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Trace elements detection in whole food samples by neutron activation analysis, k_0-method

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ABSTRACT

The increase in anthropogenic activities has been contributing to considerable increasing of the chemical elements concentration in the environment. One consequence is the need of monitoring the elemental composition of food available for consumption. Numerous techniques have been used to detect inorganic elements in biological and environmental matrices, always aiming reaching lower detection limits in order to evaluate the trace element content in the sample. This study evaluated the presence of inorganic elements in whole food samples, mainly elements on trace levels applying the neutron activation technique, k_0-method. This method produces accurate and precise results, without the need of chemical preparation of the samples. For this purpose, four 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, Brazil. It was possible to detect, in total, twenty-three elements. Nine elements are considered essentials, according to nutrition literature, thirteen are not essentials and one, classified as contaminant element by legislation. The majority of the elements determined are not reported in the TACO (Brazilian Table for Food Composition). It means that the professionals of health do not know, in fact, the real chemical elemental composition in foods and the population do not know what they are ingesting in terms of chemical elements and the risks of this ingestion. This study reaffirms the INAA, k_0–method, is an efficient technique for detecting trace elements in food samples.

Keywords: food composition, k_0-method, neutron activation analysis, trace elements.

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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 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 foods [2].

Activities such as mining, metallurgy and the indiscriminate use of fertilizers and pesticides have today resulted 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].

In the nutritional aspect, food monitoring is more directed to calorie counting from proteins, carbohydrates and fats, to the detriment of the ingestion of essential and nonessential elements - which are extremely relevant to the metabolic functions of living beings in general [6]. Thus, food 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 of elements known to be beneficial, toxic, or even with unknown effects, which makes research focused on essential elements as well as insufficient. The advancement 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 to determining lower elemental 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, thus avoiding 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, multielement technique with high accuracy and precision [8, 9, 10, 11].

In this study, samples of cereals and whole grains were analysed. These are foods 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 fibres, which act in the prevention and treatment of various 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 tables about food composition The technique selected for the determination of the elemental composition of food samples was the neutron activation analysis via k_0-method. The choice was based on the characteristics of this technique [8, 9, 10, 11].

1. MATERIALS AND METHODS

2.1 Samples

The foods selected for this study were: brown rice and flaked oats, as they are among the main existing whole grains [14], as well as golden and brown linseed, since they are quite consumed whole products currently. All products (500 g from each kind of food and from just one producer) were randomly purchased from supermarkets / markets in the city of Belo Horizonte.

2.1.1 Sample Preparation

Each food 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 weighted as they were purchased without being milling [16, 17]. The samples were stacked in other polyethylene sample holders, intercalated by neutron flux monitors, Al-Au (0.1%) alloy disks, IRMM-530, *Institute for Reference Materials and Measurements*, Belgium, 6 mm diameter and 0.1 mm thickness. The quality control was performed using reference material, that was also weighed in polyethylene vials and inserted together the food samples.

2.2 Irradiation, Gamma Spectrometry and Calculations

The irradiations of 8 hours were in the TRIGA MARK I IPR-R1 nuclear research reactor, located at Nuclear Technology Development Centre, Brazilian Commission for Nuclear Energy (*Centro de Desenvolvimento da Tecnologia Nuclear*) (CDTN/CNEN), in Belo Horizonte, Brazil, that operates at 100 kW. The irradiations were in the irradiation channels IC-6, IC-7 and IC-8 in the carrousel, with thermal neutrons flux of 6.35 x 10^{11} neutrons cm^{-2} s^{-1}, and spectral parameters *f* and α, 22.32 and -0.0022 respectively [18, 19].

After a suitable decay time - one day to one week for the determination of elements whose radionuclides have half-lives between 12 and 72 hours - and twenty days for the determination of radionuclides of long half-lives. The gamma spectrometry was performed using an HPGe detector with 50%

nominal efficiency and associated electronics. For the acquisition of gamma spectra, the Genie 2k program, CANBERRA, was used. The spectra were evaluated using the HyperLab program [20, 21]. The calculation of elemental concentration was performed using the Kayzero for Windows® program [22], version 2.46, specific for the k_0 method.

2.5 Quality Control

The quality control was performed using reference material, GBW 0805, Tea Leaves [23]. This reference was used due to inexistence of reference materials among the foods used in this study. To verify the performance of the k_0-method, the statistical test E_n-score [24] 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 the 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.

2. RESULTS AND DISCUSSION

Table 1 shows the results for reference material GBW0805, Tea leaves, used as reference. The statistical test points out that all results are ≤ 1 for $|E_n|$ in good agreement with the recommended values. It also means that the method produced results with 95% of probability to be inside a range of values that correspond to the true values.

Table 1: Results for GBW 0805, Tea Leaves.

GBW 0805, Tea Leaves (mg kg^{-1})			
El.	**Experimental Values (mg kg^{-1})**	**Certified Values (mg kg^{-1})**	***E*$_n$-score (*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*	-

El., Element; *, Informative values

Table 2 shows the experimental results and the values informed by TACO (Brazilian Table About Food Composition) [25]. This table is considered the reference for evaluation of the composition of food consumed not only by individuals but also by population by the nutritionists. It is important to enhance that the values in the TACO are general values, because they are not specific for a trade-mark or producer.

BJRS

BRAZILIAN JOURNAL
OF
RADIATION SCIENCES

07-02A (2019) 01-13

Table 2: Inorganic elements in whole food and the values informed by TACO (Brazilian Table About Food Composition) [25].

Elements	Whole food samples ($mg.kg^{-1}$) and the information available in TACO						
	Brown rice		Flaked Oats		Golden Linseed	Brown Linseed	TACO
	This Study	TACO	This Study	TACO	This Study	This Study	
As	0.13 ± 0.01	NR	< 0.06	NR	< 0.06	< 0.06	NR
Au	0.0004 ± 0.0001	NR	< 0.0003	NR	< 0.0003	< 0.0003	NR
Ba	< 4	NR	5 ± 1	NR	6 ± 1	< 4	NR
Br	0.79 ± 0.03	NR	1.14 ± 0.04	NR	2.4 ± 0.1	2.4 ± 0.1	NR
Ca	< 200	80	372 ± 85	480	3388 ± 209	2044 ± 133	2110
Co	0.15 ± 0.01	NR	0.023 ± 0.002	NR	0.95 ± 0.03	0.38 ± 0.02	NR
Cs	0.064 ± 0.003	NR	0.055 ± 0.003	NR	< 0.01	0.008 ± 0.001	NR
Fe	< 6	9	42 ± 4	44	60 ± 3	53 ± 3	47
K	1961 ± 69	1730	3551 ± 125	3360	7174 ± 252	7796 ± 276	8690
Mn	53 ± 2	29.9	51 ± 2	18.9	< 10	< 10	28,1
Mo	< 0.2	NR	1.3 ± 0.1	NR	< 0.2	< 0.2	NR
Na	111 ± 4	20	7.3 ± 0.3	50	621 ± 22	516 ± 18	90
Rb	10.5 ± 0.4	NR	6.0 ± 0.2	NR	10.6 ± 0.4	13 ± 1	NR

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Sb	< 0.005	NR	0.13 ± 0.01	NR	< 0.005	< 0.005	NR
Sc	<0.0006	NR	<0.0006	NR	<0.0006	0.0008 ± 0.0001	NR
Sr	28 ± 3	NR	< 5	NR	18 ± 1	8 ± 1	NR
Ta	< 0.005	NR	< 0.005	NR	0.008 ± 0.002	< 0.005	NR
Zn	18 ± 1	14	32 ± 1	26	44 ± 2	37 ± 1	44

NR, Not Reported

BJRS

BRAZILIAN JOURNAL
OF
RADIATION SCIENCES
XX (XXXX) XX-XX

In total, twenty-three elements were determined including those whose values were below the detection limit (Ce, < 0.2; Cu, < 0.6; La, < 0.02; Se, < 0.03 and Sm, < 0.004). Observing the elements determined in food, among the evaluated elements, only nine are known to be essential to health according to the literature - sodium, potassium, calcium, iron, zinc, copper, molybdenum, manganese and cobalt [6, 26]. According to Mahan *et al*., 2012 [26], whole foods are sources of Cr, Cu, Fe, K, Mg, Mn, Mo, P, Se, and Zn. The element Mg was not analysed because of its short half-live, 9.5 min and the element P was not also determined due to its nuclear characteristics that are unfavorable to be analysed by this technique.

Comparing the experimental results and the TACO's values it is possible to observe that the table inform values for linseed without specify which kind of linseed is, golden or brown. This study determined twenty-two elements and the table informs values only for seven elements analysed (Ca, Mn, Fe, Na, K, Cu, Zn). Besides, several of the experimental results were different from the values informed by TACO. These results suggest possible influence from soil where the plants were cultivated, or possible contamination [7].

Differently from the information available in the food composition tables, experimental values showed that when consuming any of the foods analysed, the individual may be ingesting other chemical elements different from those reported. Of the total number of elements detected in the study (twenty-three), nine are considered essential for health according to the Nutrition literature [26] (Ca, Co, Cu, Fe, K, Mn, Mo, Na, Zn), twelve are considered non-essential because they are not classified as essential by the same literature (Au, Ba, Br, Ce, La, Rb, Sc, Sm, Sr, Ta) and one, As, is classified as a contaminant by legislation [27] (Figure 1).

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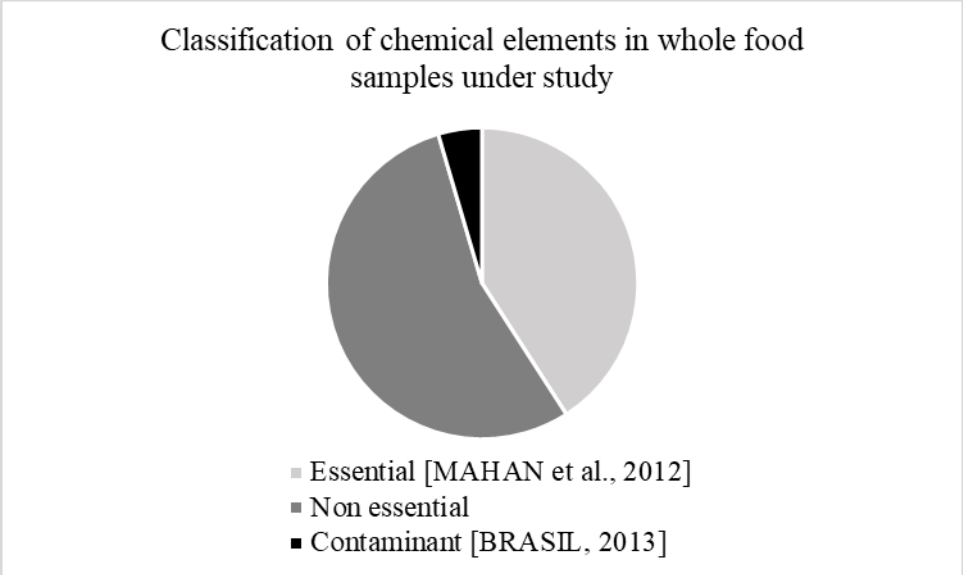
Figure 1: *Essential, non-essential and contaminant elements in food samples in this study.*



Information about the presence, concentration and origin of various components of the foods consumed is unknown by the population. Despite several techniques being 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 food consumed.

3. CONCLUSION

Despite the remarkable advances in analytical techniques for determining elements in biological matrices and also in the databases on food composition, it is observed that the available information on the elemental composition of foods is still insufficient due to the complexity of the food. The professional of health does not know, in fact, the real chemical elemental composition in foods and the population does not know what they are ingesting in terms of chemical elements and the risks of this ingestion.

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 effective 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, there-

fore, there is no risk of possible contamination, was also of great value for the reliability of the results.

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