

ESSENTIAL TRACE ELEMENTS IN EDIBLE MUSHROOMS BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Mushrooms are excellent nutritional sources since they provide proteins, fibers and mineral, such as K, P, Fe. They have also been the focus of medical research. In Brazil mushrooms are not consumed in large quantities by the general population since people know little about the nutritional and medicinal benefits that mushrooms offer. Hence, this study intends to contribute to a better understanding of the essential element content in edible mushrooms, which are currently commercialized in São Paulo state. Br Fe, K, Na and Zn concentrations were determined by Instrumental Neutron Activation Analysis in the following mushroom species: Shitake (*Lentinus edodes*), Shimeji (*Pleurotus ssp*), Paris Champignon (*Agaricus bisporus*), Hiratake (*Pleurotus ssp*) and Eringue (*Pleurotus Eryngii*). The mushroom samples were acquired from commercial establishments in the city of São Paulo and directly from the producers. Essential element contents in mushrooms varied between Br 0.03 to 4.1 mg/kg; Fe 20 to 267 mg/kg; K 1.2 to 5.3 g/kg, Na 10 to 582 mg/kg and Zn 60 to 120 mg/kg. The results confirm that mushrooms can be considered a good source of K, Fe and Zn. The low Na level is a good nutritional benefit for the consumer.

INTRODUCTION

More than a million and a half species can be found in the higher fungi, which are either macro or microscopic and most are unknown to the science. Even though there is little known about fungi, it is acknowledged that a great part of them is very important to the human health, since they contribute to the biologic diversity of our planet [1].

About 10 thousand mushroom species are known, however only about 2000 are considered edible. Out of those 2000, about 20 are cultivated for trade, and less than 10 are industrialized. The nutritional value of mushroom is superior to several vegetables. Their protein content is higher than most vegetables, but differs according to the species. Age, cultivation location and the substrate influence the nutrient composition of mushrooms [2]. Due to its high nutritional value, mushroom cultivation has been a good alternative to supply protein to countries where the nutritional food value is very low. Mushrooms also furnish

vitamins and minerals. Due to low sodium concentration in mushrooms, they are a very good food source for special diets for people with hypertension [3-4].

According to Herrera [5], mushrooms also have an immunologic function, so they are of great interest to medicinal research as an antitumoral agent. The increased interest in mushrooms and their use in the diet are not only due to their medicinal and therapeutic properties, but also due to their taste, texture and low caloric value [6].

The first species which was cultivated for trade in Brazil was the “champignon de Paris” (*Agaricus bisporus*). Other species currently cultivated are the giant mushroom or Caetetuba (*Pleurotus ostreatus*) and the Shiitake (*Lentinula edodes*) [7].

Mushrooms are cultivated in substrates such as tree trunks, eucaliptus, wood logs, straw, sawdust, berry of cane, cobs, cotton seed and cocoa seed hulls or gypsum [8]. In this way, mushroom cultivation allows for the recycling of several agricultural and agroindustrial waste products [9].

In Brazil, the main region where edible mushrooms are cultivated is Mogi das Cruzes city, in the São Paulo state, which produces about seven kilograms of fresh mushrooms for each 100 grams of humid substrate [7].

The mushroom consumption in Brazil is still very low compared to other countries in Europe and Asia. However, mushroom consumption is increasing due to the intense advertising of its benefits and cost [9]. Besides their nutritional value mushrooms present medicinal proprieties in the prevention of some diseases, such as hypertension and cancer [1].

Although there are many studies in several countries [10-12] concerning edible mushrooms, in Brazil they are still very scarce. Therefore, more studies should be undertaken for understanding of mushrooms cultivated and consumed in the country.

The Ipen Neutron Activation Analysis Laboratory has applied the Instrumental Neutron Activation Analysis method (INAA) to verify the nutritional element concentrations in foods and diets [13-14]. In this study the concentration of the essential elements Br Fe, K, Na and Zn were determined by INAA in edible mushroom samples commercialized in the São Paulo State.

EXPERIMENTAL

1. Mushrooms Sampling and Preparation:

Edible mushrooms were acquired in retail stores and directly from producers of various cities of São Paulo state. Eight species fresh were collected: Shitake (*Lentinus edodes*), Shimeji escuro (*Pleurotus ostreatus*), Shimeji branco (*Pleurotus flórida*), Paris Champignon (*Agaricus bisporus*), Hiratake (*Pleurotus ssp*), Salmão Rosa (*Pleurotus salmoneostramineus*), Porto Bello (*Agaricus sp*) e Eringue (*Pleurotus Eryngii*). Only one sample (*A. bisporus*) was in conserve. About 400g were collected for each species.

The mushroom samples were washed with Milli Q H₂O and cut in small pieces with plastic knife and put in Petri plates or plastic recipients. The samples were then freeze-dried for 10 to 15 hours in the Thermo Electron Corporation (Modulyyo Model) freeze-dryer. After the

freeze-drying process, the samples were ground and homogenized in a domestic blender with Ti blades. These mushroom samples were stored in pre-cleaned polyethylene vials until analysis.

2. Preparation of Br, Fe, K, Na and Zn Standards

Standards of Br, Ca, Fe, Na and Zn were prepared from appropriate dilutions of their Spex solutions. Aliquots (50 – 100 µL) taken from such solutions were pipetted on the Whatman 40 filter paper and dried under infrared lamp. After drying, filter papers were transferred to clean polyethylene bags.

3. Sample and Standard Irradiations

About 150 to 200 mg of mushroom samples and 200 mg of reference materials were irradiated with element standards for 8 hours under thermal neutron flux of $4.5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ at the nuclear research reactor IEA-R1 of IPEN/CNEN-SP.

4. Gamma Spectrometry

After appropriate decay periods, γ -ray spectra of mushroom samples, reference material samples and element standards were measured with a Ge detector POP TOP model of EG&G ORTEC with 20% efficiency and 1.9 keV resolution for 1332.49 keV peak of ^{60}Co . The detector is coupled an electronic system composed of multi-channel analyzer, source of high tension, amplifier and a compatible microcomputer. The gamma-ray spectra were analyzed using the VISPECT 2 software.

RESULTS AND DISCUSSION

For the validation of the methodology two reference materials were analyzed: Mixed Polish Herbs INCT-MPH-2 and Tea Leaves INCT-TL-1 from the Polish Institute of Nuclear Chemistry and Technology. Table 1 shows the mean concentration and the z-score values obtained for Br, K, Na, Fe and Zn in these materials.

Based on the ISO/IUPAC [15] the z-score values were calculated. If $|z| < 2$, the value is satisfactory at the 95% of confidence level. The values obtained varied from -1.89 to 0.73, indicating that the results are in agreement with certified values.

Table 1- Essential element results in Certified Reference Materials in µg/kg

	INCT-MPH-2			INCT-TL-1		
	$x \pm s^a$	Certified Value	z- score	$x \pm s^a$	Certified Value	z- score
Br	8.08 ± 0.36	7.71 ± 0.61	0.61	12.2 ± 0.7	12.3 ± 1.0	-0.10
K	19187 ± 1834	19100 ± 120	0.73	16773 ± 405	17000 ± 120	-1.89
Fe	523 ± 7	(460)	-	499 ± 28	(432)	-
Zn	34.5 ± 0.8	33.5 ± 2.1	0.48	33.5 ± 1.8	34.7 ± 2.7	-0.44

a: Mean value \pm standard deviation of five determinations

Hence, the concentration of Br, K, Fe, Na and Zn were determined in twelve samples of eight mushroom species by Neutron Activation Analysis.

Table 2 shows mean results for the elements Br, K, Na, Fe and Zn obtained of triplicate determinations. All results presented are related to the dry mass of the samples.

Table 2– Element concentration in different samples of edible mushrooms (mg/kg dry weight.)

Mushrooms	City	Br	K	Na	Fe	Zn
<i>Lentinus edodes</i>	São Paulo	0.18 ± 0.02	17634 ± 336	74 ± 5	18 ± 2	85 ± 2
<i>Lentinus edodes</i>	Suzano	0.13 ± 0.01	14090 ± 3589	57 ± 4	21 ± 1	33 ± 2
<i>Lentinus edodes</i>	Mirandópolis	0.17 ± 0.01	14215 ± 1212	69 ± 10	22 ± 0.5	64 ± 2
<i>Lentinus edodes</i>	Juquitiba	0.18 ± 0.01	20674 ± 994	72 ± 8	22 ± 2	44 ± 4
<i>Pleurotus almoneostramineus</i>	São Paulo	1.80 ± 0.08	24054 ± 2261	17 ± 1	101 ± 2	119 ± 3
<i>Agaricus bisporus</i>	São Paulo	1.90 ± 0.06	21960 ± 377	2437 ± 35	101 ± 7	61 ± 4
<i>Agaricus bisporus in conserve</i>	São Paulo	0.92 ± 0.02	4631 ± 1032	5556 ± 520	130 ± 5	21 ± 2
<i>Pleurotus flórida</i>	São Paulo	0.31 ± 0.03	12343 ± 705	38 ± 1	93 ± 3	79 ± 5
<i>Pleurotus ostreatus</i>	São Paulo	0.50 ± 0.01	15117 ± 737	32 ± 2	76 ± 6	97 ± 8
<i>Agaricus sp</i>	São Paulo	2.7 ± 0.16	33857 ± 1499	311 ± 60	220 ± 7	63 ± 2
<i>Pleurotus Eryngii</i>	São Paulo	0.30 ± 0.02	20887 ± 321	132 ± 4	32 ± 0.3	78 ± 2
<i>Pleurotus ssp</i>	São Paulo	0.37 ± 0.05	17535 ± 1107	27 ± 1	122 ± 3	95 ± 5
Average		0,79	18083	735	80	70
Minimum		0,13	4631	17	18	21
Maximum value		2,7	33857	5556	220	119

Large variability can be observed among mushroom species in relation to their Br, K, Na, Fe and Zn content. However, the specimens of the same species (*L.edodes*) collected in different regions showed similar levels of the essential element. The difference is not greater than twofold for K and Na. For Br and Fe the levels are almost equal. The higher difference was obtained for Zn.

Bromine content of the mushrooms ranged from 0.13mg/kg dry weight in *Lentinus edodes* to 2.7 mg/Kg dry weight in *Agaricus sp*. There are no mushroom Br levels in mushroom data available in the literature.

The highest potassium concentration (33857 mg/kg) was found in the *Agaricus sp* (Porto Belo) and the lowest value was 4631 in *Agaricus* in conserve. Manzi [3] reported the K

content of 26475 mg/kg dry weight in *Lentinus edodes*. According to Sesli [16] K concentrations in mushroom have been reported to range between 10300 – 55100 mg/kg.

Sodium contents were higher in *Agaricus* varieties than *Lentinus edodes* and *Pleorutus* varieties, in accordance with Mattila [4]. The *Agaricus bisporus* species (cultivate champignon) had significantly higher sodium content (5556 mg/kg in conserve and 2437 mg/kg fresh) than those of edible mushroom analyzed. For other species Na level varied from 17 mg/kg in *P. almoneostramineus* to 74 mg/kg for *L. edodes*. In general, edible mushrooms have low and stable Na contents. Vetter [17] analyzed Na content in several common edible mushroom species and found that the average content varied between 0.1 to 0.4 mg/g, and seemed to be independent of habitat, nutrition type or taxonomic position. Similar behavior was found for the potassium that showed relative stability and low fluctuation within the species.

Low sodium concentration and the presence of a great amount of potassium suggest the use of mushrooms in an anti-hypertensive diet.

The average iron contents for the mushrooms ranged from 18 mg/kg in *L. edodes* to 220 mg/kg in *Agaricus sp.* These values are similar with those obtained by Mattila [4] that analyzed edible mushroom in Finland (from 28 to 54 mg/kg dry weight in *A.bisporus* and *P.ostreatus*, respectively). However, higher Fe levels have been reported in the other studies which ranged of 31.3-1190 mg/kg [18], 56.1- 7162 mg/kg [11] and 568-3904 mg/kg [19].

Zinc content was lowest 21 mg/kg in *A.bisporus*, whereas in *P.almoneostramineus* it was the highest (119 mg/kg). Zinc concentrations of mushroom samples have been reported in the literature in the range of 29.3-158 µg/g [11], 33.5 – 89.5 mg/kg [20] and 45.2 -174 mg/kg [21]. Zinc is known to be involved in most metabolic pathways in humans, and zinc deficiency can lead to loss of appetite, growth retardation, skin changes, and immunological abnormalities.

CONCLUSION

In general, large variability can be observed among mushroom species in relation to their Br, K, Na, Fe and Zn content. The edible mushrooms analyzed presented high K and Zn content, confirming that mushrooms can be considered a good source for these essential elements. The low Na level is a good nutritional benefit for the consumer

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