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Elemental characterization of mineral supplements by neutron activation analysis

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Abstract Instrumental neutron activation analysis (INAA) was applied to assess element concentrations in eleven samples of mineral supplements/multivitamins acquired in drugstores and pharmacies in São Paulo city, SP, Brazil. Concentrations of Ca, Co, Cr, Cu, Fe, K, Na, Se and Zn were determined. A comparison was made between the results obtained with the labels of the mineral supplents. Certified reference materials, NIST SRM1400 Bone Ash and NIST SRM 1633b Coal Fly Ash were analyzed for quality control of the analytical results.

Keywords Mineral supplements · Neutron activation analysis · Trace elements · Multivitamins

Introduction

Over the last several years the use of dietary or mineral supplements has become very common to eliminate dietetic deficiencies, to improve nutrition, as well as, for fatigue prevention and for treatment of several diseases. Multivitamins containing mineral supplements are widely consumed mainly by elderly individuals [1, 2], lactating mothers [3], pregnant women [4] and athletes [5]. These products are acquired over-the-counter without medical prescriptions.

The control of element composition in these mineral supplements or multivitamins is of great interest due to increasingly higher consumption and a large diversity of minerals and brands offered in the market. Therefore, there is a necessity to evaluate their mineral composition and to compare with those values declared on the labels, as well as, to identify the presence of eventual toxic elements.

Several analytical techniques have been applied in the analysis of nutritional supplements such a, inductively coupled plasma mass spectrometry [6], X ray fluorescence spectrometry [7], flame atomic absorption spectrometry [8] and instrumental neutron activation analysis [9]. In this study, instrumental neutron activation analysis (INAA) was applied in the analysis of eleven samples of mineral supplements and multivitamins acquired in São Paulo city, Brazil.

Experimental

Mineral supplements and multivitamins and their preparation for analyses

The samples of mineral supplements and multivitamins were obtained from drugstores or pharmacies in São Paulo city, SP, Brazil. All of them were in solid forms in capsules, pills or tablets. Eight tablets/capsules of each sample were weighted to obtain the mean values of mass per tablet. For the analyses, the tablets or capsules were homogenized by grinding in an agate mortar and to obtain a powder form. Aliquots (500 mg) of each sample were dried at 85 °C for approximately 10 h to obtain dry mass. Table 1 presents the characteristics of the analyzed samples.

Preparation of the element standards

The synthetic standards were prepared by pippeting 50 or 100 μL of the elemental standard solutions onto sheets of

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Table 1 Mineral supplement and multivitamin sample characteristics

Sample code	Main label characteristics	MC-wet basis(g)	P, %
A	Multi-mineral with Ca, Cu, Fe and K	1.46 ± 0.02	1.50
B	Multi-mineral Ca base with Cu, Mg, Si and Zn	0.91 ± 0.02	7.85
C	Poly-vitamin and poly-mineral with Ca, Cr, Cu, Fe, Mg, Mn, P and Zn	0.619 ± 0.004	2.50
D	Poly-vitamin and poly-mineral with Ca, Cu, and Zn	1.43 ± 0.01	2.00
E	Multi mineral with Ca, Cu, I, Mn, Se and Zn	1.04 ± 0.05	2.90
F	Nutritional supplement for Se	1.71 ± 0.03	3.25
G	Nutritional supplement Ca base	1.77 ± 0.11	1.33
H	Poly-vitamin and poly-mineral with Ca, Cr, Cu, Fe, Mg, Mn, P and Zn	4.59 ± 0.03	4.77
I	Multi-mineral with Ca, K, Mg and Na	1.87 ± 0.01	2.40
J	Nutritional supplement for Zn	0.44 ± 0.01	6.30
K	Nutritional supplement for Zn	1.49 ± 0.08	1.91

MC mean mass of supplement of capsule, *P* moisture content in percent; $P = (\text{wet mass} - \text{dry mass}) \times 100/\text{dry mass}$

Whatman No. 40 filter paper. These solutions containing one or more elements were prepared using certified standard solutions provided by Spex Certiprep Chemical, USA. All the pippetors and volumetric flasks were calibrated before use. These filter sheets were dried at room temperature inside a desiccator with fresh silica and, then placed into clean polyethylene envelopes which were then heat-sealed. In these standards the quantities of each element, in μg (in parentheses) were: As (1.50), Br (5.2), Ca (1000), Cd (10.0), Co (0.150), Cr (2.0), Cu (100.0); Fe (280.0), K (1,000.0), Na (500.0), Sb (0.60), Sc (0.080) and Zn (35.0).

Neutron activation analysis procedure

Aliquots of about 180 mg of each sample weighed in polyethylene envelopes were irradiated in the IEA-R1 nuclear research reactor along with the synthetic element standards for 1 and 8 h at a thermal neutron flux of about 4×10^{12} n cm^{-2} s^{-1}. The irradiated samples and standards were measured by a High Purity Ge detector (HPGe) Model GX2020 coupled to a Model 1510 Integrated Signal Processor, both from Canberra. The resolution (FWHM) of the system was 0.90 keV for 122 keV gamma-ray peak of ^{57}Co and 1.78 keV for 1332 keV gamma ray of ^{60}Co. Each sample and standards were measured at least twice for different decay times. Counting times from 1,000 to 50,000 s were used, depending on the half-lives or activities of the radionuclides considered. The radionuclides were identified according to their half-lives and gamma-ray energies. The concentrations of elements were calculated by a comparative method. The radionuclides used in the analyses were: ^{76}As, ^{47}Ca, ^{115}Cd, ^{60}Co, ^{51}Cr, ^{64}Cu, ^{59}Fe, ^{42} K, ^{24}Na, ^{122}Sb,^{46}Sc, ^{75}Se and ^{65}Zn.

The quality of the analytical results was evaluated by analyzing the certified reference materials NIST SRM 1400 Bone Ash and NIST SRM 1633b Coal Fly Ash provided by the National Institute of Standards and Technology, USA. The element concentrations of reference materials were evaluated on a dry weight basis, as recommended in the

Table 2 Elemental concentrations obtained for NIST SRM 1633b coal fly ash and NIST SRM 1400 bone ash certified reference materials

Elements	Reference material	Mean ± S.D.	RSD[b], %	NIST values [10, 11]
As, mg kg^{-1}	Coal fly ash	137 ± 2	1.5	136.2 ± 2.6
Ca, %	Bone ash	38.7 ± 0.4	0.9	38.13 ± 0.13
Ca, %	Coal fly ash	1.5 ± 0.1	6.6	1.51 ± 0.06
Co, mg kg^{-1}	Coal fly ash	46 ± 4	8.7	(50)[a]
Cr, mg kg^{-1}	Coal fly ash	185 ± 15	8.1	198.2 ± 4.7
Fe, %	Coal fly ash	7.9 ± 0.4	5.0	7.8 ± 0.2
K, %	Coal fly ash	2.0 ± 0.1	5.0	1.95 ± 0.03
Na, %	Coal fly ash	0.21 ± 0.03	13.5	0.201 ± 0.003
Zn, mg kg^{-1}	Coal fly ash	187 ± 19	10.1	(210)
Zn, mg kg^{-1}	Bone ash	178 ± 2	1.1	181 ± 3

Mean ± SD = Arithmetic mean and standard deviation of at least 4 determinations; *RSD* relative standard deviation; [a]numbers in parenthesis are informative values

certificate. Moisture weight losses of 0.53 and 0.08% obtained, respectively, for NIST SRM 1400 Bone Ash and 1633b Coal Fly Ash were used to correct the final results.

Results and discussion

Data obtained in the analyses presented in Table 2 for the certified reference materials NIST SRM 1400 Bone Ash and NIST SRM 1633b Coal Fly Ash indicate good precision and good agreement with the certified values. Cooper was not detected in both certified reference materials (Cu detection limits obtained in these materials were lower than 188 μg g^{-1}). The relative standard deviations of the results were lower than 13.5% and relative errors varied from 0.6 to 6.6%. The standardized difference or Zscore values [12] obtained for most of the elements analyzed were $|Zscore| < 2$, indicating that our results are satisfactory and are within the ranges of certified data at the 95% confidence level.

The amounts of element present in each tablet of mineral supplements are presented in Tables 3 and 4. These quantities were calculated using element concentrations values obtained by INAA and the mass of each tablet.

Table 3 Element mass per capsule and product label values for nutritional supplements and multivitamins

Sample	Element	This study	Product label value
A	Ca, mg	167 ± 19	162
	Cr, μg	25 ± 3	25
	Cu, mg	1.9 ± 0.3	2
	Fe, mg	18 ± 5	18
	K, mg	44 ± 4	40
	Se, μg	25 ± 7	25
	Zn, mg	15.1 ± 2.5	15
B	Ca, mg	112 ± 26	125
	Cu, mg	0.23 ± 0.03	0.25
	Zn, mg	2.07 ± 0.06	2
C	Ca, mg	173 ± 15	165
	Cu, mg	3.39 ± 0.04	3.5
	Zn, mg	14.9 ± 0.3	15
D	Ca, mg	166 ± 16	162
	Cr, μg	25 ± 6	25
	Cu, mg	1.7 ± 0.4	2
	Fe, mg	15.7 ± 2.6	18
	K, mg	44 ± 7	40
	Se, μg	25 ± 1	25
	Zn, mg	13.6 ± 1.9	15

Results are given with uncertainties calculated using statistical counting errors of sample and standard and the standard deviation of tablet mean mass

Comparing the results of Tables 3 and 4 with those values indicated on the labels there was good agreement for most of the elements. Small differences occurred for Cu of sample D (Table 3) and for Cr and Fe in samples H and I, respectively (Table 4). Other elements than those printed on the labels were detected in the samples. The amounts of these elements in each tablet depended on the mineral supplement. The quantity in each tablet varied from 1.2 to 36 μg for Co, from 3.8 to 146 μg for Cr, from 0.15 to 14.9 mg for Fe, from 0.27 to 329 mg for Na and from 0.010 to 0.02 mg for Zn. Toxic elements such as As, Cd, and Sb were not detected in the supplements. Detection limit values obtained (in μg per tablet) were 40, 1.0 and 0.01 for As, Cd and Sb, respectively. High quantity of Na (329 mg) was found in each tablet of the sample coded H. if we compare it to the Adequate Intake value [13] of 1,500 mg per day for young healthy adults for this element.

In conclusion, the findings of this study suggest a careful evaluation of nutritional supplements presenting high levels of Na for hypertensive individuals. The study also showed that INAA can provide important information about the composition of minerals present in supplements and, this technique can be used as a control of mineral supplement composition. Besides, INAA presents advantages due to its simplicity and non-destructive character, and, mainly, to the possibility of simultaneous determination of several elements present in a large range of concentrations.

Table 4 Element mass per capsule and product label values for nutritional supplements and multivitamins

Sample	Element	This study	Product label values
E	Ca, mg	98 ± 7	100
	Cu, mg	2.01 ± .01	2
	Se, μg	229 ± 20	200
	Zn, mg	15.1 ± 0.2	15
F	Se, μg	51 ± 5	50
G	Ca, mg	609 ± 51	600
H	Ca, mg	48 ± 4	50
	Cr, μg	12 ± 2	10
	Cu, mg	<0.5	0.4
	Fe, mg	3.71 ± 0.09	3.6
	Zn, mg	2.9 ± 0.1	3
I	Ca, mg	51 ± 4	47
	Fe, mg	14.9 ± 0.6	18
	K, mg	5.9 ± 0.5	6
J	Zn, mg	51 ± 3	50
K	Zn, mg	21 ± 2	23

Results are given with uncertainties calculated using statistical counting errors of sample and standard and standard deviation of tablet mean mass

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