	0.9	3.15	0.09	0.065	0.0325	<0.001	0.03	0.00	0.013
16.	F-16	Cherry (Bucovat)*	3.1	118	1.15	2.25	0.08	0.08	0.04	0.001	0.025	0.035	< 0.010
17.	F-17	Raspberry (Netherlands)	7.1	121	2.3	6.75	0.25	0.28	0.14	0.0005	0.03	0.18	0.033
18.	F-18	Raspberry (Dumbrava)*	6.35	147	2.2	6.35	0.265	0.485	0.2425	<0.001	0.005	0.085	< 0.010
19.	F-19	Watermelon (Greece)	3.9	133.5	0.95	3.85	0.27	0.095	0.0475	0.0005	0.035	0.02	0.0335
20.	F-20	Watermelon (Periam)*	7.35	100	2.3	5.85	0.405	0.09	0.045	<0.001	0.01	0.065	< 0.010
21.	F-21	Melon (Periam)*	9.35	131	1.65	3.6	0.05	0.065	0.0325	0.001	0.045	0.015	< 0.010
22.	F-22	Melon (Turkey)	5.75	159	1.25	3.35	0.13	0.085	0.0425	0.0005	0.03	0.015	0.0205
23.	F-23	Grapes (Egypt)	4.95	165.5	0.85	2.95	0.275	0.075	0.0375	0.001	0.05	0.02	< 0.010

* Towns in Romania

Apricots (Greece), Raspberries (Dumbrava, Romania), Raspberries (The Netherlands) averaged in the range 5.2–7.35 mg/100g. Small concentration values were determined and were very close for samples of fruit: Plums (Chile), Plums Periam, Romania), Apples (Italy), Pears (Bucovăţ, Romania), Watermelons (Greece), Sour cherries (Bucovăţ, Romania), Sour cherries (Hungary), Cherries (Bucovăţ, Romania), Cherries (Bulgaria), Apricots (Periam, Romania), Peaches (Periam, Romania), Peaches (Greece) and Grapes (Egypt), with values in the range 3.1–4.95 mg/100g. Most samples in this category were found to have values close to 3.5 mg/100g concentration.

The element potassium values were recorded in the range 0.7–4.2 mg/100g, the highest value recorded at 4.2 mg/100g in the sample Pears (Italy).

The highest values of magnesium concentration in these tests were obtained from samples of Watermelon (Periam, Romania), Cherries (Bucovăţ, Romania), Raspberries (Dumbrava, Romania), and Raspberries (The Netherlands) in the range 5.7–6.75 mg/100g. The results for other samples ranged between 2.25–4.75 mg/100g.

Analyses made to determine the chromium and nickel content of the fruit samples purchased from supermarkets and markets in Timisoara resulted in very small values below the detection limit of the device.

Maximum concentration values in copper were obtained for the sample analysis of Watermelons (Periam, Romania) – 0.405 mg/100g. The samples Plums (Chile), Strawberries (Belgium), Strawberries (Dumbrava, Romania), Apples (Italy), Apples (Bucovăţ, Romania), Watermelons (Greece), Sour cherries (Hungary), Sour cherries (Bucovăţ, Romania), Peaches (Periam, Romania), Raspberries (The Netherlands), Raspberries (Dumbrava, Romania) showed similar values, in the range 0.15–0.28 mg/100g. For samples of Pears (Italy), Melons (Turkey), Melons (Periam, Romania), Cherries (Bulgaria), Cherries (Bucovăţ, Romania), Apricots (Greece), Apricots (Periam, Romania), and Peaches (Greece), minimum values of the concentration of this element were recorded, in the range 0.13–0.005 mg/100g.

The highest values of manganese were determined in the analysis of samples of Strawberry (Belgium), at 0.365 mg/100g, and Raspberries (Dumbrava, Romania), at 0.485 mg/100g. Average values in the concentration of this element were determined for samples analysis of Strawberries (Dumbrava, Romania) – 0.215 mg/100g, and Raspberries (The Netherlands) – 0.28 mg/100g. The other analyzed fruit samples showed low concentrations of manganese in the range 0.13–0.04 mg/100g.

Analyses made on the element iron concentration in the samples purchased from supermarkets and fruit markets in Timisoara food have resulted in high levels in samples Strawberries Belgium 0.65 mg/100g, Raspberries Netherlands 0.47 mg/100g, Peaches Periam 0.44 mg/100g, Apples Bucovăţ 100g and 0.415 mg/100g. The minimum concentration of this element was recorded for sample analysis Pears Italy 0.005 mg/100g. Other samples showed values in the range 0.16–0.4 mg/100g.

The element values registered for cadmium concentration increased in the sample Apricots (Greece) – 0.004 mg/100g, and Peaches (Greece) – 0.0025 mg/100g. In the samples Plums (Periam, Romania), Pears (Italy), Pears (Bucovăţ, Romania), Watermelons (Periam, Romania), Sour cherries (Hungary), Sour cherries (Bucovăţ, Romania), Cherries (Bulgaria), Apricots (Periam, Romania), and Raspberries (Dumbrava, Romania), the element Cd concentration was zero. Other samples analyzed showed values of 0.0005 and 0.001 mg/100g.

The results for the element lead showed evidence of an increase evidence in Apricots (Greece) – 0.085 mg/100g, Apples (Italy) – 0.05 mg/100g, and Grapes (Egypt) – 0.05 mg/100g, respectively. In the samples Apples (Bucovăţ, Romania), Pears (Italy) and Sour cherries (Hungary), no lead was found. Low concentrations of lead were determined in samples Pears (Bucovăţ, Romania), Raspberries (Dumbrava, Romania) – 0.005 mg/100g. In the samples Plums (Periam, Romania), Watermelons (Periam, Romania), Apricots (Periam, Romania), showed values of 0.01 mg/100g. For the other samples, the concentration of lead values were in the range 0.015–0.045 mg/100g.

The highest zinc content was measured in the sample Raspberries (The Netherlands) – 0.18 mg/100g. Samples Apple (Italy), Pears (Italy), Sour cherries (Hungary), Sour cherries (Bucovăţ, Romania), Cherries (Bulgaria), and Apricots (Periam, Roomania), there were no traces of this element. Close values of concentration were obtained for samples Plums (Chile), Strawberries (Belgium), Strawberries (Dumbrava, Romania), Watermelons (Periam, Romania), Peaches (Periam, Romania), and Raspberries (Dumbrava, Romania), in the range 0.05–0.085 mg/100g. Other samples analyzed showed zinc content in the range 0.015–0.04 mg/100g.

The highest cadmium content was in samples Sour cherries (Hungary) – 0.054 mg/100g. Samples Strawberries (Dumbrava, Romania), Pears (Italy), Melons (Turkey), Watermelons (Greece), Cherries (Bulgaria), Apricots (Greece), Apricots (Periam, Romania), Peaches (Greece), and Raspberries (The Netherlands), showed very low values for this element, in the range 0.002–0.0335 mg/100g. In samples Plums (Chile), Plums (Periam, Romania), Strawberries (Belgium), Apples (Italy), Apples (Bucovăţ, Romania), Pears (Bucovăţ, Romania), Melons (Periam, Romania), Watermelons (Periam, Romania), Cherries (Bucovăţ, Romania), Peaches (Periam, Romania), Raspberries (Dumbrava, Romania) and Grapes (Egypt) no cadmium was found.

The PCA analysis were used as input for the results of the analysis of macro elements content of fruit samples purchased from supermarkets (imported products) and agricultural markets (domestic products).

The multivariate data processing for macro elements allowing for a large group of diverse data samples is explained in 99% as the first principal component.

The used method centering data with system rotation axes of Varimax.

The two major groups obtained are shown in Figure 1, the first group in the top left and the second group focused on the right. These groups were responsible for the element potassium concentrations for component PC_1, concentrations of elements sodium, magnesium and calcium for component PC_2, Fig 2.

In the second stage of PCA, statistical evaluation as input, the results of analysis of trace elements content in fruit samples purchased from supermarkets (imported products) and agricultural markets (domestic products) were used.

Multivariate data processing for microelements allowed a large group of samples, the range data is explained in 94% of the first two principal components 52% PC_1, 42% PC_2. In

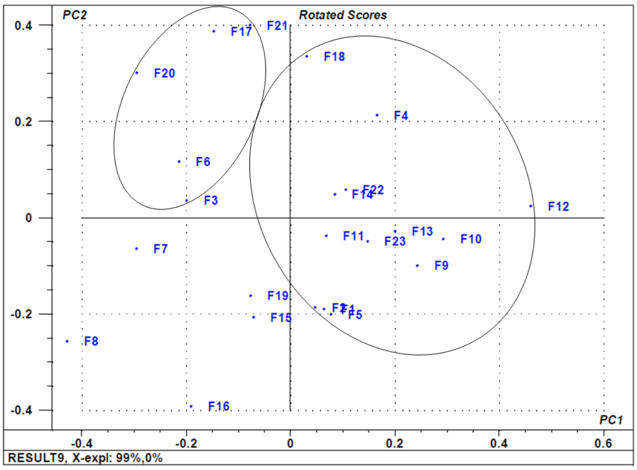

Figure 1. PC_2 vs. PC_1 scores graphic for PCA analysis using as input the macro-elements content for analysed fruits samples

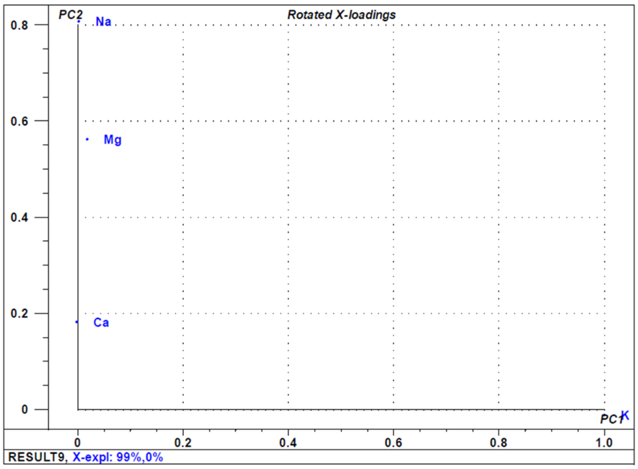

Figure 2. PC_2 vs. PC_1 records graphic for PCA analysis using as input the macroelements content in fruit samples analyzed

this case, the method centering data with system rotation axes of Varimax was used.

In Figure 3, the two groups are shown, the first group in the top left, the second group in the top right of the graph scores. Responsible for these groups, where the main component PC_1 are concentrations microelements manganese, iron

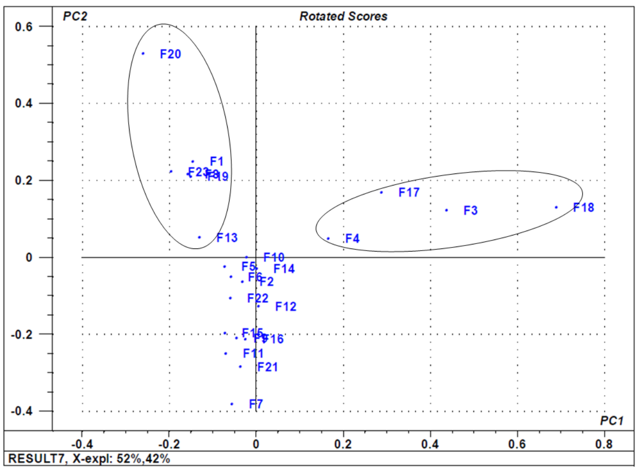

Figure 3. PC_2 vs. PC_1 scores graphic for PCA analysis using as input the contents of the microelements in fruits samples analyzed

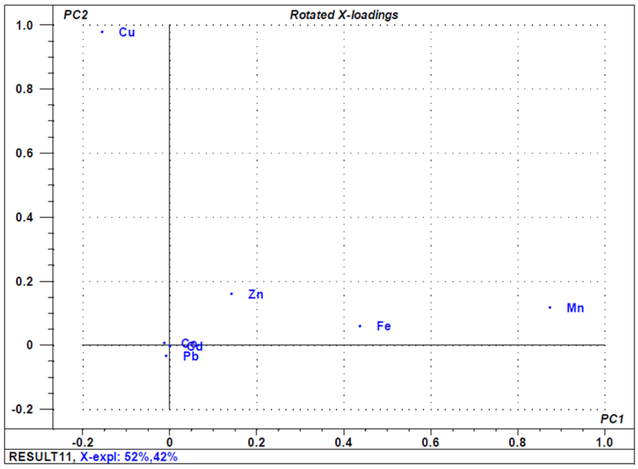

Figure 4. PC_2 vs. PC_1 records graphic for PCA analysis using as input the microelements content in fruit samples analyzed

and zinc, respectively for the main component PC_2 copper concentration (Fig. 4).

DISCUSSION

The results of macro- and micro-element fruit measurements were compared with results obtained by other researchers at home and abroad, as well as some standards in force on the fruit content of heavy metals.

Sodium is an element the human body needs to regulate fluid balance, muscle contraction and nerve impulses. To maintain the equilibrium of water/sodium, excess sodium is excreted through the kidneys [9]. Reducing sodium in the diet can reduce high blood pressure in some people. This in turn can reduce the risk of heart disease or kidney disease and stroke. Research on the sodium content of apples has been made in which Nour et al. 2010 [10] obtained values of this element in the range, 0.26–8.92 mg/100g. In the presented research, the values of sodium content obtained were in the range mentioned above. Rodríguez et. al. 1999 [11], in research for the concentration of sodium in peaches, obtained results in the range 2.94. – 4.92 mg/100g. Çalışır et. al. [12] determined from samples of plums a concentration of this element of 40.46 mg / kg.

To maintain life and health, people need to consume and absorb adequate amounts of the element potassium ions in the form (K^+) through the intestinal tract, usually eaten in the form of potassium salts of organic acids in food (e.g, potassium citrate, potassium salt of citric acid). Foods with large amounts of potassium are vegetables (vegetables and fruits), which provide the greatest amount of potassium salts.

With regard to what constitutes an ‚adequate' amount of dietary potassium, in 2004–2006, the Institute of Medicine Division of the National Academy of Science (IOM) and its Food and Nutrition Board (FNB) [13] recommended that adult humans consume 4,700 milligrams (mg) of potassium per day. Nour et al. 2010 [10] determined in analysis performed of several varieties of fresh apples, concentrations of the element potassium in the range 82.25–160.85 mg/100g. Hacıseferoğulları et. al. [13] determined concentrations of the element potassium in apricots in the range of 33.3646–22.029 mg/kg. Rodríguez et. al. 1999 [11] determined from several samples of peaches, potassium in the range 177.1

–240.8 mg/100g, whereas El Kossori et. al. [14] determined a concentration of 559 mg/100g of potassium in pears.

Calcium is an essential mineral required for diverse physiological and biochemical functions in the human body. Data from surveys by the Thai Ministry of Public Health revealed that Thai people had insufficient calcium intake to meet the national RDI during most of their lives. The last survey in 1994 showed the average calcium intake of Thai people to be 344 mg/day, which is about 43% of Thai Recommended Daily Intake (Thai RDI, 800 mg calcium per day) [15].

Nour et al. 2010 [10] analyzed several samples of different apple varieties in which the concentration of calcium in the apple samples ranged between 1.75–8.74 mg/100g. Rodríguez et. al. [11] determined element concentrations of calcium in several samples of peaches to be within the range 5.1–9.12 mg/100g. Pears in the sample were determined as having calcium concentrations much higher than those obtained in the presented study. El Kossori et. al. [14] determined the concentrations of calcium pear samples at 163 mg/100g, a value much higher than those obtained in the presented study. And investigations by Hacıseferoğulları et. al. [13], the element calcium concentration in apricot samples evaluated at 843.28–1896.53 ppm, was also much higher than the concentration obtained in the presented study. Analysis performed for samples of cherries resulted in concentrations of ppm calcium 1308.478.

Magnesium is an active component of several enzyme systems in which thymine pyrophosphate is a co-factor. Oxidative phosphorylation is greatly reduced in the absence of magnesium. Magnesium is also an essential activator for the phosphate-transferring enzymes myokinase, diphophopyridinenucleotide kinase, and creatine kinase. It also activates pyruvic acid carboxylase, pyruvic acid oxidase, and the condensing enzyme for the reactions in the citric acid cycle. It is also a constituent of bones, teeth, enzyme co-factor, (kinases, etc). The health status of the digestive system and the kidneys significantly influence magnesium status. Magnesium is absorbed in the intestines and then transported through the blood to cells and tissues. Approximately one-third to one-half of dietary magnesium is absorbed into the body.

Nour et al. [10] have determined from analyzed Apple samples, magnesium concentrations in the range 5.02–11.83 mg/100g. Research has also been conducted on the concentration of the element magnesium in different samples of fruit. The results obtained by other researchers were 402.82–765.62 ppm for apricots [13], for peaches 8.62–9.93 mg/100g [11], and for pears – 76.1 mg/100g [14]. In the presented study, the magnesium content of the fruit samples are much smaller than those obtained by other researchers.

Copper is a constituent of enzymes, such as cytochrome c oxidase, amine oxidase, catalase, peroxidase, ascorbic acid oxidase, cytochrome oxidase, plasma monoamine oxidase, erythrocuprin (ceruloplasmin), lactase, uricase, tyrosinase, cytosolic superoxide dismutase, etc., and it plays a role in iron absorption. Copper is an essential micro-nutrient necessary for the haematologic and neurologic systems. It is necessary for the growth and formation of bone, formation of myelin sheaths in the nervous system, assists in the incorporation of iron in haemoglobin, assists in the absorption of iron from the gastrointestinal tract (GIT), and in the transfer of iron from tissues to the plasma [6].

Nour et al. 2010 [10] have determined in samples of several varieties of apples, copper element concentrations in the range 0.003–0.007 mg/100g. Other measurements on the copper content of fruit were made by several researchers as follows: for cherries, Kalyoncu et al. [16] determined a concentration of 5.797 ppm copper, for watermelons, Sobukola et. al. [17] determined the concentration of the element copper at 0.004 mg/kg for grapes, melons, peaches, pears, strawberries and apricots, while Olalla et. al. 2004 [18] presented the following concentrations 0.052 mg/100g, 0.06 mg/100g, 0.06 mg/100g, 0.11mg/100g, 0.048 mg/100g, mg/100g 0.088 mg/100g.

Research carried out by the authors of the presewnted study in terms of copper concentration in fruit samples were within the values obtained by other researchers.

Manganese is a co-factor of hydrolase, decarboxylase, and transferase enzyme. It is involved in glycoprotein and proteoglycan synthesis and is a component of mitochondrial superoxide dismutase. Manganese is a co-factor in phosphohydrolases and phosphotransferases involved in the synthesis of proteoglycans in cartilage. Manganese is a part of the enzymes involved in urea formation, pyruvate metabolism, and the galactotransferase of connective tissue biosynthesis [6].

Manganese was analyzed from different varieties of apples by Nour et al. [10] who obtained results in the range 0.02–0.06 mg/100g. Other researchers have collected and examined samples of fruit, for which the results were: for cherries Kalyoncu et. al. [16] determined the values of 4.649 ppm of manganese concentration; for more samples of peaches, Rodríguez et. al. [11], determined manganese concentrations in the range 0.06–0.09 mg/100g; for pears, El Kossori et. al. [14] obtained 6.99 mg/100g. And in the presented study, concentration of manganese were mostly in agreement with the results obtained by other researchers.

Iron functions as haemoglobin in the transport of oxygen. In cellular respiration, it functions as essential component of enzymes involved in biological oxidation, such as cytochromes c, c_1, a_1, etc. Iron is an important constituent of succinate dehydrogenase as well as a part of the haeme of haemoglobin (Hb), myoglobin and the cytochromes. Iron is required for proper myelination of the spinal cord and white matter of the cerebellar folds in the brain, and is a co-factor for a number of enzymes involved in neurotransmitter synthesis. Iron is involved in the synthesis and packaging of neurotransmitters, their uptake and degradation into other iron-containing proteins which may directly or indirectly alter brain function [6].

Research carried out with respect to the element iron concentration in samples of fruit were conducted by researchers with the following results: for several varieties of apples, Nour et al. 2010 [10] obtained concentrations of the element iron in the range 0.19–0.40 mg/100g; for cherries, Kalyoncu et al. [16] determined concentrations of 23.21 ppm of iron; for peaches, Rodríguez et. al. [11] determined concentrations of this element in the range 0.18–0.24 mg/100g; while El Kossori et. al. [14] determined concentrations of the element iron at 16.5 mg/100g.

Cadmium has a long residence time in human tissues (10–40 years), especially in the kidneys. The toxic effects of cadmium are noticeable in various ways. It can interfere with some of the organism's enzymatic reactions, substituting zinc and other metals, manifesting its action in several pathological processes, such as renal dysfunctions, hypertension, arteriosclerosis, inhibition of growth, damage to the nervous system, bone demineralisation and endocrine disruption [19].

Previous research conducted by other researchers on the element cadmium have produced in the following results: Sobukola et. al. [17] obtained for watermelons – 0.004 mg/kg, apples – 0.004 mg/kg, grapes – 0.005 mg/kg, and Hakala et. al. [20] obtained a concentration in strawberries of 0.016 mg/kg. Results obtained in the presented study on the cadmium content of fruit samples were within the results obtained by other researchers.

The element lead bio-accumulates in plants and animals, and its concentration is generally magnified in the food chain. Airborne lead can be deposited on soil, water and plants, thus reaching humans via the food chain. Lead is accumulated in the skeleton and causes renal tubular damage and may also give rise to kidney damage [21].

Research on the lead content of fruit have also been conducted by other researchers whose results were as follows: Sobukola et. al. [17], for watermelons – 0.108 mg/kg, grapes – 0.092 mg/kg and apples – 0.112mg/kg; Krejpcio et al. [22], for strawberries – 0.074 mg/kg, cherries – 0.059 mg/kg, pears – 0.042 mg/kg, and apples – 0.078 mg/kg. The results obtained for lead in fruit in the presented study are similar to results obtained by other researchers.

The element zinc is necessary for numerous enzymatic reactions and the absorption of diverse vitamins, mainly vitamins of the B complex. It is very important to maintain healthy skin, self-immunity, and good functioning of the prostate gland. Zinc is also necessary for the protection of the sexual hormones and for natural growth. In the same way as magnesium, zinc participates in about 200 metallo-enzymatic reactions [19].

Results for this element were compared with results obtained by other researchers: Nour et al. [10] analyzed several varieties of apples and obtained the element concentrations in the range 0.07–0.26 mg zinc/100g. Krejpcio et. al. [22] took more samples and analyzed the fruit, obtaining the following results for zinc concentrations: strawberries – 3.43 mg/kg, cherries – 1.49 mg/kg, pears – 2.059 mg/kg, and apples – 1.72 mg/kg. Sobukola et. al. 2010 [65] analyzed several samples of fruits and obtained the following results: watermelon – 0.047 mg/kg, grapes – 0.073 mg/kg, and apples – 0.045 mg/kg. Olalla et. al. [18] obtained for melons – 0.09–0.29 mg/100g, peaches – 0.02 mg/100g, 0.1–0.12 – apples mg/100g, apricots – 0.07–0.1 mg/100g, pears – 0.16–0.23 mg/100g, and strawberries – 0.09–0.22 mg/100g.

Cobalt is an indispensable element which is scattered in the atmosphere in a concentration of about 0.001%. It is found in the bivalent as well as trivalent state. Vegetables and fruits contains 0.009 mg/kg. Cobalt is usually included in vitamin $B_{12,}$ and its deficiency in that vitamin affects the consistency in the body. Cobalt deficiency is rare in humans, but cattle are effected with symptoms such as like anemia. The daily recommended range of cobalt in the human diet is 0.005 mg/day, and cobalt deficiency plays an additional role in producing anoxia and injuring the heart muscles [23].

Sobukola et. al. [17] obtained the following results for the element cobalt: watermelons – 0.021 mg/kg, grapes – 0.025 mg/kg, and apples – 0.02 mg/kg. Zahir et. al. [82] determined for samples of apples and apricots element concentrations of 0.407 µg/g and 1.049 µg/g of cobalt. Hussain et. al. [24] analyzed several varieties of apricots, the results of which were within the range 0.05–0.09 mg/100g. The results of the prsented study for concentrations of cobalt in fruit samples analyzed were within the results obtained by other researchers.

CONCLUSIONS

Following the results obtained in the analysis of mineral elements, macro- and micro-elements, the following conclusions were drawn: the maximum sodium values recorded for samples of Melon Periam were 9.35 mg/100g and Watermelon Periam – 7.35. mg/100g; potassium showed the highest values in the tests performed on samples of Apricots (Periam, Romania) – 210.5 mg/100g and Peaches (Periam, Romania) – 186.5 mg/100g. The largest calcium concentration values were determined from samples of Pears (Italy) – 4.2. mg/100g' and Sour cherries (Bucovăţ, Romania) – 2.5 mg/100g. Maximum values of the element magnesium in samples were obtained in Raspberries (The Netherlands) – 6.75 mg/100g and Raspberry (Dumbarva, Romania) – 6.35 mg/100g. PCA statistical analysis, using as input concentration values in the macro-elements (sodium, potassium, calcium and magnesium) led to very good correlation being obtained in samples of fruit affected by assimilation, to a greater extent, of the element sodium; to a lesser extent – magnesium and calcium, in the case of principal components PC1, PC2 component element potassium respectively**.**

The results obtained in terms of content in micro samples of fruit have resulted in the following conclusions.

Fruit samples analyzed showed higher assimilation for micro-elements, copper, manganese, iron and zinc. Thus, the maximum concentration of copper in the sample was recorded in Watermelons (Periam, Romania) – 0.405 mg/100g and Plums (Chile) – 0.28 mg/100g.

The element manganese showed high concentrations for samples: Raspberries (Dumbrava, Romania) – 0.485 mg/100g and Strawberries (Belgium) – 0.365 mg/100g. A greater assimilation of the element iron in the samples were recorded in Raspberries (Dumbrava, Romania) – 0.24 mg/100g and Strawberries (Belgium) – 0.18 mg/100g. The element cadmium in a sample of Apricots.

(Greece) was recorded at the highest concentration of 0.004 mg/100g. In Apricots (Greece) and Melons (Periam, Romania) samples the largest element assimilation was recorded – 0085 mg/100g and 0.042 mg/100g, respectively.

The highest concentrations of zinc were found in samples of Raspberries (The Netherlands) – 0.18 mg/100g and Raspberries (Dumbrava, Romania) – 0.085 mg/100g.

The element cobalt in samples of Sour cherries (Hungary), Watermelons (Greece) and Raspberries (The Netherlands) recorded the highest concentrations: 0.054 mg/100g, 0.0335 mg/100g and 0.033 mg/100g, respectively.

PCA statistical analysis, using as input values the concentrations of micro-elements (Cu, Mn, Fe, Cd, Pb, Zn and Co) resulted in very good correlations in the fruits samples. The first component PC_1 had a major influence in the classification of the samples in the form of the element manganese, followed to a lesser extent by the elements iron and zinc. In the groups obtained for $PC_{2,}$ the principal components were influenced by the concentration of the element.

When comparing the allowable limits for heavy metals [25], concentrations of the microelements studied did not exceed thee limits.

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