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Evaluation of the level of chromium and nickel in selected dietary supplements (containing antioxidant compounds) available in Poland

Ocena poziomu chromu i niklu w wybranych suplementach diety (zawierających związki przeciwutleniające) dostępnych w Polsce

INTRODUCTION

A healthy body of man (under the conditions of due nutrition and the clean environment) produces an adequate amount of antioxidants in order to neutralize the harmful effect of free radicals arising in physiological conditions. With the progressing ageing process of the organism, the effectiveness of the internal, anti-oxidant organic protection decreases. Antioxidants delivered with food assist natural protective mechanisms of the organism allowing to preserve the appropriate balance, but these are sometimes insufficient [4].

Some civilization factors, e.g. chemicals polluting the food, air pollution through the exhaust fumes or cigarette smoke, electromagnetic radiation from different emitters act disadvantageously on people and can cause a increase of free radicals in human bodies. For this reason applying anti-oxidant supplementation is recommended [10].

In recent years many dietary supplements with antioxidants have emerged in the market. These preparations often contain ingredients of natural origin – plant parts which are rich in mineral substances: macro- and microelements necessary in the body, including chromium and nickel [4, 6].

Chromium (mainly Cr^{3+}) is the element necessary for the normal development of man: it accomplishes a substantial role in the metabolism of glucose, some proteins and fats; its participation in the metabolism of cholesterol is unexplained. It is a component of some enzymes (e.g. trypsins) and it stimulates the activity of others. The most significant combination of chromium in the body is a compound with the nicotinic acid and the glutathione known as GTF (Glucose Tolerance Factor) [15, 16].

Recently it was shown that the popular dietary supplement chromium picolinate complex generates chromosome damage in hamster ovary cells [14]. Release of chromium from chromium picolinate for use in cells requires reduction of the chromic center, a process that can potentially

lead to the production of harmful hydroxyl radicals [15]. Nickel has only recently been started to be regarded as the essential element for man. The basic physiological role of this microelement consists in the activation of enzymes, e.g. of some dehydrogenases and carboxylases. This element combines with plasmin and it probably regulates its functions. In humans, nickel influences iron absorption and metabolism, and may be an essential component of the haemopoietic process. An increased amount of this element in the body causes changes in the metabolism of other metals, e.g. lowering the level of magnesium, manganese and zinc in some parenchymal organs. It has been suggested that high levels of nickel may impair absorption or utilization of iron when iron status is low [8].

The purpose of this work was the examination of nickel and chromium levels appearing in chosen dietary supplements (often applied due to their composition and purpose) and whether they are threatening the health of man.

MATERIALS AND METHODS

Dietary supplements containing antioxidant compounds applied in the prophylaxis and therapy of the organs of sight – *Aronia z luteiną (Chokeberry with luteine), Bilberin, Maxi Vision, Naturapia wzrok, Oculobon, Pro-wzrok, Vitalux* and the preparations containing garlic in their composition – *Aktiv Kapseln, Aliovital, Alitol, Bio-czosnek (Bio-garlic), Czosnek forte (Garlic forte), Czosnek z pietruszką (Garlic with parsley), Garlicin, Tabletki z czosnkiem (Tablets with garlic)* were analyzed and they were the subject of the research (Table 1).

4–5 different series of production of individual supplements in two parallel runs were tested. Samples of 4–5 gram of these preparations were mineralized ”dry” at the temperature of 450˚C. Pills were previously fragmented in the mortar and capsules were weighed in one piece. The process of mineralization was sped up using 30% of water solution of nitric acid (V) - (HNO_3 - Suprapur, Merck). Ashes were dissolved in 15% water solution of hydrochloric acid (HCl - Suprapur, Merck).

The amounts of the studied elements were determined in Pye Unicam SP 192 atomic absorption spectrometer: content of chromium – directly from water phase, but nickel with the extraction method from the organic phase, according to Sapek [12]. With a view of indicating the content of nickel, 2 cm^3 of 2% water solution of APDC solution (1-ammonium-pyrrolidinedithiocarbamate) was added to the appropriate amount of the mineralisate in order to conduct nickel into a complex with this compound, in the environment citrate buffer of pH = 6.8. The MIBK (methyl-isobutyl ketone) was an organic phase saturated with deionised water.

The content of chromium was marked from the water phase applying two-time strengthening of the signal and the following parameters: analytical wavelength – 257.9 nm, breadth of the crack – 0.4 nm, situation of the burner – 10 cm, the intensity of the current of the hilar cathode – 10 mA, flow of air – 5 dm^3 min., flow of acetylene – 0.8 dm^3/min. [11].

Determining nickel from the organic phase was conducted with the application of the following parameters: analytical wavelength – 232.0 nm, breadth of the crack – 0.2 nm, situation of the burner – 10 cm, the intensity of the current of the hilar cathode – 10 mA, flow of air – 5 dm^3/min, flow of acetylene – 0.8 dm^3/min. [11].

Table 1. Name and composition of dietary supplements containing antioxidants

Name of preparation	Composition
Dietary supplements used auxiliary in prophylaxis and therapy the organ of vision	
Aronia z luteiną – Chokeberry with luteine (caps.) AGROPHARM SA Tuszyn	Aronia fruit dry extract, calendula dry extract
Bilberin (caps.) HASCO–LEK SAWrocław	*Myrtilli fructus* extractum siccum, beta-carotene
Maxi Vision (caps.) A.S.A Sp. z o.o. Głubczyce	*Myrtilli fructus* extractum siccum, vitamins: E, C; Zn, Se
Naturapia wzrok (caps.) Le Laboratoire de la Nature, Francja	Standardized extract from grapes, the fruit of bilberry or blackberry, Zn, β- carotene, lutein, lycopen
Oculobon (caps.) Laboratorium Medycyny Naturalnej BONIMED, Żywiec	*Vaccinium myrtillus*, lutein, beta- caroten, vitamin E, C, $B_{1,}$ $B_{2,}$ $B_{5,}$ B_6, B_{12}, H, PP, folic acid
Pro-wzrok (caps.) HASCO–LEK SA Wrocław	Billberry dry extract, beta-caroten, vitamin E
Vitalux (caps.) EXCELVISION, Francja	Beta-carotene, vitamins: C and E, PP, microelements: Zn, Se, Mn
Dietary supplement containing garlic	
Aktiv Kapseln (caps.) Mcm Klosterfrau, Niemcy	*Allii sativi* maceratio oleosa, *Hyperici herbae* maceratio oleosa, vitamins: E, A; lecithin
Aliovital (caps.) AGROPHARM S.A.Tuszyn	Garlic macerate (*Allium sativum*)
Alitol (caps.) KRKA, Słowenia	Oil garlic extract (*Allii sativi*)
Bio-czosnek – Bio-garlic (tabl.) Pharma Nord APS, Dania	Powdered garlic
Czosnek forte – Garlic forte (caps.) Naturell AB, Szwecja	Garlic extract, soy oil
Czosnek z pietruszką – Garlic with parsley (caps.) Herbapol Kraków	*Allii sativi bulbus* siccum, *Petroselini herba*
Garlicin (caps.) Olimp Laboratories Sp. z o.o. Dębica)	Garlic extract
Tabletki z czosnkiem – Tablets with garlic (tabl.) Labofarm, Starogard Gdański, Polska	*Allii sativi* bulbus pulv.siccum

In the same conditions the analysis was performed of the certified material of reference - blends of Polish herbs – „Mixed Polish Herbs" (INST-MPH- 2) [4]. The declared amounts of the examined elements in this material were: of chromium – 1.69 ± of 0.13 µg/g and nickel – 1.57 ± 0.16 µg/g, and they marked in it: of chromium – 1.73 ± of 0.15 µg/g and nickel – 1.48 ± 0.10 µg/g.

RESULTS AND DISCUSSION

Results were presented in tables: 2 and 3, giving the arithmetic means, the standard deviation and the content range (minimal and maximum) – for preparation of every kind. Contents of chromium in all examined dietary supplements were diversified. In preparations applied in the prevention and as supplements, amounts of this element in the therapy of the sight organ ranged, on average from 0.20 μg/g in the Vitalux supplement and 0.24 μg/g (Pro-wzrok) to 6.85 μg/g in Maxi Vision preparation (3.14 μg of this element in 1 capsule). In supplements containing garlic or extract from garlic, contents of chromium fluctuated, on average from 0.04 μg/g in preparation *Czosnek forte (Garlic forte)* to 1.01 μg/g in preparation *Czosnek z pietruszką – Garlic with parsley* (0.42 μg of this element in 1 capsule).

The determined levels of nickel were found to be in a wide range, too. In supplements applied in the prevention of sight problems, the smallest content of this element was stated, like in the case of chromium, in Vitalux preparation, on average 0.05 μg/g and the biggest, also like in the case of chromium, in Maxi Vision preparation, on average 1.98 μg/g (0.88 μg of nickel in 1 capsule). In dietary supplements with garlic, Alitol preparation contained the paucity of nickel, on average 0.03 μg/g, and the biggest amount was noted for *Czosnek z pietruszką – Garlic with parsley*, on average 1.01 μg/g (0.42 μg of this element in 1 capsule).

The microelements essential for the man, among others chromium and nickel should be provided to the organism in appropriate amounts and proportion, otherwise manifestations of their deficiency or the excess can appear [8].

Despite a wide assortment of dietary supplements available at present, there are few studies concerning determination of the content of chromium and nickel in them.

Trivalent chromium is regarded essential for the human development of the organism. Demand of an adult person for Cr^{3+} is from 25 μg per day for women to 35 μg/24-hours – for men. Chromium taken up with food and water is poorly absorbed from the digestive tract – from 0.5 to 3% [7, 8].

Findings published so far on the content of chromium in supplements of food and other preparations in the form of capsules or pills have been in a wide range. In preparations supporting slimming it was stated, on average, from 0.15 μg of this element in 1 g to 50.64 μg of chromium in 1 gram of the supplement (preparation with the addition of chromium) [2]; in preparations with phytoestrogens – from 0.12 μg/g to 4.57 μg/g [3].

Leśniewicz et al. [9] determined, on average, from 0.30 μg/g to 63.1 μg of chromium in one gram of *Tonic tablets* Tonic preparation. Nickel was relatively recently recognized as the element essential for the human organism, but the AI (Adequate Intake), neither RDA (Recommended Dietary Allowances) have not been established so far. It was accepted, that maximally, the amount per day is 1 mg of this element for the body of adult man [8]. According to Anke et al. [1] 25–35 μg of this element per day will be enough for the correct functioning of the body of an adult man. Nickel taken up with food and water is poorly absorbed in the digestive tract (about 5% of the total number) and quickly excreted.

In earlier published research papers, levels of nickel in dietary supplements were also diversified. Preparations supporting slimming contained, on average, from 0.07 μg/g to 2.74 μg of nickel in 1g of *Slim Trio* [2], and with phytoestrogens, on average from 0.23 μg/g to 1.56 μg of nickel in 1 gram of *Fito-Fem Forte* [3]. Higher contents of this element were found in some preparations: Leśniewicz et al. [9], on average – to 32.3 μg/g.

Table 2. The levels of chromium and nickel in dietary supplements used additionally in prophylaxis and therapy of the organ of vision (µg/g and µg/ caps., tabl.) and intake of these elements with maximal daily dose (µg)

Name of preparation	The arithmetical means ± standard deviation, content (min.-max.)		Intake of Cr with maximal of daily dose	The arithmetical means ± standard deviation, content (min.-max.)		Intake of Ni with maximal of daily dose (µg of Ni)
	Chromium content (µg/g)	Chromium content (µg/caps. tabl.)	(µg of Cr)	Nickel content (µg/g)	Nickel content (µg/caps. tabl.)	
Aronia z luteiną - Chokeberry with luteine (n = 5; $\overline{m}$ = 0.139 g)	0.62 ± 0.31 0.36 – 0.95	0.09 ± 0.04 0.05 – 0.13	0.09 ± 0.04	0.26 ± 0.06 0.20 – 0.33	0.04 ± 0.01 0.03 – 0.05	0.04 ± 0.01
Bilberin (n = 5; $\overline{m}$ = 0.722 g)	0.32 ± 0.05 0.26 – 0.39	0.23 ± 0.03 0.19 – 0.28	0.92 ± 0.12	0.45 ± 0.03 0.42 – 0.49	0.32 ± 0.02 0.31 – 0.35	1.28 ± 0.08
Maxi Vision (n = 5; $\overline{m}$ = 0.454 g)	6.85 ± 2.68 3.05 – 9.56	3.14 ± 1.23 1,38 - 4.33	3.14 ±1.23	1.98 ± 1.05 0.80 – 2.99	0.88 ± 0.51 0.30 – 1.35	0.88 ± 0.51
Naturapia wzrok (n = 5; $\overline{m}$=0.367 g)	0.58 ± 0.23 0.37 – 0.86	0.21 ± 0.09 0.13 – 0.32	0.84 ± 0.36	0.18 ± 0.03 0.15 – 0.21	0.07 ± 0.01 0.06 – 0.08	0.28 ± 0.04
Oculobon (n = 4; $\overline{m}$ = 0.329 g)	6.45 ± 3.04 3.82 – 9.17	2.11 ± 0.98 1.26 - 2.98	4.22 ± 1.96	1.12 ± 0.07 1.06 – 1.22	0.37 ± 0.02 0.35 - 0.40	0.74 ± 0.04
Pro-wzrok (n = 5; $\overline{m}$ = 0.424 g)	0.24 ± 0.05 0.20- 0.30	0.11 ± 0.02 0.09 – 0.13	0.22 ± 0.04	0.47 ± 0.07 0.38 – 0.54	0.20 ± 0.03 0.16 - 0.23	0.40 ± 0.06
Vitalux (n = 5; $\overline{m}$ = 0.612 g)	0.20 ± 0.03 0.18 – 0.23	0.14 ± 0.03 0.11 - 0.19	0.14 ± 0.03	0.05 ± 0.02 0.03 – 0.08	0.03 ± 0.01 0.02 – 0.05	0.03 ± 0.01

*n – number of series, $\overline{m}$ – mean mass of caps. or tabl. [g]

Table 3. The levels of chromium and nickel in dietary supplements containing garlic (µg/g and µg/caps., tabl.) and intake of these elements with maximal daily dose (µg)

Name of preparation	The arithmetical means ± standard deviation, content (min.-max.)		Intake of Cr with maximal of daily dose (µg of Cr)	The arithmetical mean ± standard deviation, content (min.-max.)		Intake of Ni with maximal of daily dose (µg of Ni)
	Chromium content (µg/g)	Chromium content (µg/caps., tabl.)		Nickel content (µg/g)	Nickel content (µg/caps., tabl.)	
Aktiv Kapsel (n = 5; $\overline{m}$ = 0.403 g)	0.07 ± 0.03 0.05 – 0.10	0.03 ± 0.01 0.02 – 0.04	0.18 ± 0.06	0.08 ± 0.03 0.02 – 0.10	0,03 ± 0,01 0.01 - 0,04	0.18 ± 0.06
Aliovital (n = 5; $\overline{m}$ = 0.397 g)	0.11 ± 0.03 0.09 – 0.14	0.05 ± 0.01 0.04 – 0.06	0.50 ± 0.10	0.08 ± 0.02 0.06 – 0.11	0,03 ± 0,01 0,02 - 0,04	0.30 ± 0.10
Alitol (n = 5) $\overline{m}$ = 0.394 g)	0.11 ± 0.05 0.05 – 0.15	0.04 ± 0.02 0.02 – 0.06	0.24 ± 0.12	0.03 ± 0.02 0.02 – 0.07	0.01 ± 0.01 0,01 – 0.03	0.06 ± 0.06
Bio-czosnek – Bio-garlic (n = 4; $\overline{m}$ = 0.715 g)	0.21 ± 0.07 0.13 – 0.29	0.15 ± 0.05 0.09 – 0.21	0.15 ± 0.05	0.22 ± 0.04 0.16 – 0.26	0.16 ± 0.03 0.12 – 0.19	0.16 ± 0.03
Czosnek forte – Garlic forte (n = 5; $\overline{m}$ = 0.431 g)	0.03 ± 0.02 0.02 – 0.05	0.01 ± 0.01 0.01 – 0.02	0.02 ± 0.02	0.08 ± 0.02 0.07 – 0.10	0.03 ± 0.01 0.03 – 0.04	0.06 ± 0.02
Czosnek z pietruszką – Garlic with parsley (n = 5; $\overline{m}$ = 0.422 g)	1.01 ± 0.30 0.75 – 1.34	0.42 ± 0.13 0.31 – 0.56	1.69 ± 0.52	1.01 ± 0.14 0.88 – 1.20	0.42 ± 0.06 0.38 – 0.50	1.68 ±0.24
Garlicin (n = 4; $\overline{m}$ = 0.308 g)	0.62 ± 0.03 0.59 – 0.65	0.19 ± 0.01 0.18 – 0.20	0.19 ± 0.01	0.66 ± 0.07 0.60 – 0.72	0.20 ± 0.02 0.18 – 0.22	0.20 ± 0.02
Tabletki z czosnkiem – Tablets with garlic (n = 5; $\overline{m}$ = 0.300 g)	0.63 ± 0.03 0.58 – 0.67	0.19 ± 0.01 0.18 – 0.20	1.14 ± 0.06	0.49 ± 0.07 0.39 – 0.58	0.15 ± 0.02 0.12 – 0.18	0.90 ± 0.12

*n – number of series; $\overline{m}$ – mean mass of caps. or tabl. [g]

CONCLUSIONS

1. Indicated amounts of chromium and nickel in the studied dietary supplements were diversified depending on the composition of the preparation.

2. Contents of the examined elements taken with the maximum daily dose declared by the producer can be regarded safe for the body of a man.

3. Stated amounts of chromium and nickel in inspected supplements can supplement the daily demand of the organism for these microelements taken with these preparations.

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SUMMARY

Among the dietary supplements whose assortment is still increasing, preparations containing antioxidants constitute an important group protecting the human organism against free radicals. As there is a scarcity of studies concerning the content of the microelements essential for human the body in dietary supplements, contents of chromium and nickel in preparations applied in the prevention of illnesses and in the therapy of the sight organ were studied *Aronia z luteiną (Chokeberry with luteine), Bilberin, Maxi Vision, Naturapia wzrok, Oculobon, Pro-wzrok, Vitalux)* and those containing garlic in their composition – *Aktiv Kapseln, Aliovital, Alitol, Bio-czosnek (Bio-garlic), Czosnek forte (Garlic forte), Czosnek z pietruszką (Garlic with parsley), Garlicin, Tabletki z czosnkiem (Tablets with garlic)*. Samples (4–5 gram) were mineralized "dry" in temperature of 450˚C. The amounts of the studied elements were determined in of the Pye Unicam SP 192 atomic absorption spectrometer: chromium directly from the mineralisate, and nickel after the extraction up to the organic phase (MIBK). Contents of chromium ranged, on average from 0.04 μg/g to 6.85 μg/g, and those of nickel from 0.03 μg/g to 1.98 μg/g. The indicated amounts of chromium and nickel in inspected dietary supplements were diversified and they depended on the composition of the preparation. Contents of these elements taken with the maximum daily dose declared by the producer can be regarded safe for the human body and they supplement the daily demand of the organism for these microelements in the supplementation process.

Keywords: dietary supplements, chromium, nickel, flame atomic absorption spectrometer (FAAS)

STRESZCZENIE

Wśród suplementów diety, których asortyment ciągle wzrasta, ważną grupę stanowią preparaty zawierające związki antyutleniające chroniące organizm przed wolnymi rodnikami. W związku z niewielką ilością badań dotyczących zawartości mikroelementów niezbędnych dla organizmu człowieka w suplementach diety oznaczono zawartość chromu i niklu w preparatach stosowanych w profilaktyce i pomocniczo w terapii narządu wzroku (*Aronia z luteiną, Bilberin, Maxi Vision, Naturapia wzrok, Oculobon, Pro-wzrok, Vitalux)* oraz zawierających czosnek w swoim składzie (*Aktiv Kapseln, Aliovital, Alitol, Bio-czosnek, Czosnek forte, Czosnek z pietruszką, Garlicin, Tabletki z czosnkiem)*. Próbki (4–5 gramowe naważki) mineralizowano metodą „na sucho" w temperaturze 450˚C. Zawartość niklu i chromu oznaczono stosując płomieniową absorpcyjną spektrometrię atomową (FASA) w spektrometrze Pye Unicam SP 192: chrom bezpośrednio z mineralizatu, a nikiel po ekstrakcji do fazy organicznej (MIBK). Zawartości chromu mieściły się w przedziale średnio od 0,04 μg/g do 6,85 μg/g, a niklu od 0,03 μg/g do 1,98 μg/g. Oznaczone ilości chromu i niklu w badanych suplementach diety były zróżnicowane i zależały od składu preparatu. Zawartości tych pierwiastków pobrane wraz z maksymalną dzienną dawką zadeklarowaną przez producenta mogą być uznane za bezpieczne dla organizmu człowieka i uzupełniać dzienne zapotrzebowanie organizmu na te mikroelementy w czasie trwania suplementacji.

Słowa kluczowe: suplementy diety, chrom, nikiel, płomieniowa absorpcyjna spektrometria atomowa (FASA)