EVALUATION OF MINERAL ELEMENT CONTENT IN GRAPE SEED AND DEFATTED GRAPE SEED

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Abstract: *A study of the grape seed and of the defatted grape seed has been made in order to evaluate the content of mineral elements, with the purpose of investigating the possibility of using them for human/animal consumption. The research was made individually for each grape seed sample, defatted grape seed respectively. The total ash content was determined according to SR ISO 2171:2009, as a percent of dry substance. The determination of mineral content was performed by the energy dispersive spectrometer, using Röntgen radiation, Shimadzu type (EDX 900HS) with high resolution and sensibility. The results obtained show that the grape seed and defatted grape seed contain macro elements such as calcium (Ca), phosphorus (P), potassium (K) and sulphur (S) and trace elements such as: zinc (Zn), copper (Cu) and manganese (Mn).*

The seeds of the studied grape varieties and the defatted grape seed have proven to be good sources of mineral elements. Both varieties of seeds can be considered an important source used for fortifying aliments in order to obtain food products with higher nutritional characteristics. At the same time, these products can be valued to obtain new products which result in diminishing waste.

The data regarding the mineral content of the grape seeds are useful for the formulation of new diets and food processing techniques.

Keywords: *cakes, X-ray, Fluorescence spectrometer*

Introduction

The study of the physical and mechanical properties of grape seeds, including the chemical composition and obtaining new products through the active natural components are the source of many researches. The grape seed contains: oil, protein, cellulose, mineral elements and other components, with benefits for the human health [1]. In larger or smaller quantities, such as salts (cations and ions), especially in the solid part of the grape–peel, seeds, the cellular walls of the core, soluble elements from the soil can be found [2].

Mineral elements play an important role in the human metabolism and the interest for investigating them is rising [3, 4]. Although, they do not produce energy, the mineral elements have an important role in many activities of the human body [5, 6] and are necessary in order to maintain certain chemo-physical processes which are essential for life. Mineral elements represent inorganic components which are vital because they contribute to the normal development of vital activities and to the development of organism. As ions are linked to vitamins, minerals play important functional roles of metabolic nature,

activating numerous enzymatic systems, of chemo-physical nature, controlling the pH, electrical neutrality, and the gradients of the chemical potential [7]. The mineral substances from vegetables and fruit help the ossification of the skeleton, growth, maintaining different functions of the internal secretion glands and the forming of blood.

The mineral elements are a part of the chemical composition of enzymes, pigments, nucleic acids, peptic substances. These have an important role in nutrition because they are necessary in the development of the metabolic processes in the human body. No matter of quantity existing in the human body, mineral elements are essential because the body cannot synthesize or replace them. For this reason, they must be consumed together with nourishment [8]. In accordance with the quantity that exists in the organism, mineral elements are classified into three categories: macro elements, microelements and ultra microelements. Macro elements include: calcium, phosphorus, sodium and chloride and microelements include iron, copper, cobalt, potassium, magnesium, iodine, zinc, manganese, molybdenum, fluoride, chromium, selenium and sulphur [6]. Macro-minerals are necessary for the organism in larger quantity than 100 mg/day and micro-minerals, in smaller quantities than 100 mg/day [9]. The lack and the excess of macro elements produce metabolic disorders. Trace elements are essential in the maturation, activation and functions of host defence mechanism [10; 11]. Essential components of the enzymatic systems, biological and of structural portions of the biologically active components [12] are used by the immune system in order to face infectious agents [13, 14]. Ultra micro elements can be found as traces and include boron, silicon, arsenic, nickel, cadmium, lead, tin, lithium, vanadium, uranium, radium, thorium and a part of these have an essential metabolic effect. As regards cadmium, lead, tin, lithium and vanadium there is not enough evidence that could indicate their essential role in the organism [15].

The diversity of mineral elements which exist in the seed constitutes an important source of macro and microelements which are necessary in covering the needs of the human body [16] and contributes to the increase of food value of the products obtained from these. An exception is made by the contaminating materials (lead, cadmium), which can appear in seeds due to the pollution of soil, water, in contact with processing equipment and are toxic for the organism.

Analyzed macro elements and their role in the organism

Calcium (Ca) is present in the organism in larger quantities than other mineral substances. Together with phosphor, calcium contributes to the formation of the skeleton and teeth and insures their growth. *Ca* is important in the formation and consolidation of the cellular walls, and maintains the structure and permeability of the membrane, activating the enzymes [17]. It facilitates the normal activity of the neuromuscular system, of the heart, it intervenes in the blood coagulation process, it increases the water in protoplasm and the possibility of synthesizing cellular albumin. *Ca* decreases the size of allergic processes, it increases the resistance of organism to infectious diseases, activates an important number of metabolic processes, stimulates the enzymatic equipment of the organism, regulates energetic processes and tissue regeneration, participates in the stimulation of gastric secretion, the use of iron and the absorption of vitamin B_{12} [18].

Potassium (K) is an essential nutrient for the life and the human health. In the organism, *K* participates in the water circulation process, intervenes in the muscular and myocardial contraction, participates in the protein synthesis and it is a diuretic. Potassium ions participate in the forming of acetylcholine and in the transmission of nervous excitation

to the muscles. The increase of *K* in the organism will result in lower sodium and it emphasizes its elimination because there is a conflict between the potassium and sodium metabolism. The lack or insufficiency of *K* determines the growth of enzymes which distorts the nutritional balance, especially through the collapse of the phosphorylation process [8]. This maintains the acid-basic balance of the living cell, activating a series of enzymes. The components of *K* influence the tissue colloids. Through the reduction of the hydration level of proteins from tissues, these determine the elimination of liquid from the organism [7].

Phosphorus (P) is a part of the nucleic amino acids structure, of the phospholipids and participates in the division and multiplication process of cells. In living matter, phosphorous has an important role in growth. In medicine, *P* is used to treat rickets, functional disorder of the nerve system [19]. *P* is a partner of the majority of oxidation stages of sugar and lipids. These are a part of adenosine triphosphate (ATP) structure, made of a high quantity of energy, which plays an essential role in the release of energy from food products and supplies the energy necessary for the organism to function. Moreover, *P* has an important role in the activity of vitamins from group B, the majority of these become active only after combining with phosphoric acid [7].

Sulphur (S) is present in all the cells of the organism. It is a component of: amino acids with sulphur, vitamin B_1, biotin, coenzyme A and the insulin hormone. This mineral element has an important role in the process of substance exchange of the organism and especially in detoxification. *S* participates in expiration, has a favourable action in a balanced diet. Through the bridges S-S, sulphur is one of the major elements of the protein tertiary structure, and the radicals -SH are involved in the activity of some enzymes. *S* represents an integrated part of the food protein.

Analyzed micro elements and their role in the organism

Iron (Fe) is a component of vegetal and animal organisms and it participates in metabolic oxidation. This element is a part of the chemical composition of some enzymes and participates in the substance exchange of the organism; it is an oxygen carrier and plays an important role in cellular respiration. *Fe* balances the blood forming processes. The value of a food product as a *Fe* source is influenced more by the chemical state of this micro element than the total content of *Fe*. Solubility, slight ionization and the *Fe* balance state are properties which determine the absorption of *Fe*. Ascorbic acid, sulphide groups and other reduction substances, and normal gastric acidity facilitate the absorption of integrated iron [7].

Zinc (Zn) participates in the metabolism of sugar and, especially, of protein, it stimulates the activity of some enzymes, and is involved in digestion. Also, *Zn* has a specific role in the metabolism of essential fatty acids [7]. In the human organism, *Zn* is a part of insulin, stimulating its secretion, of some enzymes, it takes part in the synthesis of vitamins C, D and P [20], it facilitates the normal absorption and the vitamin action, especially those in the B_1 complex and provitamin A. *Zn* participates in the biosynthesis of nucleic acids and of proteins while being an essential nutrient for the growth and development of children. *Zn* influences the memory and the behaviour of the individual. *Zn* has an important role in the metabolism of sugar and lipids influencing the concentration of cholesterol. One of the first effects of *Zn* deficiency is loss of appetite which is established very early. Along with this, growth stops and the individual can even experience weight loss.

Copper (Cu) is present in all the fruits in variable quantity and has an essential role in the carbohydrate metabolism. In the human organism, *Cu* participates in the formation of haemoglobin and of erythrocytes, facilitating the absorption of *Fe*.

Manganese (Mn) together with iron, zinc and copper stimulates the activity of some

enzymes, takes part in the synthesis of some vitamins, the synthesis of proteins, lipids and carbohydrates. At the same time, *Mn* participates in the vitamin activity, improves the activity of the central nervous system and contributes to the forming of urea and of blood, of milk, intervenes in the development of the skeleton; also in the processes of reproduction contributes at maintaining the production rhythm of sexual hormones. The lack of *Mn* can delay the child's growth; it can lead to deafness and blindness, and in adults it can produce ear noises or hearing loss.

Cobalt (Co) is found in the organism in the smallest quantity, but it has a very intensive activity. It is a component of vitamin B_{12} and it participates in the proper functioning of red blood cells. Recent studies have provided information on the biochemistry and bioinorganic chemistry of several proteins containing cobalt in a form other than that in the corrin ring of vitamin B_{12} [21]. The level of cobalt in the organism is dependent on the hexogen, greater than in the case of other nutrients, considering that there are no tissues that can accumulate it directly.

*Nickel (Ni***)** takes part in blood formation and plays an important biological role, generally similar to that of *Co*. *Ni* activates several enzymes [7] and is involved in preserving the integrity of cell membranes [18].

A comprehensive synthesis of the influence of minerals on the organism has been presented by Soetan [17].

Materials and methods

Seeds – study material. The grape seeds come from grapes picked in 2009, from different geographical regions of the country, during the wine making season. The seed of the grape varieties have been separated from the dry grape pomace (Mixtures of white varieties of Aligoté and Frăguţă *b*) and from wet grape pomace (white Nohan, Frăguţă *a*) which were dried in open air at that moment, at temperatures between 20°C and 25°C. The separation was made by eliminating the impurities from seeds by sifting and free falling in air. The seed were minced mechanically as powder.

The *defatted grape seed* was also a study material in the present paper.

Chemical analysis. Determination of ash and mineral content. In order to remove carbon, every 2 g of powdered seeds of each variety were weighed and put into a crucible and then incinerated in oven at 550 Celsius degrees for 6 hours. The total ash content, determined according to SR ISO 2171:2009, is the percentage of dry matter. The determination of mineral content, from each seed sample, and defatted grape seed respectively, was performed by an energy dispersive spectrometer using Röntgen radiation, Shimadzu EDX type 900HS, of high sensitivity and resolution. Before the analysis, the homogenization of the samples was taken into consideration so that the radiation could penetrate each cell of the sample.

Analytical methods. All analytical determinations were performed at least three times and the value of each determined parameter is the average of the three values, which is added with ± the standard deviation values. The veracities of the obtained results and the ones presented in the paper are confirmed at the signification level of 0,95.

Results and Discussion

The results obtained at the determination of the total mineral elements (in %, dry matter basis) from the grape seed, and from the defatted grape seed respectively are given in Table 1.

Table 1
The total mineral elements from grape seed and defatted grape seed

Grape varieties	Total mineral elements	
	grape seeds [% s.u.]	defatted grape seed [% s.u.]
White variety Mix	3.18	2.73
Aligoté	3.35	2.84
Hybrid variety Nohan white	2.14	1.80
Hybrid variety Frăguţă *a*	3.20	2.86
Hybrid variety Frăguţă *b*	3.28	2.80

The way in which the content of mineral elements from the grape seed varies in report with the defatted grape seed for the white Mix variety is given in the graphic from Figure 1.
For the white Mix varieties, a larger concentration of calcium in seeds is obtained (55.74%) than from the defatted grape seed (49.51%), and the other predominant mineral elements, *K*, *P* and *S* are found in larger concentration in the defatted grape seed than in seeds. Also, in the defatted grape seed from the white Mix variety the element *Ti* (0,090%±0,006) is present. *Ti* is non-toxic even in larger quantities and has no natural role in the human organism. A quantity of 0,8 milligrams is ingested by humans on a daily basis, but the majority passes through the organism without being absorbed [22].
The content of mineral elements from the grape seed and defatted grape seed, from the Aligoté variety is given in Figure 2.
In the case of seeds from the Aligoté variety, the mineral elements *Ca*, *K*, *S* are found in larger quantities in the defatted grape seed than in seeds; only *P* is in a smaller percentage in the defatted grape seed (13.12%) than in the seeds (16.632%). The concentration of *Ca* from the defatted grape seed (53.477%) does not differ significantly from the concentration of *Ca* in grape seed (54.11%).
The variation of mineral elements from the grape seed and defatted grape seed of Nohan variety is given in Figure 3. The predominant mineral elements *Ca*, *K*, *S* from the seeds of Nohan hybrid variety can be found in smaller concentration than in the defatted grape seed. In seeds, just *P* is found in large concentration (18,853%) than in the defatted grape seed (14,364%).
The content of mineral elements from grape seed and defatted grape seed for Fraguţă hybrid variety is presented in Figure 4 and for Fraguţă *b* in Figure 5.

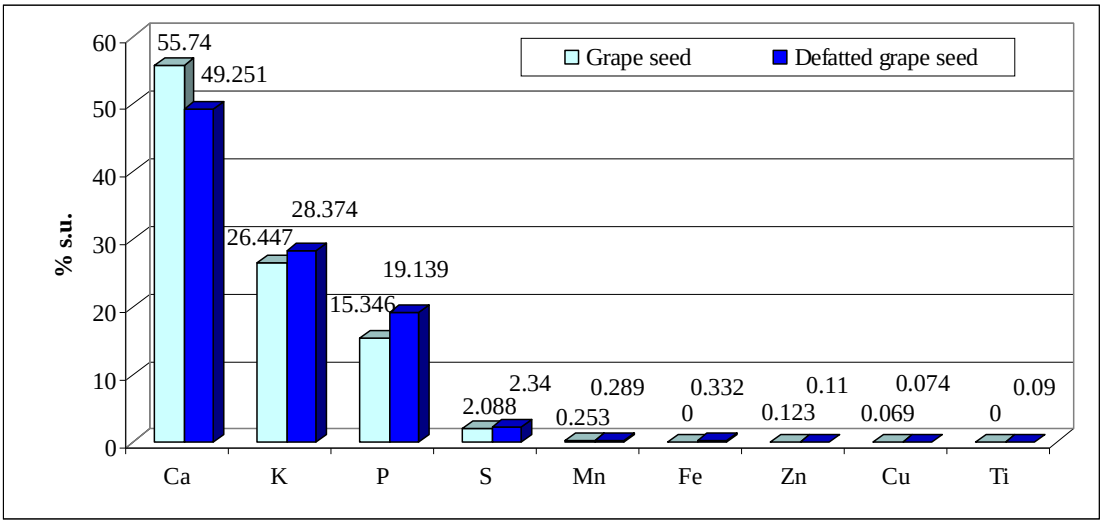

Figure 1. The content variety of mineral elements from grapes and defatted grape seed for the white variety Mix

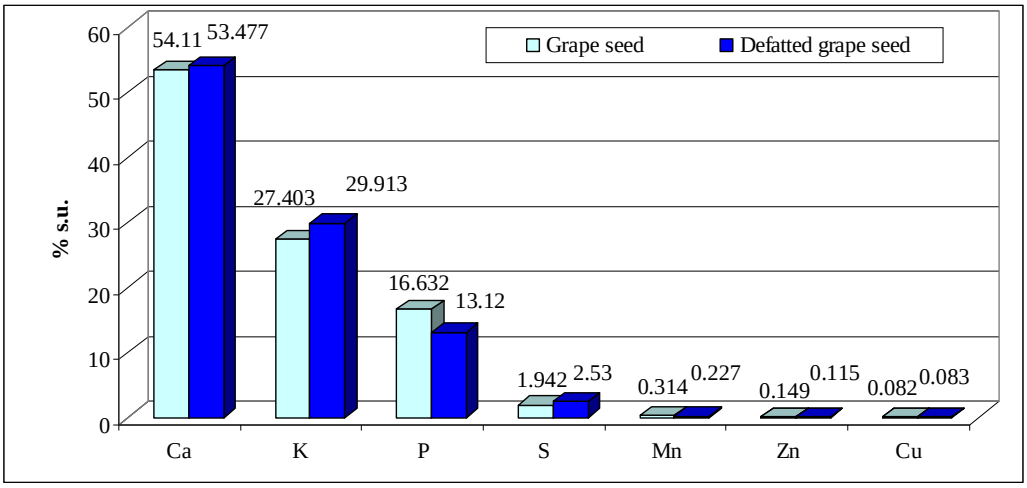

Figure 2. The content of mineral elements form seeds and defatted grape seed – Aligoté variety

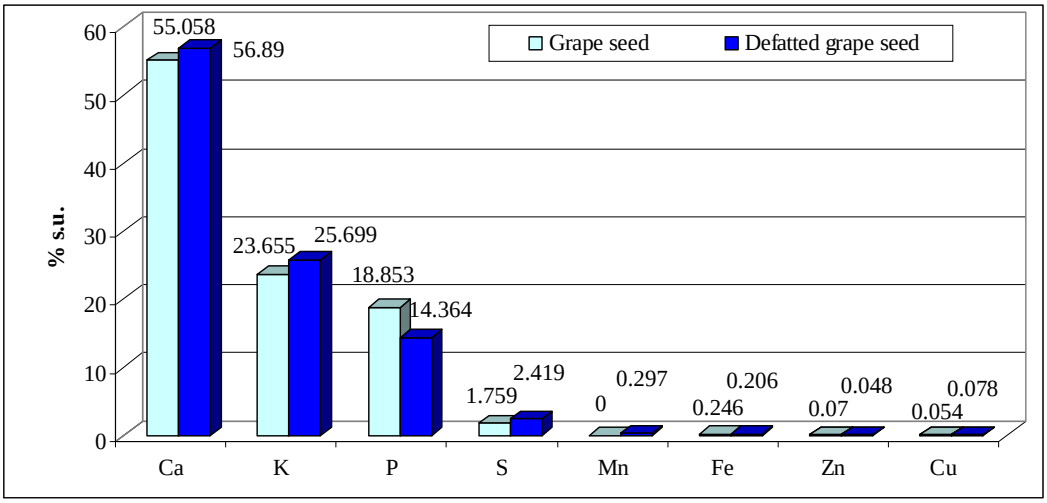

Figure 3. The content of mineral elements form seeds and defatted grape seed – Nohan hybrid variety

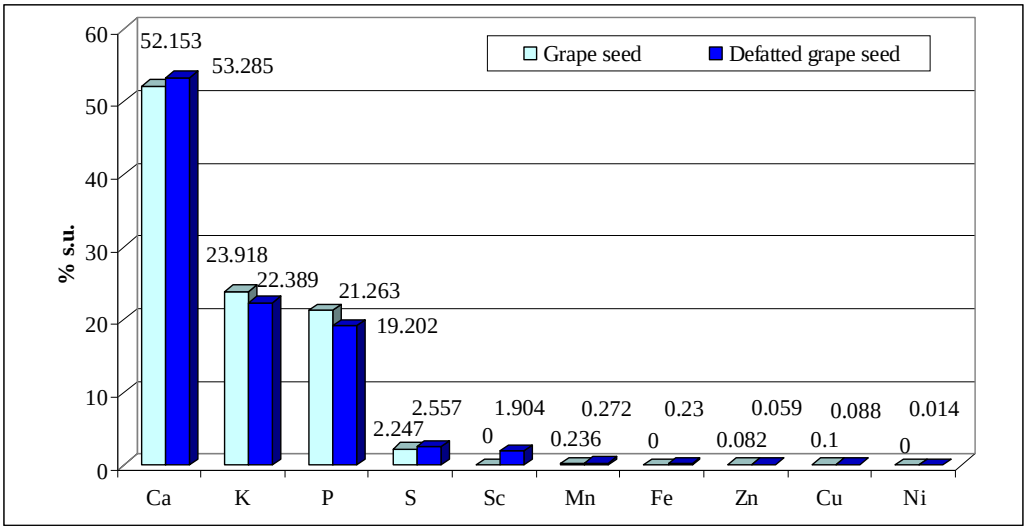

Figure 4. The content of mineral elements form seeds and defatted grape seed – Frăguţa *a* hybrid variety

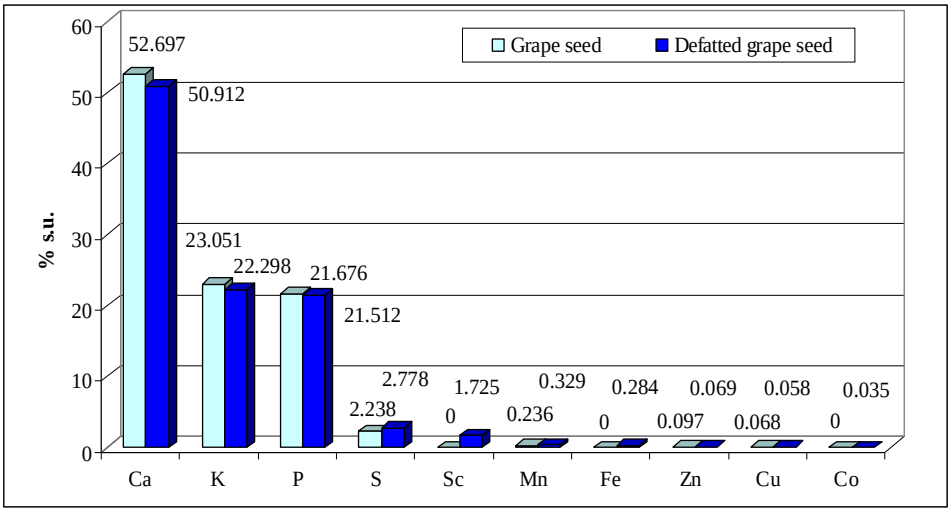

Figure 5. The content of mineral elements form seeds and defatted grape seed – Frăguţa *b* hybrid variety

When compared with the other varieties - varieties from Vrancea, in the hybrid variety Fraguţă – variety from the Suceava county, a new element appears – scandium (*Sc*). In the defatted grape seed which results after the extraction of oil, the nickel (*Ni*) cation contamination can be found in concentration of 0,014%.

From the comparative analysis of the content of mineral elements of the Fraguţă hybrid variety, it can be observed that seeds gathered from the dry pomace – Fraguţă *b* have a larger concentration of *Ca* (52,697%) when compared to the seeds gathered from the wet pomace – Fraguţă *a* (52,153%).

Moreover, in the seeds gathered from the dry pomace, *Ni* is not present but a new element appears - *Co*.

Generally, the chemical composition of the mineral elements of the tested samples is comparable with the one presented in the specialty literature [23, 24].

From the analysis of the obtained results for the mineral content, it can be observed that in the grape seed and also in the defatted grape seed, there is a predominant quantity, in the specified order, of calcium, potassium, phosphor and sulphur. It has been found that cations such as arsenic, cadmium, selenium, mercury, etc. do not exist. The only cation that appears is nickel, in the case of the defatted grape seed from the Frăguţă *a* hybrid variety, variety gathered from humid marc. Its occurrence may be due to the contact with processing machinery. Its concentration is in the allowed limits.

Conclusion

The results of the mineral elements show that all the studied grape seed variety and the defatted grape seed contain considerable quantities of mineral elements: calcium, potassium and phosphorus which can be used to improve the nutritional value of the human diet. The grape seed and the defatted grape seed, due to their high content of mineral elements, can constitute an alternative in the manufacture of products which ensure benefits for health, following the acceptance of the idea that diet plays a decisive role in the prevention and treatment of disease. Such products, in addition to having appropriate nutritional effects - they improve health and/or reduce the risk of disease - also have components which are derived from natural ingredients that provide additional health benefits.

References

1. MIRONEASA, S., LEAHU, A., CODINĂ, G.G., STROE, S.G. and MIRONEASA, C. *Grape Seed: physico-chemical, structural characteristics and oil content,* Journal of Agroalimentary Processes and Technologies 2010, 16 (1), 1-6.
2. POMOHACI, N., STOIAN, V., GHEORGHIŢĂ, M., SÎRGHI, C., COTEA, V. V. and NĂMOLOŞANU, I., Oenologie vol. I, *Prelucrarea strugurilor şi producerea vinurilor*, Editura Ceres, Bucureşti, 2000.
3. PELUS, E., ARNAUD, J., DUCROS, V., FAURE, H., FAVIER, A. and ROUSSEL, A.M., *Trace element (Cu, Zn, Fe, Mn, Se) intakes of a group of French men using the duplicate diet technique*. Int. J. Food Sci. Nutr. 1994, 45, 63 –70.
4. FENNEMA, O.R., *Food Chemistry*. New York: Marcel Dekker, 2000.
5. MALHOTRA, V.K., *Biochemistry for Students*, Tenth Edition, Jaypee Brothers Medical Publishers (P) Ltd, New Delhi, India, 1998.
6. ERUVBETINE, D., *Canine Nutrition and Health*. A paper presented at the seminar organized by Kensington Pharmaceuticals Nig. Ltd., Lagos on August 21, 2003.
7. SEGAL, R., *Principiile nutriţiei*, Galaţi, Editura Academica, 2002.
8. JAMBA, A. and CARABULEA, B. *Tehnologia păstrării şi industrializării produselor horticole*, Chişinău, Editura Cartea Moldovei, 2002.
9. MURRAY, R.K., GRANNER, D.K., MAYES, P.A. and RODWELL, V.W., *Harper's Biochemistry*, 25th Edition, McGraw-Hill, Health Profession Division, USA, 2000.
10. BENDICH, A., *Antioxidant micronutrients and immune responses*, Ann. N.Y. Acad. Sci., 1990, 587, 180.
11. ROMERO, R., *Intra-uterine infection, premature birth and the Fetal Inflammatory Response Syndrome*. J. Nutr. 2003, 33, 1668-1673.
12. ARINOLA, O.G., NWOZO, S.O., AJIBOYE, J.A. and ONIYE, A.H. *Evaluation of trace elements and total antioxidant status in Nigerian cassava processors*, Pak. J. Nutr., 2008, 7(6), 770-772.
13. SPALLHOLZ, E.J., BOYLAN, M.L. and LARSEN, S.H., *Advances in understanding selenium's role in the immune system*, Ann. N.Y. Acad. Sci., 1990, 587, 123-139.
14. SHERMAN, R.A., *Influence of iron on immunity and disease resistance*, Ann. N.Y. Acad. Sci., 1990, 587, 123-139.
15. ALBION RESEARCH NOTES. *A compilation of vital research updates on human nutrition*, 5: 2, Albion Laboratories, Inc. May, 1996.
16. FAUR, V. and GOIAN, M. *Fitoterapie şi fitoprotecţie alimentară*, Editura Dacia, Europa Nova, Lugoj, 1998.
17. SOETAN, K. O., OLAIYA, C. O. and OYEWOLE O. E., *The importance of mineral elements for humans, domestic animals and plants*: *A review.* African Journal of Food Science, 2010, 4(5), 200-222.
18. DUMBRAVĂ, D.G., *Contribuţii la studiul, izolarea şi purificarea pigmenţilor carotenoidici din produsele naturale*. Teze de doctorat ale UPT, Seria 4, Nr. 11, Editura Politehnica, 2008.
19. SEGAL, B., COTRĂU, M. and SEGAL, R., *Factori de protecţie prezenţi în produsele alimentare*, Editura Junimea, Iaşi, 1996.
20. ŢÂRDEA, C., *Chimia şi analiza vinului*, Editura „Ion Ionescu de la Brad", Iaşi, 2007.
21. KOBAYASHI, M. and SHIMIZU, S., 1999, *Cobalt proteins*, European Journal of Biochemistry, 1999, 261 (1), 1–9.
22. EMSLEY, J., *"Titanium"*. Nature's Building Blocks: An A-Z Guide to the Elements. Oxford, England, UK: Oxford University Press, 2001.
23. GURIN, A.A., *Razrabotka tehnologhii proizvodstva ăkstaktov, konţentratov i vin iz sladkoi vinogradnoi vîjimki*. Avtoreferat kand. Disertaţii, Moskva, 1991.
24. GASANOV, D.H.A., *Razrabotka tehnologhii proizvodstva kormovogo belkovogo producta iz vinogradnîh bîjimok*. Ealta, Avtoreferat kad.diss, 1990.