Chia trace elements detection by neutron activation analysis

Detecção de elementos traço de chia por análise de ativação neutrônica

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ABSTRACT
Chia seed is an ancient grain that is becoming popular in modern food regimen for their nutritional value and functional properties, although many tables of food composition do not provide complete information about it. Trace and ultra-trace elements are indispensable for human health as they are involved in biochemistry regulations, such as transport and oxygen activation, electron transport, catalytic center in oxide reduction processes, catalytic center in acid-base processes and structural function. For both diet assessment and prescription, reference values for trace elements as recommended daily intake, recommended dietary allowance and tolerable upper intake level were established. Instrumental neutron activation analysis (INAA) is a noble method to identify and quantify trace and ultra-trace elements that has high sensitivity for many elements, has little or no sample contamination, resulting in low blank values, has virtually no matrix effects and multi-element capability. The aim of the present work was to identify and quantify by INAA mineral elements of chia seeds. The results showed higher content of Ca, K, Zn and Fe when compared with data from the literature obtained by other analytical methods. Besides that, using INAA was possible to detect elements that was not commonly verified with others measuring methods.

Keywords: Chia (Salvia hispanica L.), Trace Elements, Neutron Activation Analysis.

RESUMO
A semente de chia é um grão antigo que está se tornando popular no regime alimentar moderno por seu valor nutricional e propriedades funcionais, embora muitas tabelas de composição alimentar não fornecem informações completas sobre ele. Os elementos traços e ultra-traços são indispensáveis para a saúde humana, pois estão envolvidos nos regulamentos bioquímicos, como transporte e...
ativação de oxigênio, transporte de elétrons, centro catalítico em processos de redução de óxidos, centro catalítico em processos ácido-base e função estrutural. Para avaliação e prescrição da dieta, foram estabelecidos valores de referência para elementos traço, como ingestão diária recomendada, subsídio dietético recomendado e nível de ingestão superior tolerável. A análise instrumental por ativação de nêutrons (INAA) é um método nobre para identificar e quantificar elementos traços e ultra-traços que possui alta sensibilidade para muitos elementos, possui pouca ou nenhuma contaminação da amostra, resultando em baixos valores de branco, praticamente sem efeitos de matriz e capacidade de multi-elementos. O objetivo do presente trabalho foi identificar e quantificar, por INAA, elementos minerais das sementes de chia. Os resultados mostraram maior teor de Ca, K, Zn e Fe quando comparados com dados da literatura obtidos por outros métodos analíticos. Além disso, o uso do INAA foi possível detectar elementos que não eram comumente verificados com outros métodos de medição.

Palavras-chave: Chia (Salvia hispanica L.), elementos traço, análise de ativação de nêutrons.

1 INTRODUCTION

Chia seeds (Salvia hispanica L.) are native of Mexico and north of Guatemala and was an important staple Mesoamerican food and medical plant in pre-Columbian times [1]. Chia is a popular food due its nutritional value and functional properties. It contains approximately 30–34 g dietary fiber (insoluble fraction approximately 85–93%, soluble fraction approximately 7–15%), high contents of polyunsaturated fatty acids (mainly linoleic and oleic that represent approximately 60% all fatty acids), some important vitamins (B1, B2 and niacin), rich in polyphenols (gallic, caffeic and chlorogenic acids) and high content of important minerals and trace elements (phosphorus, calcium, potassium, magnesium, zinc, copper and manganese) [2]. Besides that, many tables of food composition do not present chemical composition of chia seeds.

Trace minerals are inorganic substances that, along with vitamins and other micronutrients, belong to those constituents in the human diet that are needed in very small quantities. Some trace minerals are essential components of enzymes and other proteins. The deficiency of these elements is cause of several physiological diseases and disorders. Trace and ultra-trace elements are indispensable for biochemistry regulations in the human organism, such as transport and oxygen activation, electron transport, catalytic center in oxide reduction processes, catalytic center in acid- base processes and structural function [3, 4].

Instrumental neutron activation analysis (INAA) stands out among other similar techniques in terms of its relative simplicity and high sensitivity when analyzing trace elements in food samples. 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 INAA for the determination of the elemental composition of food samples, recognized
by World Health Organization, was based on the fact that it is a multi-elementary technique with high accuracy and precision, but can be employed only where a nuclear reactor is available [5]. This comparative method consists of irradiating together with the samples appropriate patterns with well-known concentrations under a same neutron flux. From this, nuclear reactions occur forming radioactive isotopes with the emission of characteristic gamma rays for each radioisotope, which can be measured in a gamma ray spectrometer. After detection of this radiation by the equipment and with the help of pre-set calibrations, it is possible to calculate the concentrations of the elements of interest by comparing the peak area generated by counting the samples and the standards [6].

The aim of the present work was to identify and quantify by INAA mineral elements of chia seeds.

2 MATERIALS AND METHODS

Chia seeds supplied by Casa Forte Distribuidora de Produtos Alim. Ltda. were ground in a conventional mill. Five aliquots where weigh in polyethylene envelopes appropriate for irradiation process. Two subsamples of chia flour and standard reference samples where irradiated on Research Nuclear Reactor (IEA-R1) of IPEN by neutron flux of $9 \times 10^{11} \text{n cm}^{-2} \text{s}^{-1}$, for 30 sec for analysis of Ba, Cl, Cu Mg, Mn, Ti and V. For analysis of As, Br, Ca, Cr, Co, Fe, K, La, Mo, Na, Rb, Sb, Sc, Se and Zn three subsamples of chia flour and standard reference samples where irradiated for 8 h, by neutron flux of $0.97 \times 10^{12} \text{n cm}^{-2} \text{s}^{-1}$. In both cases, standard references samples (Rice Flour - NIES- CRM-10C and Soil 7) certify by AIEA where irradiated simultaneously. Measurements of gamma radiation emitted by the radionuclides produced in the neutron irradiation were performed with a gamma spectrometer Canberra model GX 2020 hyper-pure Ge detector, with a resolution of 1.90 keV for the 1332.49 keV peak of $^{60}\text{Co}$ coupled to a model 1510 Integrated Signal Processor and MCA 100 System.

3 RESULTS AND DISCUSSION

The values of mineral content of chia, radionuclides and respective value of energy emission are expressed in Table 1.
The results show important information about nutritional value of chia. Dietary Reference Intakes (DRIs) represent the most current scientific knowledge on nutrient needs. According RDC 59/2012 - ANVISA [7], a food classified as source of determined mineral if it have more than 15% of the DRI value in a portion of 100g. The reference values of selenium intake for adults of both sexes is 55 µg/day, so the results of Tab. 1 show that chia can be consider a source of selenium. Selenium-containing proteins are widely distributed in the body. Among functionally characterized selenoproteins are five glutathione peroxidases (GPX) and three thioredoxin reductases, (TrxR/TXNRD) [8]. Besides that, chia has a high content of Cr, Fe, Mg, Mn, Mo, Zn, and Ca, although the last one is not trace element. Classifying according ANVISA [7], a food classified as high content of determined mineral if it have more than 30% of the DRI value in a portion of 100g.

Health professionals, mainly nutritionists, commonly use table of chemical composition of food to calculate calories, macro and micronutrients diets content. Table values must be as accurate as possible due many pathologies required diets with different nutritional values. Trace elements detection by neutron activation technique could improve the databases quality of chemical composition tables due the method accuracy. Table 2 shows the comparison of values obtained with three different analytical methods and values from the Tabela Brasileira de Composição de

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Table 1. Chia mineral content

| Element | Radionuclide (energy in keV) | Concentration | Content Mean ± Standard derivation |
|---------|------------------------------|---------------|----------------------------------|
| K       | ^{42}K (1524.7)              | mg. 100g⁻¹    | 790 ± 40                         |
| Ca      | ^{43}Ca (1296.9)             | mg. 100g⁻¹    | 750 ± 50                         |
| Mg      | ^{77}Mg (1014.4)             | mg. 100g⁻¹    | 310 ± 30                         |
| Fe      | ^{56}Fe (1099.32)            | mg. 100g⁻¹    | 11.1 ± 0.6                       |
| Mn      | ^{56}Mn (846.6)              | mg. 100g⁻¹    | 7.1 ± 0.4                        |
| Zn      | ^{64}Zn (1115.5)             | mg. 100g⁻¹    | 6.9 ± 0.3                        |
| Ba      | ^{133}Ba (165.85)            | mg. 100g⁻¹    | 6.2 ± 1.1                        |
| Cl      | ^{35}Cl (1642.7)             | mg. 100g⁻¹    | 5.2 ± 1.1                        |
| Cu      | ^{63}Cu (1039)               | mg. 100g⁻¹    | 2.5 ± 0.4                        |
| Rb      | ^{87}Rb (1076.6)             | mg. 100g⁻¹    | 0.99 ± 0.05                      |
| Ti      | ^{47}Ti (320)                | mg. 100g⁻¹    | 0.94 ± 0.17                      |
| Br      | ^{82}Br (776.5)              | mg. 100g⁻¹    | 0.9 ± 0.07                       |
| Na      | ^{23}Na (1368.53)            | mg. 100g⁻¹    | 0.24 ± 0.02                      |
| Mo      | ^{99}Mo (140.51)             | µg. 100g⁻¹    | 39.9 ± 0.7                       |
| Co      | ^{60}Co (1332.5)             | µg. 100g⁻¹    | 30.7 ± 0.9                       |
| Cr      | ^{51}Cr (320.1)              | µg. 100g⁻¹    | 14.4 ± 3                         |
| Se      | ^{75}Se (264.5)              | µg. 100g⁻¹    | 11.6 ± 5                         |
| V       | ^{52}V (1434.4)              | µg. 100g⁻¹    | 10.4 ± 1.9                       |
| La      | ^{138}La (1596.2)            | µg. 100g⁻¹    | 7.6 ± 0.5                        |
| As      | ^{75}As (559)                | µg. 100g⁻¹    | 1.72 ± 0.35                      |
| Se      | ^{36}Se (889.30)             | µg. 100g⁻¹    | 1.16 ± 0.06                      |
| Sb      | ^{125}Sb (564.08)            | µg. 100g⁻¹    | ND                                |
Alimentos (TBCA) and United States Department of Agriculture Food Composition Databases (USDA).

Table 2. Comparison of mineral content of chia seeds with different methods

| Mineral | INAA [present work] | Flame atomic absorption spectrometry [9] | Plasma atomic emission spectrometry* [10] | TBCA/USDA [11, 12] |
|---------|---------------------|------------------------------------------|------------------------------------------|---------------------|
| Ca      | 750                 | 694                                      | 566.64                                   | 631                 |
| Na      | 0.24                | 3.68                                     | 58.04                                    | 16                  |
| Mg      | 310                 | 378                                      | -                                        | 335                 |
| K       | 790                 | 871                                      | 635.17                                   | 407                 |
| Zn      | 6.9                 | 5.50                                     | 4.96                                     | 4.58                |
| Fe      | 11.1                | 2.12                                     | 7.76                                     | 7.72                |

*Mean of values obtained of three trades evaluated in the work.

Values of Ca, K, Zn and Fe from INAA were higher than other methods and table values, in particular K of INAA were almost double of registered on TBCA/USDA, emphasizing the nutritional quality of chia seeds.

Values of Na and Mg from INAA were smaller than those detected by other methods and recorded on tables. Similarly to the sort of analysis performed in the present work, other authors applied INAA for the for mineral analysis of brown rice, flaked oats, golden and linseed [5].

4 CONCLUSIONS

Instrumental neutron activation analysis (INAA) allows identify and quantify many elements of chia seed and permit been classified as high content of Cr, Fe, Mg, Mn, Mo, Zn, Ca according ANVISA rules. This technique detects also the presence of Mo, Co, Cr, Se, V, La, As, Sc. The sensitivity of INAA varies considerably among elements; nevertheless, it can be used as an important reference for other analysis methods. In that sense, present results will contribute with important information on detailed chia composition, highlighting the nutritional value of chia seeds responsible for their health benefits.

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