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ARTÍCULO ORIGINAL – ORIGINAL ARTICLE

Study of *Araucaria angustifolia* nuts by Gamma Spectrometry and X-Ray Fluorescence

Estudio de semillas de Araucaria angustifolia por Espectrometría Gamma y Fluorescencia de Rayos X

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Abstract: The seed of *Araucaria angustifolia* is largely produced and consumed in Parana state, Brazil. It has an estimated annual consumption of approximately 0.167 kg per capita. The samples of seeds were acquired in 8 different commercial points of Londrina city in the state of Paraná, Brazil. To determine the natural level of radiation and elemental composition were analysed the seed pulp and peels, to determine the level of radiation in these samples and to calculate the effective dose per intake, the gamma ray spectrometry was applied using the HPGe detector with a 60% relative efficiency, and the X-rays Fluorescent by Dispersive Energy (EDXRF) was applied for elemental identification of the composition with a spectrometer from Shimadzu EDX-720 model. The samples were qualitatively analyzed by EDXRF, where the elements K, Fe, Cu, Zn, Rb, Ca, P, Mg and Sr were found in pulp and peels of seed, however, the elements Mg and Sr were detected only in the peel samples. The results obtained by gamma spectrometry showed that the radioactive activities in the *Araucaria angustifolia* pulp per kilogram in nature, for 226Ra ranged from 0.691 to 2.269 Bq/kg, the interval activity measured for the 228Ra were 0.386 to 1.767 Bq/kg and the 40K were 283.405 to 1,536.820 Bq/kg. Activities of 137Cs were detected in the pulp and peels of seed. The average dose per intake was 0.68 μSv/year for 226Ra and 0.35 μSv/year for 228Ra.

Keywords: Araucaria angustifolia, EDXRF, dose, radiation.

Resumen: La semilla de Araucaria angustifolia es producida y consumida en gran medida en el estado de Paraná, Brasil. Tiene un consumo anual estimado aproximado de 0.167 kg per cápita. Las muestras de semillas fueron adquiridas en 8 puntos comerciales diferentes de la ciudad de Londrina en el

estado de Paraná, Brasil. Para determinar el nivel de radiación natural y la composición elemental, se analizaron la pulpa y las cáscaras de las semillas, para determinar el nivel de radiación y dosis efectiva por ingesta, se aplicó la espectrometría de rayos gamma utilizando el detector HPGe con un 60% eficiencia relativa, se utilizó fluorescencia de rayos X por energía dispersiva (EDXRF) para la identificación elemental de la composición con un espectrómetro fabricado por Shimadzu modelo EDX-720. Las muestras fueron analizadas cualitativamente por EDXRF, donde los elementos K, Fe, Cu, Zn, Rb, Ca, P, Mg y Sr se encontraron en la pulpa y cascara de las semillas, sin embargo, los elementos Mg y Sr se detectaron solo en las cascaras de la semilla. Los resultados obtenidos por espectrometría gamma muestran que las pulpas de *Araucaria angustifolia* in natura por kg, poseen actividades de 226Ra en el rango fue 0.69 a 2.26 Bq/kg, para el 228Ra el rango fue de 0.38 a 1.76 Bq/kg, para el 40K el rango de actividad fue de 283.40 a 1,536.82 Bq/kg. Se detectaron actividades de 137Cs en la pulpa y las cáscaras de semillas. La dosis promedio por ingesta fue de 0,68 μSv/año para el 226Ra y 0.35 μSv/año para el 228Ra.

Palabras clave: Araucaria angustifolia, EDXRF, dosis, radiación.

1. INTRODUCTION

Radioactivity is present in all moments of our daily life. The radiation that exists in nature without human intervention is called natural radioactivity and it is present in the ground, in the air, etc. The radioactivity generated by human intervention is called artificial radioactivity (1–5). Its applications have increased in the last few years. Therefore, it is necessary a periodical environmental control to monitor human activities such as the analysis of different types of food in order to guarantee their quality (6–13).

The pulp of the araucaria's seed is suitable for human consumption, it can be ingested naturally, roasted or boiled, the peel is used in medical infusions for the treatment of muscle tension of varicose vein. In addition, the araucaria's resin is used for the treatment of respiratory infections and the leaves to treat scrofula, fatigue, and anemia (14–19). The commercialized volume of Araucaria nuts reached over 10 thousand tons of Araucaria nuts from August 1994 to June 2002 by the Parana City Supply Centers (CEASA, in Portuguese) from Curitiba, Maringá, Londrina, Foz do Iguaçu and Cascavel, which corresponds to an approximated average of 1300 ton per year (20).

The research often focuses on the nutritional content, chemistry characterization and some physicochemical properties of the Araucaria nuts (6, 7). However, due to its wide distribution and high amount of consumption,

there is a concerning risk of exposure to natural radioactivity from the Araucaria nuts. This study aims to determine the activity of ^{232}Th, ^{238}U, ^{40}K, and ^{137}Cs and to perform a multi-element analysis of the seed of Parana pine tree (*Araucaria Angustifolia)*, commonly known as Pinhão (Araucaria nut) (15, 21).

2. MATERIALS AND METHODS

2.1. Preparation of samples

The samples were acquired in the city of Londrina (Parana, Brazil) between May and July of 2014. Among 8 batches were bought in different commercial centers and informal stores found around the city. During the purchase of Araucaria nuts, their origin and time of harvest were consulted, however, some traders could not specify this information.

The Araucaria nuts were roasted on a hot plate between 100°C and 150°C, simulating cooking procedures for human consumption. Later, their pulp and peel were separated, grounded manually in a mortar and stored in neutral plastic containers of 300mL of volume. At the end, 16 containers were used for the seed's pulp and 8 containers for the seed's peel which were sealed for 40 days in order to achieve the secular balance for the upcoming analysis.

For the X-ray fluorescence analysis, the pulp was dehydrated, sieved and pressed into tablets to achieve homogeneous samples. A binding agent (0.250 g of boric acid - H3BO3) was used for every 1000 g of seed powder. Two 2.5 mm thick tablets were prepared for each batch by applying 9 tons of uniaxial pressure over the mix for 2 minutes. In addition, the powder samples were also measured for elementary identification of the composition, putting 1 gram of Araucaria pulp powder and the peels over a chemplex (samples holder).

2.2. Gamma-ray spectrometry

A high-resolution gamma-ray spectrometer system setup was a HPGe (hyper-pure germanium) detector, manufactured by CANBERRA (model GC6020) with a relative efficiency of 60% and the shield elaborated by ORTEC model HPLBS1 designed for environmental applications. This setup was used to measure the radionuclides of interest.

All spectra were collected during a 24-hour period, preceded by the acquisition of the background spectrum produced by natural radiation for the calculation of the activity and committed effective doses.

2.2. Energy dispersive X-ray fluorescence spectrometry (EDXRF)

A commercial equipment of X-ray fluorescence by dispersive energy (EDXRF) manufactured by Shimadzu (model EDX-720) with an Rh target (X-rays source) was used for the qualitative elemental analysis of the Araucaria nuts. A solid-state detector was used with the following experimental set up parameters: 10 mm collimator, 100 s of measurement time, 50 kV of voltage and 487 – 604 μA of current.

EDXRF analysis was performed for the elemental identification of the composition of the araucaria seeds and control of contamination with heavy metals. Because of the lack of certified material, it was not possible to quantify elements.

2.3. Estimation of the consumption per capita

Information and analysis about Araucaria nuts consumption per capita was not found in the literature. Due to this fact, the value was estimated through the quantity of Araucaria nuts commercialized among the different supply centers from Parana State and the Brazilian Institute of Geography and Statistics (IGBE, in Portuguese) shown in Table 1.

Table 1: Commercialized Araucaria nuts among the different supply centers of Parana State (22).

District or city	Quantity (ton)	Population	Consumption per capita
Curitiba	511.04	1751907	0.292
Cascavel	106.1	286205	0.371
Foz do Iguaçu	30.25	256088	0.118
Londrina	14.68	357077	0.041
Maringá	14.68	357077	0.012
		Average	**0.167**

The official figures might contain considerable discrepancy because of the informal or clandestine sales in rural areas, and because not all the Araucaria nuts sold, is consumed (23).

3. RESULTS AND DISCUSSIONS

3.1. Quantitative results

Figure 1 presents gamma spectrum pulps of araucaria, obtained with a 24 hours measure time. Peaks of interest from radionuclides are indicated. Because it is the most abundant in nature, the peak belonging ^{40}K is the most intense in comparations with others peaks.

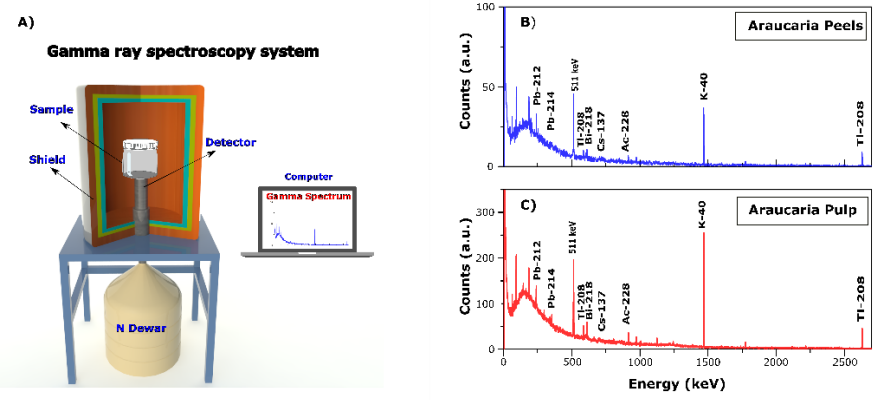

Figure 1: A) Gamma acquisition system scheme and typical spectrum of araucaria B) peels and C) pulp.

Using the spectra obtained in gamma spectrometry, the Bq / kg activities of ^{226}Ra, ^{228}Ra, ^{40}K, and ^{137}Cs in the araucaria seed and bark samples were calculated.

Due to the different ways of consumption of Araucaria seeds the activities are calculated per kg in nature.

The radioactivity of the desired radionuclides for each sample is presented in Table 2. This table organizes the average activity of ^{226}Ra, ^{228}Ra, ^{40}K, and ^{137}Cs from 16 pulp samples and 8 Araucaria nuts samples *in nature* per kilogram.

Table 2: The average activity of ^{226}Ra, ^{228}Ra, ^{40}K, and ^{137}Cs per kilogram for pulp and peel of Araucaria nuts *in nature*.

Powdered Samples	Average activity (Bq/kg)			
	^{226}Ra	^{228}Ra	^{40}K	^{137}Cs
Pulp	0.93 ± 0.05	0.62 ± 0.02	498 ± 1	0.65 ± 0.04
Peel	5.8 ± 0.4	3.9 ± 0.2	730 ± 6	2.4 ± 0.4

The radionuclides analyzed presented higher levels of activity in the Araucaria nuts peel. In all 8 batches of pulp of Araucaria nuts purchased, the presence of ^{137}Cs was registered, but just in the batch number 6 was registered the presence of ^{137}Cs in the peel.

In Figure 2 it is observed that all batches shown an activity of ^{137}Cs and ^{228}Ra, but the activity of ^{226}Ra is similar in all samples. The ^{137}Cs is absorbed by the tree roots due to similar properties that own the K (24–26), the activities of ^{37}Cs in all samples are below the concentration level of 600 Bq/kg for the sum of activities of ^{134}Cs and ^{137}Cs respectively.

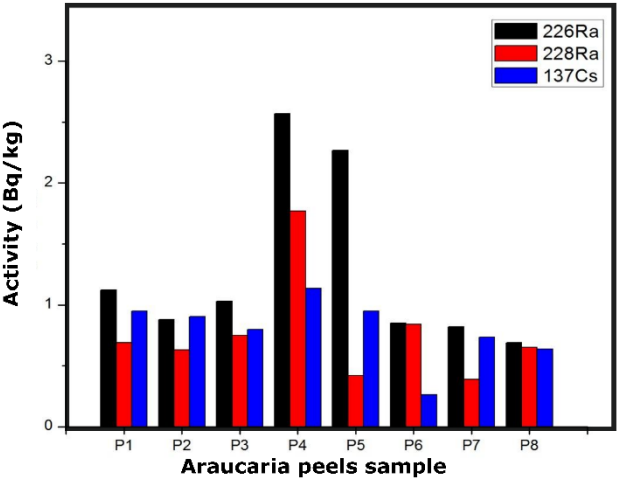

Figure 2. The activity of ^{226}Ra, ^{228}Ra, ^{40}K, and ^{137}Cs for each batch of pulp of Araucaria nuts per kilogram *in nature*.

Has been calculated the effective dosage committed by ingestion *(DEC)* with the average of ^{226}Ra and ^{228}Ra and average Commercialized Araucaria nuts

among the different supply centers of Parana of araucaria nuts. Using the following expression for the calculated *(DEC)* (27–29).

$$Dec=e(g)A.C \quad [1]$$

Where *C* is the consumption per capita in *Kg/years, A* is the activity of radionuclide *Bq/kg* and *e(g)* Is the effective dose compromised per unit in *Sv/Bq.*

The Table 3 shows the effective dosage committed by ingestion (*Dec*) with the UNSEAR reference value.

Table 3: Effective dosage committed by ingestion (DEC) calculated with the average of ^{226}Ra and ^{228}Ra.

Age (years)	***Committed effective doses (µSv/year)***					
	Araucaria nuts consumption			**Reference values [UNSCEAR]**		
	^{226}Ra	**^{228}Ra**	**Sum**	**^{226}Ra**	**^{228}Ra**	**Sum**
2 a 7	0.96	0.58	1.54	7.5	31	38.5
7 a 12	0.8	0.39	119	12.0	40.0	52.0
>17	0.28	0.07	0.35	6.3	11	17.3
Average	0.68	0.35	1.03	8.1	21	29.1

According to the average values of effective doses per radionuclide, it was verified that the ^{228}Ra present on the effective committed dose of 0.35 *µSv/year*, which is two orders of magnitude lower than the reference values of UNSCEAR, 21 µSv/year. For ^{226}Ra, the average effective dose weighted was 0.68 *µSv/year*, approximately 13 times lower than the one of reference of 8.1 µSv/year. The differences obtained for the doses and the reference values are expected since the calculations in the current research refer only to the dose of the Araucaria nuts consumption, while the reference values contain other daily diet food.

Furthermore, the *DEC* for ^{40}K was not calculated since the dose of this radionuclide is controlled by the organism through homeostatic control. The annual equivalent doses for tissues from ^{40}K are 165 and 185 µSv/year for adults and children, respectively. The effective dose is 170 µSv (29, 30).

3.2. Qualitative results by EDXRF

Figure 3 shows typical spectra of X Ray Fluorescence spectra on the Araucaria pulp and shield powdered. In all the pulp powder samples was detected the presence of P, S, K, Ca, Fe, Rb, Zn and Cu. However, in the pulp tablets, the frequency of Zn and Cu detection was lower than the frequency in the pulp.

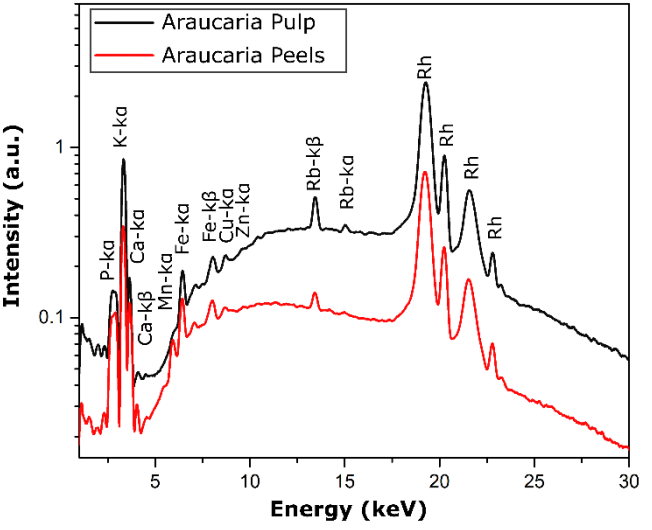

Figure 3: Araucaria shield and pulp powders X-ray fluorescence spectra.

In the Table 3 shows element intensity of major elements present in the araucaria measurements with X-ray fluorescence and standard deviation in the Araucaria nuts powdered tablet, pulp and peel. No significant difference between powder and tablet peaks intensity was observed, except for the increased presence of Zn in the powdered pulp.

Table 3: Major elements intensity detected in Araucaria nuts powdered pulp, tablet, and peel.

	Intensity		
Element	**Peel**	**Pulp Powder Tablet**	**Pulp powder**
K	1.865±0.081	3.417±0.635	3529±0.626
S	0.039±0.001	0.073±0.003	0.074±0.003
Fe	0.879±0.014	0.83±0.054	0.43±0.02
Cu	0.612±0.014	0.663±0.024	0.707±0.019
P	0.27±0.011	0.051±0.005	0.0495±0.005
Ca	0.34±0.014	-	-
Mn	0.29±0.013	-	-
Rb	-	3.940±0.106	3.714±0.061
Zn	-	-	0.587±0.014

In all the pulp powder samples was detected the presence of P, S, K, Ca, Fe, Rb, Zn and Cu. However, in the pulp tablets, the frequency of Zn and Cu detection was lower than the frequency in the pulp.

P, K, Rb, Fe, S, Ca, Cu and Zn were detected both in the pulp and the peels. Sr and Mn were observed only in the peels. No trace of Sr was detected in the pulp and the peel is consumed as a medicinal tea. As the Sr is not soluble in water and as the consumption is not frequent, this practice does not generate a risk.

The Cu is a transition non-ferrous metal abundant on earth, however, our interaction with this element is not daily. It is present in almost all types of food and in the air. Considered a micronutrient, Cu is only dangerous at high concentration and long periods of exposition, in which cases, it can cause damage to the liver and the kidney. It was not yet confirmed if Cu is a carcinogenic element (31, 32).

4. CONCLUSIONS

Araucaria nuts are not consumed in high amounts by the population, they are a typical food but not popular in Brazil.

The values of Dec calculated by gamma spectrometry show that the consumption of araucaria nuts are in acceptable values of ^{226}Ra and ^{228}Ra, in addition to verifying that the levels of activity of ^{137}Cs and ^{46}K are in the range accepted by UNSCEAR(33).

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