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Investigation of declared values of iodine in food supplements on the Slovene market

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ABSTRACT

The essentiality of iodine for man is well recognized. The primary sources of iodine in a normal, balanced diet are fish, shellfish, milk and iodinated salt. Alternative sources of iodine meant to complement the normal diet are food supplements containing iodine. The complex composition of food supplements, due to their content of various vitamins and minerals, makes determination of iodine very difficult. In our work we employed radiochemical neutron activation analysis to determine the content of iodine in different series of seven different food supplements available on the Slovene market intended for adults, children and sportsmen. The levels of iodine found ranged from 21 to 231 µg/g. Three food supplements were not in agreement with the declaration made by the producer and two food supplements were not in agreement with the recommendations made by U.S. Pharmacopoeia that dietary supplements should contain not less then 90 % and not more then 200 % of the declared amount of substance.

Keywords: food supplements, iodine, RNAA

IZVLEČEK

PREVERJANJE DEKLARIRANIH VREDNOSTI JODA V PREHRANSKIH DOPOLNILIH NA SLOVENSKEM TRŽIŠČU

Pomembnost joda za človeka je dobro znana. Osnoven vir joda v normalni, uravnoteženi prehrani predstavljajo ribe, lupinarji (školjke, polži, raki), mleko in jodirana sol. Alternativen vir joda so prehranska dopolnila, ki vsebujejo jod. Njihova uporaba je upravičena predvsem v primerih, kadar je težko zagotoviti uravnoteženo prehrano in so nepogrešljivi med nosečnostjo ter v času bolezni, poškodb, izrednega stresa ali telesnih obremenitev. Vsakršno prekomerno ali nesorazmerno vnašanje v zdravo telo pa je zanj le obremenitev metabolizma ali pa celo vodi v kopičenje v določenih organih, kjer povzročajo nekateri elementi celo toksične učinke. Prehranska dopolnila imajo kompleksno sestavo, saj vsebujejo številne vitamine in minerale, kar precej otežuje določanje joda. Pri našem delu smo uporabili radiokemijsko nevtronsko aktivacijsko analizo ter določili vsebnost joda v sedmih različnih prehranskih dopolnilih, iz različnih proizvodnih serij, ki so dosegljiva na slovenskem tržišču in

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so namenjena odraslim, otrokom in športnikom. Vsebnost joda je bila v območju od 21 do 231 µg g^{-1}. Pri treh prehranskih dopolnilih se določena vrednost joda ni ujemala z deklarirano vrednostjo proizvajalca, pri dveh pa se določena vrednost ni ujemala z priporočilom U.S. Pharmacopoeia, ki navaja, da prehranska dopolnila naj ne bi vsebovala manj kot 90 % in ne več kot 200 % deklarirane vrednosti določene sestavine.

Ključne besede: prehranska dopolnila, jod, RNAA

1 INTRODUCTION

Iodine is a mineral essential for normal functioning of the thyroid gland and for mental and physical development. Lack of iodine results in insufficient production of thyroid hormones, which are involved in the regulation of various enzymes and metabolic processes. When physiological requirements for iodine are not satisfied iodine deficiency effects, known as "iodine deficiency disorders" occur (DRI, 2000).

The recommendations for minimum daily iodine intake differ among different institutions. The U.S. Food and Nutrition Board recommends for adults a daily iodine intake of 150 µg/day (DRI for Vitamin C…, 2000). In contrast, the German Nutrition Society recommends for adults a daily iodine intake of 200 µg/day (Reference Values for Nutrient Intake, 2002). The main sources of iodine in an average diet are marine fish, shellfish, milk, dairy products and salt fortified with iodine (Haldimann et. al., 2005). With a well balanced diet the nutritional requirements for iodine can be met, but some groups of people like vegetarians, sufferers from milk allergy, those with lactose intolerance, fish allergy or persons on a low salt diet can develop iodine deficiency. For these people food (dietary) supplements containing iodine are an important source of iodine in the daily diet (DRI, 2000; European Commission, 2002).

The term dietary supplement is used in the United States for a wider range of products. At the moment the term food supplement is used in the European Union for foodstuffs containing vitamins and minerals. The definitions are as follows:

a) Food supplements in the European Union are defined in Directive 2002/46/EC, which become law in August 2005, as foodstuffs meant to supplement the normal diet and which are concentrated sources of nutrients or other substances with a nutritional or physiological effect, alone or in combination (nutrients means vitamins and minerals) (Directive 2002/46/EC, 2002).
b) Dietary supplements in the United States are defined in the Dietary Supplement Health and Education Act (DSHEA) of 1994 as a product intended to supplement the diet and that contains a "dietary ingredient" (vitamins, minerals, herbs or other botanicals, amino acids, and substances such as enzymes, organ tissues, glands and metabolites) (DSHEA, 1994).

Dietary and food supplements may be found in forms such as tablets, capsules, pastilles, pills, soft gels, gelcaps, liquids or powders. They are sold in the United States and in the European Union with little or no regulation. In the European Union only herbal products in Germany are regulated by the same standards as drugs (Directive 2002/46/EC, 2002; DSHEA, 1994).

The Directive 2002/46/EC of the European Parliament and of the Council introduces rules for the labelling of food supplements and introduces specific rules for vitamins and minerals; medicinal products as defined by Directive are excluded (Directive 2001/83/EC, 2001). It prescribes which vitamins and minerals (Annex 1) and in which chemical form (Annex 2) may be used for the production of food supplements (positive lists). Trade in products containing vitamins and minerals not listed was prohibited from the 1st of August 2005. For example, iodine may be present in the form of sodium iodide/iodate or potassium iodide/iodate. (Directive 2002/46/EC, 2002).

Dietary and food supplements are not under strict regulations like drugs, which must be proven safe and effective before marketing and before they reach the costumer. The institutes responsible for food safety focus their resources first on products that may cause injury or illness, meaning that they do not monitor all dietary supplements. The information about a specific dietary supplement is provided on its label or declaration and the costumer has to trust the producer to whom control and quality assurance in the production of dietary supplements is left (DRI, 2000).

Food supplements contain a variety of different vitamins and minerals in different chemical forms, which can interact with each other and make the determination of an individual element (mineral) very difficult. For example, the presence of ascorbic acid (vitamin C), a reducing agent, can change the chemical form of the element selenium (Shaker, 1996).

From the point of view of human nutrition and metabolism the fact that some minerals decrease the absorption of others is important, because they compete for the same binding sites, and transport pathways in the cell. Iodine absorption is reduced by iron, calcium and magnesium. Iron may impair zinc absorption, which is needed especially by lactating women for milk production (Carolyn et. al., 2002; Ubom, 1991).

The aim of our work was to determine the content of iodine in some commercially available food supplements on the Slovene market and to find out whether consumers can trust the declared values on the label. To our knowledge there are no data concerning iodine in food supplements available in literature. Radiochemical neutron activation analysis (RNAA) was employed as a sensitive, accurate and reliable method.

2 MATERIALS AND METHODS

2.1 Samples

From each food supplement ten to twenty tablets/capsules were taken and ground in an agate mortar. Two to four aliquots of each homogenised sample of food supplement were taken to determine the content of iodine.

The samples investigated, bought on the Slovene market in period of two years (2003-2005), were as follows: ABC plus® (3 lots), Centrum from A to Zinc® (3 lots), Centrum Junior® (3 lots), Daily one caps®, Sport fuel with Iron®, Unicap M® (3 lots) and Unicap T® (3 lots). These so called multivitamin-mineral supplements contain different vitamins and minerals (Table 1) and are intended to provide balanced nutritional support for children, adults and sportsmen.

Table 1: Labelled content of each tablet/capsule of food supplement

Vitamin, mineral	Food supplements						
	A	B[1]	C	D	E	F[2]	G[3]
Vitamin A (µg)	1000	1200	375	800	800	3000	3750
Vitamin C (mg)	60	60	30	60	90	150	500
Vitamin D (µg)	10	10	3	5	5	10	5
Vitamin E (mg)	20	20	7.5	10	10	67	268
Vitamin K (µg)	-	25	10	-	-	-	-
Thiamin (mg)	1.5	1.5	0.7	1.4	2.1	25	25
Riboflavin (mg)	1.7	1.7	0.9	1.6	2.4	25	25
Niacin (mg)	20	20	11.5	18	27	100	75
Vitamin B6 (mg)	2	2	0.95	2	3	25	25
Folic Acid (µg)	-	400	125	200	200	400	200
Vitamin B12 (µg)	6	6	0.9	1	2	100	50
Biotin (µg)	30	30	50	-	-	300	150
Pantothenic Acid (mg)	10	10	3	6	9	50	125
Calcium (mg)	162	162	162	-	160	25	12.5
Iron (mg)	18	18	4.4	14	14	10	5
Phosphorus (mg)	109	125	125	-	-	-	-
Iodine (µg)	150	150	65	150	150	150	75
Magnesium (mg)	100	100	60	75	75	7.2	300
Zinc (mg)	15	15	4	15	15	15	15
Selenium (µg)	20	25	15	50	50	200	100
Copper (mg)	2	2	0.4	2	2	2	1
Manganese (mg)	2.5	2.5	0.5	2.5	2.5	5	2.5
Chromium (µg)	25	25	12.5	50	50	200	200
Molybdenum (µg)	25	25	12.5	-	-	150	75
Chloride (mg)	36.3	36.3	-	-	-	-	-
Potassium (mg)	40	40	-	-	-	5	50

Also incorporated:
[1] B, Ni, Si, Sn, V, Lutein and Lycopene
[2] Para-aminobenzoic Acid, Choline Bitartrate and Inositol
[3] Para-aminobenzoic Acid, Choline Bitartrate, Inositol, Co-Enzyme Q10, L-Glutathione, N-Acetyl-Cysteine, Alpha Lipoic Acid and L-Carnitine

2.2 Iodine determination method

In brief, samples were heat sealed in a plastic tube and irradiated simultaneously with an appropriate aliquot of standard iodine solution in a rabbit for approximately 20-30 seconds in the pneumatic system of our TRIGA Mark II Reactor at a neutron fluence of 4×10^{12} $n \cdot cm^{-2}$ s^{-1}. The irradiated samples were then combusted with iodine carrier in an oxygen atmosphere (4L Schöniger flask) containing a reducing acid solution (0.05 M H_2SO_4 and 10 % Na_2SO_3), followed by extraction and purification of iodine by a selective extraction-stripping-reextraction cycle via $NaNO_2/CHCl_3$ and Na_2SO_3. The purified organic solution of iodine in $CHCl_3$ was transferred to a 10 mL vial for gamma-ray measurement of the induced radionuclide $^{128}I(^{127}I(n,\gamma)^{128}I$; $t_{½}$ = 25 min, E_γ = 443 keV).

The chemical yield for each sample aliquot was determined spectrophotometrically at 517 nm with an MA 9525 – Spekol 210 spectrophotometer from the recovery of the added carier. The method for iodine determination by RNAA is described in more detail elsewhere (Dermelj et. al., 1990).

3 RESULTS AND DISCUSSION

The critical step in iodine determination is sample decomposition, because iodine is highly volatile and the reagents used should have a low blank and not cause interference with the measurement. Procedures such as dry (alkaline) ashing, wet ashing using oxidizing acids or acid mixtures and combustion with oxygen in closed systems are used. For measurement of iodine at μg/g levels ion selective electrodes, X-ray fluorescence, ion chromatography, cathodic stripping voltammetry, ICP-MS and radiochemical neutron activation analysis are suitable, but for its determination in foods only the high selectivity ICP-MS and RNAA have low enough detection limits (Knapp et al, 1998).

The main advantage of the RNAA method used is that the sample is not subjected to any chemical treatment before irradiation, so the possibility of sample contamination is minimal, i.e. virtually blank free. The method is not time consuming but costly and requires special equipment. During irradiation the iodine present in the sample (and standard) is activated via the (n, γ) nuclear reaction induced by thermal neutrons to ^{128}I, and then extracted from the combusted matrix during the radiochemical purification with chloroform via the redox reaction with $NaNO_2$ in H_2SO_4 medium. Stripping of elemental iodine from the organic phase with Na_2SO_3 followed to separate iodine from any traces of bromine and chlorine. The purified iodine was then re-extracted into chloroform. The separation step is performed after irradiation, meaning that there is no influence from the reagents used for the isolation of iodine on the activity of ^{128}I separated. The detection limit of the method is about 1 ng/g. There is no reference material with a similar matrix to food supplements on the market. So we tested the method with the reference material NIST 1549 Whole milk powder. Good agreement with the certified value was obtained (3.37 ± 0.12 μg/g, certified value 3.38 ± 0.02 μg/g).

The levels of iodine in seven investigated food supplements ranged from 21 to 231 μg per g and they were in most cases, with the exception of three (A, F and G), in agreement with the declaration made by the producer (Table 2). The levels of iodine were constantly lower for food supplement A found in period of two years. Two food supplements (A and G) were not in agreement with the recommendations made by U.S. Pharmacopoeia, that dietary supplements should contain not less then 90 % and not more then 200 % of the declared amounts of iodine (U.S. Pharmacopoeia, 2004). Variability between each batch of production was observed. A possible explanation for this difference could be, as already mentioned in the Introduction of the present work, the huge variety of different vitamins and minerals present in food supplements. Vitamins and minerals can interact with each other and thereby change their chemico–-physical properties, causing loss of some vitamins, and/or minerals by making them volatile (Table 2).

Table 2: Comparison of levels of iodine determined in food supplements and those declared by the label

Sample[a]	Iodine determined (µg/g)	Declared values of Iodine (µg/g)	Ratio "between determined and declared value" (%)	Range allowed according to U.S. Pharmacopoeia
A_1	62.90 ± 3.50		58	
A_2	77.74 ± 4.03	108	72	97 – 216
A_3	55.43 ± 2.34		51	
B_1	104.81 ± 7.82		101	
B_2	102.96 ± 5.16	104	99	94 – 208
B_3	112.50 ± 6.16		108	
C_1	28.20 ± 1.39		95	
C_2	37.00 ± 1.84	30	124	27 – 60
C_3	35.77 ± 2.40		120	
D_1	212.00 ± 11.00		92	
D_2	207.27 ± 11.22	232	89	208 – 463
D_3	227.64 ± 15.12		98	
E_1	126.71 ± 6.51		95	
E_2	123.14 ± 6.37	134	92	121 – 268
E_3	129.49 ± 7.53		97	
F	230.77 ± 12.02	155	149	140 – 310
G	21.13 ± 0.74		26	
	69.89 ± 2.60		85	
	14.65 ± 0.54	83	18	74 – 165
	56.96 ± 2.10		69	
	36.17 ± 1.20		44	

Results are given with measurement uncertainty (k=2.0)

a) Numbers represent different lots, letters represent different food supplements

Sample G caused problems. The scattering of results was very high. We made five determinations and the results are listed in Table 2. As shown, they range from 21 to 70 µg per g, and the iodine content is evidently non-homogeneous.

Amount of iodine consumed based on the determined and declared values is presented in Table 3. One can see that, with the exception of food supplement A and F, there is good agreement between the actual amount of iodine consumed and the declared values as labelled by the producer. This result is much better than in the case of study of the iodine content of infant formulae (Osterc et al., 2005) where infant starting, follow-on and special formulae were investigated. From the results obtained it was clear that only three from eighteen investigated infant formulas were in good agreement with the declared values.

The same food supplements were analysed by Stibilj et al. (2005) to investigate the declared value of selenium. They found that two of the nine food supplements do not comply with the U.S. Pharmacopoeia and also revealed variability between different lots of the same brand. Their findings for selenium are comparable to ours for iodine in the same food supplements.

Table 3: Comparison of iodine intakes from food supplements based on declared values and experimentally determined values

Sample[b]	**Iodine determined** (µg/ tablet, capsule)	**Recommended portion**	**Amount of iodine consumed based on declared value** (µg/day)	**Amount of iodine consumed based on determined value** (µg/day)
A_1	87.48 ± 4.87			90
A_2	108.11 ± 5.60	1 tablet/day	150	110
A_3	77.10 ± 3.25			80
B_1	150.83 ± 11.25			150
B_2	148.17 ± 7.43	1 tablet/day	150	150
B_3	161.89 ± 8.86			160
C_1	61.49 ± 3.03			60
C_2	80.69 ± 4.01	1 tablet/day	65	80
C_3	78.00 ± 5.23			80
D_1	137.27 ±7.12			140
D_2	134.21 ± 7.26	1 tablet/day	150	130
D_3	147.40 ± 9.79			150
E_1	141.83 ± 7.29			140
E_2	137.83 ± 7.13	1 tablet/day	150	140
E_3	144.94 ± 8.43			140
F	223.13 ± 11.62	1 tablet/day	150	220

Results are given with measurement uncertainty (k=2.0)

b) Numbers represent different lots, letters represent different food supplements

Rasmussen et al. (2002) investigated the effect of geography, supplements and food choice on iodine intake in a Danish population. They estimated the iodine intake by measuring the iodine excretion in urine samples. The iodine excretion was significantly higher in participants who took a daily dietary supplement with 150 μg of iodine in form of a multivitamin-mineral supplement and slightly higher in participants who consumed at least 200g of fish/week and 0.5 L of milk/day, but who did not get enough iodine. Rasmussen et al. concluded that the iodine deficiency problem could not be overcome by dietary changes [9].

Haldimann et al. (2005) investigated the iodine content of several kinds of foods representing different product groups available on the Swiss market. The samples included foods such as cereals, meat, dairy products, fruit and vegetables. They estimated per capita iodine intakes from the investigated foods using statistics on food consumption and the corresponding mean iodine concentrations. They found bread and milk to be significant daily sources of iodine in the Swiss diet, contributing 58 and 29 μg/day, respectively. The sum of the contributions of all basic food groups to the total dietary iodine intake for the average consumer was estimated to be approximately 140 μg/day, which is comparable to the food supplements investigated in this study.

4 CONCLUSIONS

The intake of iodine per day declared by the producer was not always in agreement with the actual contents of the supplements found experimentally. It would make sense to introduce controls in the field of food supplements so as to assure the safety and quality of these products.

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