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TRACE ELEMENTS DETECTION IN WHOLE FOOD SAMPLES BY NEUTRON ACTIVATION ANALYSIS, k_0-METHOD

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ABSTRACT

Inorganic elements, from natural and anthropogenic sources are present in foods in different concentrations. With the increase in anthropogenic activities, there was also a considerable increase in the emission of these elements in the environment, leading to the need of monitoring the elemental composition of foods available for consumption. Numerous techniques have been used to detect inorganic elements in biological and environmental matrices, always aiming at reaching lower detection limits in order to evaluate the trace element content in the sample. Neutron activation analysis (INAA), applying the k_0-method, produces accurate and precise results without the need of chemical preparation of the samples – that could cause their contamination. This study evaluated the presence of inorganic elements in whole foods samples, mainly elements on trace levels. For this purpose, seven samples of different types of whole foods were irradiated in the TRIGA MARK I IPR-R1 research reactor – located at CDTN/CNEN, in Belo Horizonte, MG. It was possible to detect twenty two elements above the limit of detection in, at least, one of the samples analyzed. This study reaffirms the INAA, k_0–method, as a safe and efficient technique for detecting trace elements in food samples**.**

1. INTRODUCTION

Several studies have been conducted in recent decades about the determination of trace elements in biological samples. Due to the increase of environmental pollution, other researches have also been developed about the impact that the exposure to those trace elements can cause to human and animal health [1, 2]. Chemical elements present in the environment come from many different natural and anthropogenic sources [2, 3]. Some of them are essential to the growth and development of plants, animals and people, however, others that can cause damage to human health and also to the ecosystem due to their potential toxicity, tendency to bioaccumulation and long residence in the environment [2,3,4]. In recent years, emissions of metals from anthropogenic sources have reached values several times higher than natural emissions, characterizing a potential threat to the health of living beings and the environment [2, 3]. These elements accumulate in the atmosphere, soil, crops and

reservoirs near urban areas and can reach the human body, mainly by inhalation and ingestion of water and food [2].

Activities such as mining, metallurgy and the indiscriminate use of fertilizers and pesticides have resulted today in increased concentrations of potentially toxic elements such as cadmium, mercury, arsenic and lead in the environment. When exposed to the weathering and microbiological activity of the soil, the movement of these elements is facilitated, being able to reach areas more distant from the place of origin. As a result, urban areas and planting of food are affected and, if ingested or inhaled in large concentrations, such elements can cause neurological diseases, encephalopathies, renal and hepatic damage, abdominal pain, cardiovascular and gastrointestinal symptoms, as well as different types of cancer [5].

Under the nutritional point of view, food monitoring is concerned to calorie counting in proteins, carbohydrates and fats, instead of taking care about the ingestion of essential and nonessential elements - which are extremely relevant to the metabolic functions of living beings in general [6]. Thus, foods composition databases, although very useful in assessing the quality of nutritional intake of individuals and populations, are usually quite deficient in relation to components such as bioactive compounds, contaminants and trace elements [7]. When it is carried out, the monitoring of chemical elements occurs almost exclusively in a way restricted to those essential elements [6], which causes a false impression that the food consists only of nutrients beneficial to health.

In general, food is exposed to an environment composed by elements known as beneficial, toxic, or even with unknown effects, which makes research focused on essential elements as well as insufficient. The improvement of analytical methods has made the detection of metals and other chemical elements relatively simple to perform, with high sensitivity and precision [6]. Nowadays, numerous techniques are used to detect the presence of inorganic elements in biological and environmental matrices, aiming at reaching lower detection limits, in order to evaluate elements contained in very small concentrations. They are well established, such as inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled atomic emission spectroscopy (ICP-AES), inductively coupled mass spectrometry (ICP-MS), fluorescence spectrometry (XRF), neutron activation analysis (NAA), among others considered efficient and with low detection limits [17].

Neutron activation analysis (NAA) stands out among other similar techniques in terms of its relative simplicity and high sensitivity when analysing this kind of sample [1]. Neutron activation analysis can bring even more accuracy and safety of the results, at the moment that the chemical preparation of the sample is dispensed, avoiding thus its contamination. The choice of NAA for the determination of the elemental composition of food samples was based on the fact that it is a non-destructive, multielementar technique with high accuracy and precision [8, 9, 10, 11].

In this study, samples of cereals and whole grains were analysed. This is the kind of food whose nutritional importance has been greatly enhanced. Currently, there is a consensus regarding the benefits of replacing refined foods with whole grains, opinion of health professionals. They justify this mainly due to the presence of dietary fibers, which act in the prevention and treatment of several pathologies [12,13,14,15]. The aim of this study is to show that there are more chemical elements in the composition of this food than those reported in labels and tables about food composition. Other objective is to demonstrate the

effectiveness of the NAA technique for the evaluation of the elemental composition of biological samples, even in the presence of elements at the trace level.

2. MATERIALS AND METHOD

2.1. Samples

The foods selected for this study were: brown rice, flaked oats and wheat grains, as they are among the main existing whole grains [14], as well as chia, golden and brown linseed and quinoa, since they are quite consumed whole products currently. All products were randomly purchased from supermarkets / markets in the city of Belo Horizonte.

2.1.1. Sample preparation

Each of the foods selected for analysis was identified, weighed in analytical balance with calibration certified and conditioned in polyethylene vials containing approximately 1g of product. The samples were stacked in other polyethylene sample holders, intercalated by neutron flux monitors, Al-Au (0.1%) alloy disks, 6 mm diameter and 0.1 mm thickness.

2.2 Irradiation

The irradiation of 8 hours was carried out in the TRIGA MARK I IPR-R1 nuclear research reactor, located at Centro de Desenvolvimento da Tecnologia Nuclear (CDTN/CNEN), 100 kW, in the irradiation channels in the carrousel - IC-6, IC-7 and IC-8 - with thermal neutron flux of 6.35 x 10^{11} neutrons cm^{-2} s^{-1}, and spectral parameters f equal to 22.32 and α, – 0.0022 [16, 17, 18].

2.3 Gamma Spectrometry

After a suitable decay time - one day to one week for the determination of elements with half-lives between 12 and 72 hours -and twenty days for the determination of radionuclides of long half-lives. The gamma spectrometry was performed on an HPGe detector with 50% nominal efficiency and associated electronic. For the acquisition of gamma spectra, the Genie 2k program, CANBERRA, was used. The spectra were evaluated using the HyperLab program [19, 20].

2.4 Calculation of Elemental Concentration

The calculation of elemental concentration was performed using the Kayzero for Windows program [21], version 2.46, specific for k_0 method.

2.5 Quality Control

The quality control was performed using certified reference material. To verify the performance of the k_0-method, the statistical test E_n-number [22] was applied. The E_n-number was calculated to measure the agreement between the experimental result and the assigned

value, taking into account the expanded uncertainty (k = 2) of both values. To compare the results, the criterion $|E_n| \leq 1$ was applied, meaning that the evaluation of the performance of the method was satisfactory and if $|E_n| > 1$, the performance was unsatisfactory.

E_n-number:

$$E_n = \frac{Value_{Experiment\ al} - Value_{Assigned}}{\sqrt{U^2_{LabExpand} + U^2_{Assigned}}} \quad (1)$$

where$U_{LabExpand}$ and $U_{Assigned}$ are the expanded uncertainties (k = 2) of the experimental result and the assigned result, respectively, and

$$U_{LabExpand} = 2 \cdot U_{Experiment\ al} \quad (2)$$

$$U_{Assigned} = 2 \cdot St.Dev._{Assigned} \quad (3)$$

3. RESULTS AND DISCUSSION

Table 1 shows the results for reference material GBW0805, Tea leaves [23], used as reference material due to inexistence of reference materials similar to the foods used in this study. Table 2 displays the values for elemental concentrations in whole foods samples.

Table 1: Results for GBW 0805, Tea Leaves

Elements	GBW 0805 (mg kg^{-1})		
	Experimental Values (mg kg^{-1})	Certified Values (mg kg^{-1})	E_n-number k=2
As	0.20 ± 0.01	0.191 ± 0.025	+0.33
Ba	14.0 ± 0.7	15.7 ± 2.4	–0.61
Br	2.06 ± 0.05	2*	-
Ca	3088 ± 184	2840 ± 227	+0.57
Ce	0.76 ± 0.03	0.686 ± 0.096	+0.69
Co	0.22 ± 0.01	0.2*	-
Cr	0.98 ± 0.03	0.8*	-
Cs	0.147 ± 0.004	0.13*	-
Fe	390 ± 10	373 ± 63	+0.26
K	21010 ± 537	19700 ± 1379	+0.75
La	0.44 ± 0.01	0.458 ± 0.023	–0.56
Na	157 ± 4	142 ± 14	+0.94
Rb	39 ± 1	36.9 ± 1.5	+0.70
Sb	0.041 ± 0.001	0.037 ± 0.003	+0.98
Sc	0.121 ± 0.003	0.1*	-

*, Informative values

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Table 2: Inorganic elements in whole food samples (mg.kg^{-1})

Element	Brown rice	Oats	Wheat grain	Chia	Golden linseed	Brown linseed	Quinoa
As	0.13 ± 0.01	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
Au	0.0004 ± 0.0001	<0.0003	0.00039±0.00005	<0.0003	<0.0003	<0.0003	<0.0003
Ba	< 4	5 ± 1	5 ± 1	40 ± 2	6 ± 1	< 4	< 4
Br	0.79 ± 0.03	1.14 ± 0.04	0.68 ± 0.02	1.9 ± 0.1	2.4 ± 0.1	2.4 ± 0.1	2.0 ± 0.1
Ca	< 200	372 ± 85	208 ± 52	6778 ± 306	3388 ± 209	2044 ± 133	594 ± 69
Ce	< 0.2	< 0.2	0.3 ± 0.1	< 0.2	< 0.2	< 0.2	< 0.2
Co	0.15 ± 0.01	0.023 ± 0.002	0.015 ± 0.001	0.65 ± 0.02	0.95 ± 0.03	0.38 ± 0.02	0.09 ± 0.01
Cs	0.064 ± 0.003	0.055 ± 0.003	0.033 ± 0.002	0.025 ± 0.002	< 0.01	0.008 ± 0.001	0.051 ± 0.004
Cu	< 0.6	< 0.6	< 0.6	21 ± 3	< 0.6	< 0.6	< 0.6
Fe	< 6	42 ± 4	40 ± 2	81 ± 3	60 ± 3	53 ± 3	44 ± 3
K	1961 ± 69	3551 ± 125	4153 ± 146	7707 ± 273	7174 ± 252	7796 ± 276	6591 ± 232
La	< 0.02	< 0.02	<0.02	0.033 ± 0.002	< 0.02	< 0.02	< 0.02
Mn	53 ± 2	51 ± 2	47 ± 2	63 ± 2	< 10	< 10	26 ± 1
Mo	< 0.2	1.3 ± 0.1	0.4 ± 0.2	< 0.2	< 0.2	< 0.2	0.24 ± 0.05
Na	111 ± 4	7.3 ± 0.3	7.4 ± 0.3	1.5 ± 0.1	621 ± 22	516 ± 18	61 ± 2
Rb	10.5 ± 0.4	6.0 ± 0.2	3.3 ± 0.1	9.3 ± 0.4	10.6 ± 0.4	13 ± 1	9.6 ± 0.4
Sb	< 0.005	0.13 ± 0.01	0.013 ± 0.001	0.008 ± 0.002	< 0.005	< 0.005	< 0.005
Sc	<0.0006	<0.0006	0.0041 ± 0.0003	0.0026 ± 0.0003	<0.0006	0.0008 ± 0.0001	0.0013±0.0002
Sm	<0.004	<0.004	<0.004	0.006 ± 0.001	<0.004	<0.004	<0.004
Sr	28 ± 3	< 5	< 5	53 ± 2	18 ± 1	8 ± 1	< 5
Ta	< 0.005	< 0.005	< 0.005	< 0.005	0.008 ± 0.002	< 0.005	< 0.005
Zn	18 ± 1	32 ± 1	33 ± 1	54 ± 2	44 ± 2	37 ± 1	27 ± 1

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According to Mahan *et al*., 2012 [24], the whole foods are sources of Cr, Cu, Fe, K, Mg, Mn, Mo, P, Se, and Zn. The element P was not determined due to its nuclear characteristics that are unfavorable to be analyzed by this technique. The others were successfully analyzed in the samples and some of them were assayed in high concentrations. On the other hand, it was also observed that among the evaluated elements, only nine are known to be essential to health according to literature - sodium, potassium, calcium, iron, zinc, copper, molybdenum, manganese and cobalt [6, 24]. The remaining elements (approximately 64% of the evaluated elements), even present, are neither in the tables for food composition and not in their labels. Information about the presence, concentration and origin of various components of the foods consumed is unknown by the population.

Despite several techniques are available for the detection of numerous chemical elements in biological samples, such elements remain unreported or not informed to the consumer, causing the false impression that they are not present in the foods consumed. To illustrate this fact, Table 2 presents a comparison between the elements present in brown rice, according to the results of k_0, with the Taco - main Brazilian table of foods composition [25] - and with the product label. For the construction of the table, only those elements whose values were above the limit of detection were used.

Table 3: Experimental values and available information on brown rice in Taco (Brazilian Table for Food Composition)

El.	**Brown rice**		
	Average of elements / Consumption portion of the label *(1/4 cup) (mg/50g)*		
	Experimental Values	Taco [25]	Label
As	0.007	NR	NR
Au	0.00002	NR	NR
Br	0.04	NR	NR
Co	0.008	NR	NR
Cs	0.003	NR	NR
K	98	87	NR
Mn	3	1.5	NR
Na	6	1	0
Rb	0.5	NR	NR
Sr	1	NR	NR
Zn	1	1	NR

El, Element; NR, Not Reported

As it can be seen in the table above, labels and databases on foods composition, although they are very useful in clinical practice, do not exactly match the actual composition of the food consumed. It is the duty of the inspection agencies and researchers in the field, to monitor variations in the elemental composition of foods and to alert to any type of nonconformity in order to maintain the guarantee of food safety. Even though little is known about non-essential elements, it is known that some have the capacity to accumulate in the human body over time, which can generate toxic effects to the body [6]. As an example, the presence of the arsenic element in rice is already evident in the table, which is already a widely publicized issue [26, 27], and becomes an even bigger problem as foods consumption has

increased considerably replacing wheat since the recent condemnation of one of its main nutrients - gluten - by some researchers and practitioners in the area.

4. CONCLUSIONS

Despite the remarkable advances in analytical techniques for determining elements in biological matrices and also in the databases on foods composition, it is observed that the available information on the elemental composition of foods is still insufficient. It is expected that this work presents the k_0-method of neutron activation as a valuable technique for the performance of food analysis, proving effectiveness for the detection of even elements present in minimum concentrations with the need for small amounts of sample. The fact that the technique does not involve any chemical preparation of the samples and, therefore, there is no risk of possible contamination, was also of great value for the reliability of the results.

For a future work, it is suggested that not only other foods should be monitored as well as other elements should be analyzed in order to contribute to food and nutrition security.

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