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# Mineral Composition of Fruits in Different Walnut (*Juglans regia* L.) Cultivars

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**Abstract**

Walnuts are considered to be a good source of dietary minerals. Mineral composition was determined in nine walnut cultivars ('Mihaela', 'Roxana', 'Velnita', 'Geoagiu 65', 'Jupanesti', 'Valcor', 'Valmit', 'Valrex', 'Argesan') originated from Romania. A Milestone digestion microwave system was used for mineralization of solid samples. Microelements: Na, Ca, Mg, Fe, Mn, Cu, Se, Al, Cr, Zn, Sr and Rb were determined by using ICP-MS as measurement tool, and K content was determined with an atomic absorption spectrometer in flame, by using as excitation source the cavitar cathode lamp for potassium. Mineral elements content presented significant differences from a cultivar to another. Potassium content has varied between 357.1 mg/100g in 'Valmit' cultivar, and 499.6 mg/100g, in 'Geoagiu 65' cultivar, recording significant differences from the average (414.0 mg/100g) in 'Velnita', 'Roxana'and 'Argesan'cultivars. Magnesium content varied between 189.2 mg/100 g in 'Mihaela' cultivar and 278.1 mg/100 g in 'Argesan' cultivar, significant differences from the average (216.6 mg/100g) were obtained in cultivars 'Geoagiu 65', 'Valrex', 'Argesan'. The order of nutritive elements depending on their content/100 g of produce was K>Mg>Ca>Mn>Fe> Cu>Zn>Na>Cr>Al>Rb>Sr. Comparing obtained data with the ones existing in the literature, Romanian walnut cultivars proved to be important sources of nutritive elements, and walnut kernel consumption can contribute to a well balanced diet.

***Keywords:*** kernel walnut, ICP-MS system, atomic absorption spectrometry, minerals

## Introduction

Walnut (*Juglans regia* L.) is quite widespread in Romania. Walnut assortment is generally local. Walnut's fruit (nut) has a remarkable nutritional composition. Walnut contains quinones, oils, tannins; nuts contain essential fatty acids, including cis-linoleic and alfa-linolenic acid. The kernels contain oil, mucilage, albumin, mineral matter, cellulose and water. Walnut is considered a good source of dietary minerals. Potassium, phosphorus, magnesium and iron are found in significant quantities in these nuts. A number of research works were conducted to find the content of nutritive elements in cultivated walnut and on their impact on human health. The walnut's health benefits include cholesterol lowering, reducing inflammation, and improving arterial function (Nash *et al.*, 2005; Patel, 2005).

Lavedrine *et al.* (2000) in analyzing mineral composition in two walnut cultivars ('Franquette', 'Hartley') with origin in France and California, has found significant differences for three mineral elements (potassium, sodium, magnesium) depending on cultivar and origin. Walnuts (*Juglans regia* L.) are rich in valuable minerals like phosphorus, potassium, sodium, magnesium and zinc (Lavedrine *et al.*, 2000).

Analysis of twelve cultivars in New Zealand, two in the US ('Tehama' and 'Vina'), three cultivars ('Esterhazy', 'G139', 'G120') in Europe, and eight cultivars ('Rex', 'Dublin's Glory', 'Meyric', 'Stanley', '150', '151', '153') from New Zealand, has shown that the oil content has varied between 62.6% and 70.3%, and the protein content was between 13.6% and 18.1%. Dietary fiber ranged from 4.2 to 5.2%, while the starch content made up no more than 2.8% of the remaining portion of the kernel. The amino acid content of walnuts was similar between cultivars and the patterns of essential amino acids were characteristic of a high quality protein (Savage, 2001).

Chemical composition of tree cultivars ('Jupiter', 'Sejnov' and 'Elit') of walnut (*Juglans regia* L.) harvest from Cacak, Central Serbia, including moisture, total oil content, crude protein, ash, and carbohydrates, was determined. The fatty acid composition of walnut oils was determined by using gas chromatography with flame ionization detector. The oleic acid content ranged between 15.9-23.7% of total acids, while linoleic acid content ranged from 57.2% to 65.1% and the linolenic acid from 9.1%-to 13.6% ( Rabrenovic *et al.*, 2008).

Research of mineral composition in walnut genotypes ('Sebin-Type-I', 'Körcegöz', 'Karabodur', 'Tozam' and 'Güvenli'), cultivated in Turkey, outlined the average mineral content (mg/100 g) as follows: P-316.0; K-270.0; Ca-85.0; Mg-90.0; Zn-2.01; Mn-2.46; Cu-1.01; Fe-2.90; B-1.03 (Caglarirmak, 2003).

Determination of sterol and fatty acid composition, oxidative stability, and nutritional value of six walnut (*Juglans regia* L.) cultivars grown in Portugal, shown that fat was the predominant component, ranging from 62.3% to 66.5%. Eighteen fatty acids were quantified. Polyunsaturated fatty acids and, in particular, linoleic acid were predominant. Beta-Sitosterol, delta(5)-avenasterol, and campesterol were the major sterols found (Amaral, 2003).

Regarding chemical composition and antioxidant potential, in six walnuts (*Juglans regia* L.) cultivars (cvs. 'Franquette', 'Lara', 'Marbot', 'Mayette', 'Mellanaise' and 'Parisienne') produced in Portugal, the main constituent of fruits was fat, ranging from 78.83% to 82.14%, having nutritional value around 720kcal per 100 g of fruits. Linoleic acid was the major fatty acid reaching the maximum value of 60.30% (cv. Lara) followed by oleic, linolenic and palmitic acids (Pereira, 2008).

The present study deals with determination of mineral contents of nine walnut cultivars ('Mihaela', 'Roxana', 'Velnita', 'Geoagiu 65', 'Jupanesti', 'Valcor', 'Valmit', 'Valrex', 'Argesan') originated from Romania.

**Materials and methods**

The study was conducted by using nine local walnut cultivars ('Mihaela', 'Roxana', 'Velnita', 'Geoagiu 65', 'Jupanesti', 'Valcor', 'Valmit', 'Valrex', 'Argesan') for determinations. The study material comes from collection orchard of the Valcea Research Station (SCDP Valcea), located in Sub-Carpathian area in Oltenia (45°6′17″ N, 24°22′32″ E), with temperate climate, an area which is known as favourable to walnut culture.

*Instrumentation*

A commercial ICP-MS system (Perkin-Elmer Elan 9000), the atomic absorbtion spectometer in flame (Avanta PM), and Milestone digestion microwave system were used. The experimental operating parameters are summarized in Tab. 1.

*Reagent and chemicals*

Etalon standards were obtained from multi-element stock solutions ICP –MS calibration STD 3, etalon solutions mono-element 1000 ppm K, azotic acid 65% puriss p.a (Fluka), oxygenated water 33% reactive p.a and ultra pure water, 1st degree according to ISO 3696 :1987.

*Method*

For solid sample mineralization, a Milestone digestion microwave system was used. Quantities of approximately 0.5 g sample, weighed with 0.0001g precision, 6 mL azotic acid 65 % and 2 ml oxygenated water 33% were introduced in Teflon recipients and a thermic treatment programme under pressure was applied: heating up to 180 0C, by a rate of 4,5 0C/min, and keeping them for 20 minutes at 180 0C.

After cooling them down, liquid samples were transferred into marked glass balloons; ultra pure water was added to obtain a 50 mL volume, .The samples were analyzed according to specific procedures in two spectrometer instruments.

Control sample (blank) was made from 6 mL azotic acid 65 % and 2 mL oxygenated water 33 %, and it was processed in the same conditions as the analyzed sample.

Microelements: Na, Ca, Mg, Fe, Mn, Cu, Se, Al, Cr, Zn, Sr, V, Rb - were determined by using the ICP-MS as measurement tool, while the K content was determined with the atomic absorption spectrometer in flame, using as an excitation source the cavitar cathode lamp for potassium.

Tab. 1. ICP-MS and the atomic absorption spectrometer in flame operating conditions

| ICP-MS, model Elann9000 | |
|---|---|
| Rf power(W) | 1000 |
| ICP torch | fassele type |
| Torch injector | ceramic alumina |
| Nebulizer | Tip cross flow |
| Nebulizer gas flow (l/min) | 0.93 |
| Spray chamber | |
| Sweeps/reading | 20 |
| Reading/replicate | 2 |
| Number of replicates | 5 |
| Atomic absorption spectrometer in flame Model AvantaPM | |
| Optics | Double fascicle |
| Flame | Air –Acetylene |
| Falme Control | Programmed |

**Results and discussions**

Walnuts are considered a good source of dietary minerals. Walnuts contain almost similar quantities of minerals, except calcium, which is present only in moderate amounts in black walnuts. Potassium, phosphorus, magnesium and iron were found in significant quantities in these nuts. The highest content was recorded for potassium (K), a cardiac tonic and muscular tonic element, with large variation limits, comprised between 357.1 mg/100 g ('Valmit' cultivar) and 499.6 mg/100 g ('Geoagiu 65'cultivar), with a very significant difference, compared to the average values. In nine walnut cultivars, the average of potassium content was 414.01 mg/100 g.

Tab. 2. Mineral concentration of nine walnut (*Juglans regia)* cultivars

| No. | Analyzed produce | Determined elements, mg/100 g of produce | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Na | K | Ca | Mg | Fe | Mn | Cu | Se | Al | Cr | Zn | Sr | V | Rb |
| 1 | 'Mihaela' | 0.633 | 394.5 | 46.26 | 189.2 | 3.815 | 10.15 | 1.643 | 0.003 | 0.141 | 0.539 | 1.948 | 0.246 | 0.001 | 1.162 |
| 2 | 'Roxana' | 0.134 | 471.5 | 48.08 | 207.6 | 3.842 | 9.845 | 2.162 | 0.002 | 0.169 | 0.568 | 2.054 | 0.16 | 0.001 | 1.099 |
| 3 | 'Velnita' | 0.479 | 428.7 | 63.62 | 209.7 | 4.708 | 9.229 | 2.44 | 0.002 | 0.245 | 0.596 | 2.056 | 0.269 | 0.002 | 1.25 |
| 4 | 'Geoagiu-65' | 0.654 | 499.6 | 37.00 | 234.2 | 3.876 | 3.134 | 1.41 | 0.002 | 0.189 | 0.692 | 2.844 | 0.315 | 0.001 | 0.356 |
| 5 | 'Jupanesti' | 0.358 | 368.1 | 79.48 | 200.8 | 4.525 | 18.37 | 1.946 | 0.001 | 0.525 | 0.525 | 2.292 | 0.537 | 0.001 | 0.967 |
| 6 | 'Valcor' | 0.261 | 369.3 | 76.27 | 204.9 | 5.103 | 6.835 | 2.075 | 0.001 | 0.397 | 0.544 | 2.59 | 0.431 | 0.001 | 2.607 |
| 7 | 'Valmit' | 2.387 | 357.1 | 90.84 | 199.8 | 4.696 | 17.59 | 2.386 | 0.003 | 0.143 | 0.419 | 3.613 | 0.408 | 0.001 | 2.165 |
| 8 | 'Valrex' | 0.734 | 409.1 | 64.15 | 224.9 | 5.927 | 16.82 | 3.223 | 0.005 | 0.102 | 0.255 | 3.529 | 0.418 | 0.001 | 1.958 |
| 9 | 'Argesan' | 1.072 | 428.3 | 51.64 | 278.1 | 4.965 | 11.88 | 2.857 | 0.002 | 0.142 | 0.607 | 2.679 | 0.273 | 0.001 | 1.738 |
| Average | | 0.745 | 414.0 | 61.92 | 216.6 | 4.60 | 11.54 | 2.24 | 0.0023 | 0.229 | 0.527 | 2.622 | 0.339 | 0.0011 | 1.478 |
| Standard error | | 0.225 | 16.16 | 5.918 | 8.91 | 0.232 | 1.725 | 0.189 | 0.0003 | 0.047 | 0.041 | 0.206 | 0.038 | - | 0.231 |
| Standard deviation | | 0.676 | 48.47 | 17.76 | 26.73 | 0.697 | 5.175 | 0.567 | 0.001 | 0.142 | 0.125 | 0.619 | 0.117 | - | 0.694 |
| Confidence level 95% | | 0.519 | 37.35 | 13.65 | 20.55 | 0.54 | 3.97 | 0.436 | 0.0009 | 0.108 | 0.096 | 0.475 | 0.089 | - | 0.533 |
| LSD5% | | 0.63 | 45.23 | 16.57 | 24.94 | 0.32 | 2.43 | 0.26 | 0.001 | 0.067 | 0.059 | 0.292 | 0.055 | - | 0.327 |

mineral composition of nine cultivars of walnut is given in Tab. 2. In kernels of nine walnut cultivars originated from Romania, the following mineral elements were determined: Na, K, Ca, Mg, Fe, Mn, Cu, Se, Al, Cr, Zn (Tab. 2). Tab. 2 contains the average values, standard deviations and standard error. The described data have an 95% interval of confidence .. In these data, we can observe that potassium, magnesium and calcium showed the highest levels of concentration. In general, the order depending on content of elements/100 g of produce, was as follows: K> Mg> Ca> Mn> Fe> Cu> Zn> Na> Cr> Al> Rb> Sr.

Depending on composition, after potassium comes magnesium (Mg), with limits of variation between 189.2 mg/100g ('Mihaela' cultivar) and 278.1 mg/100g ('Argesan' cultivar), with higher values than average (216.57 mg/100 g) in three out of nine cultivars analyzed ('Geoagiu 65', 'Argesan', 'Valrex') (Tab. 4). Magnesium is considered a regenerative and cell tonic, brain balance maker, and a general antiseptic; human organism needs approximately 300 mg magnesium per day (Neamtu *et al.*, 1995), and walnut kernel consumption can meet the daily-required amount.

Tab. 3. Mineral content of walnut (*Juglans regia)* kernels (mg/100g) reported in the literature*

| Minerals | Units | Value per 100 grams | Number of Data Points | Std. Error |
|---|---|---|---|---|
| Calcium, Ca | mg | 98 | 7 | 3.009 |
| Iron, Fe | mg | 2.91 | 7 | 0.086 |
| Magnesium, Mg | mg | 158 | 7 | 1.204 |
| Phosphorus, P | mg | 346 | 7 | 3.689 |
| Potassium, K | mg | 441 | 7 | 6.471 |
| Sodium, Na | mg | 2 | 7 | 0.837 |
| Zinc, Zn | mg | 3.09 | 7 | 0.083 |
| Copper, Cu | mg | 1.586 | 7 | 0.026 |
| Manganese, Mn | mg | 3.414 | 7 | 0.122 |
| Selenium, Se | mcg | 4.9 | 6 | 0.417 |

*Sources: USDA National Nutrient Database for Standard Reference, Release 21 (2008)

Calcium (Ca) follows, with variation limits between 37 mg/100 g ('Geoagiu 65') and 90.8 mg/100g ('Valmit'), the recorded average value being 61.92 mg/100g.

Tab. 4. Mineral content of Romanian walnut (*Juglans regia* L.) kernels (mg/100g)

| Minerals | Units | Value per 100 grams | Number of Data Points | Std. Error |
|---|---|---|---|---|
| Calcium, Ca | mg | 61.926 | 9 | 5.918 |
| Iron, Fe | mg | 4.606 | 9 | 0.232 |
| Magnesium, Mg | mg | 216.578 | 9 | 8.910 |
| Potassium, K | mg | 414.012 | 9 | 16.160 |
| Sodium, Na | mg | 0.745 | 9 | 0.225 |
| Zinc, Zn | mg | 2.622 | 9 | 0.206 |
| Copper, Cu | mg | 2.237 | 9 | 0.189 |
| Manganese, Mn | mg | 11.540 | 9 | 1.725 |
| Selenium, Se | mg | 0.0023 | 9 | 0.0003 |
| Aluminum, Al | mg | 0.228 | 9 | 0.0471 |
| Chromium, Cr | mg | 0.527 | 9 | 0.0418 |

Manganese (Mn) content in kernel varied between 3.134 mg/100g in 'Geoagiu 65' cultivar and 18.37 mg/100 g in 'Jupanesti' cultivar (a very significant difference, compared to the average), with an average of 11.54 mg/100 g. In human body, manganese is an important glandular regulator, being involved in metabolism of glucydes, lypides and protides (Neamtu *et al.*, 1995).

According to USDA National Nutrient Database for Standard Reference (Tab. 3), the order depending on concentration in listed mineral elements was kept (K>Mg>Ca>Mn), but values are different if we compare them with Romanian walnuts analyzed.

With values of more than 1 mg/100 g weight, the next mineral elements follow : iron (Fe), copper (Cu), zinc (Zn) and sodium (Na). Mineral iron is a key element for health and proper working of organism. Variation limits of this element in the analyzed walnut cultivars were 3.81 mg/100 g in 'Mihaela' cultivar, and 5.92 mg/100g in 'Valrex' cultivar, with an average of 4.6 mg/100g.

Copper (Cu) is a dynamic element, anti-infectious, antiviral, anti-inflammatory. Daily required amount of copper for an adult human is 2.5 mg (Neamtu *et al.*, 1995). Walnuts are rich sources of copper (Cu), the variation limits of this element, in the analysed cultivars , was 1.41 mg/100g ('Geoagiu 65') and 3.22 mg/100g ('Valrex'), and the average was 2.237 mg/100g of kernel.

Zinc (Zn) is a key element in cell division and growth, the variation limits in analyzed walnut cultivars were 1.94 mg/100g ('Michaela') and 3.61 mg/100g ('Valmit')and the recorded average was 2.62 mg/100 g of kernel (Tab. 4). Sodium (Na) is an important mineral element, very present in the organism, especially in plasma (Neamtu *et al.*, 1995); walnut kernel composition, in cultivars analyzed, has varied between 0.261 mg/100g ('Valcor') and 2.387 mg/100g ('Valmit'), with an average of 0.745 mg/100 g of kernel. Values under 1 mg/100 g weight were recorded for the next elements: aluminum (Al), chromium (Cr), strontium (Sr), rubidium (Rb), selenium (Se). Among many roles with which selenium (Se) was accredited, the antioxidant effect one is the first one. The content of selenium in cultivars analyzed varied between 0.001 and 0.005 mg /100 g. In agreement with the previously reported data, high selenium levels were found in Brazil walnuts (those purchased without shells contained approximately a quarter of the content than those purchased with shells) and significantly lower levels in walnuts, cashews, and pecans nuts (Kannamkumarath Sasi *et al.*, 2002).

The obtained values for Se, Zn, Fe, Na, Cu in the analyzed Romanian cultivars (Tab. 4) compared to the data from USDA National Nutrient Database for Standard Reference (Tab. 3), are complying to variation limits of mineral content in walnut kernels. However, the average content in selenium (Se), zinc (Zn), sodium (Na), was lower in Romanian studied cultivars.

According to determinations conducted by Moodley *et al.* (2007) on elemental composition and chemical characteristics of five edible nuts (almond, Brazil, pecan, macadamia and walnut) consumed in Southern Africa, in generally, the order of elements' concentrations in all nut samples was found to be: Mg > Ca > Fe > Cu > Cr > As > Se. The Mn and Zn concentrations showed greater variation amongst different types of walnuts.

## Conclusions

Walnut cultivars analyzed have recorded rich mineral composition, especially potassium, magnesium, calcium. The mineral elements content was different from a cultivar to another. Potassium varied between 357.1 mg/100g in 'Valmit' and 499.6 mg/100g in 'Geoagiu 65', magnesium between 189.2 mg/100 g in 'Mihaela' and 278.1 mg/100 g in 'Argesan', etc. The order of nutritive elements depending on content/100 g of kernel was: K>Mg>Ca>Mn>Fe>Cu>Zn>Na>Cr>Al>Rb>Sr.

Walnut kernel consumption (Romanian cultivars) can cover the required amount of mineral elements in a well-balanced diet.

In breeding programme of walnut species, cultivars having high content of mineral elements are recommended to be used as genitors.

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