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# Application of INAA technique for analysis of essential trace and toxic elements in medicinal seeds of *Carum carvi* L. & *Foeniculum vul-gare* Mill. used in Algeria

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## ABSTRACT

Traditional medicinal seeds such as caraway “*Carum carvi* L.” and *Foeniculum vulgare* Mill. commonly called fennel have been largely used since several centuries for a wide range of ailments related to digestive, endocrine, reproductive, and respiratory systems. Additionally, it is also used as a galactagogue agent for lactating mothers. The Algerian neutron activation analysis laboratory is highly involved in nutrition applications in the framework of research activities using the Es-Salam research reactor. The objective of this work is to contribute by using nuclear analytical techniques, for studying a large number of natural food samples consumed in Algeria related to nutrition and human health. The present study focuses on the analysis of the seeds of caraway and fennel used in our country by using instrumental neutron activation analysis (INAA) technique. Twenty-seven elements were assessed (As, Ce, Co, Cr, Cs, Eu, Hf, La, Mo, Lu, Nd, Sb, Sc, Se, Sm, Tb, Yb, Th, Ba, Br, Rb, Sr, Zn, Ca, K, Na and Fe) and the accuracy of the method was evaluated by analyzing the Certified Reference Materials (CRMs). The daily intake of essential and toxic elements was determined and compared with the recommended values and was found to be well below the tolerance limits.

## 1. Introduction

As of late years many authors over the world reported several studies on the importance of elemental constituents of the plant food, seeds, herbal drug plants, fruits and vegetable most of these studies concluded that essential metals can produce toxic effects when the metal intake is in high concentrations, whereas non-essential metals are toxic even in very low concentrations in human health (Arzani and Ashraf, 2017; Alamin et al., 2007; Naidu et al., 1999; Reddy et al., 1998; Kumar et al., 2005; Bacha et al., 2017; Waheed and Siddique, 2009; Messaoudi et al., 2018; Nedjimi and Beladel, 2016).

Plant foods can contributes significantly to human nutrition and health, because they contain almost all of the mineral and organic nutrients established as essential for human nutrition, the vast majority of trace element determinations in food and beverage are carried out because of their nutritive importance and toxic effects. The toxic elements in food are defined as those present in food in amounts that can be potentially hazardous to human health. Toxic elements in food originate from several different sources among which the most frequently studied are agricultural production of plants and animals, industrial or household processing, and migration from packaging during storage of final products health (Naidu et al., 1999; Reddy et al., 1998; Kumar et al., 2005; Waheed and Siddique, 2009; Alamin et al., 2007; Obi et al., 2001). The recommended dietary allowances (RDAs) are defined as the levels of essential nutrients intakes considered to be adequate to meet the known nutrient needs of all healthy persons based on scientific knowledge (WHO/FAO, 1999). Thus, persons with special nutritional needs are not included in the RDAs. Furthermore, the RDAs are categorized according to the needs for some nutrients based on age group (e.g., infants, children, adolescents, and adults), sex (male/female) and physiological requirements (e.g., pregnancy, lactation) (Recommended Dietary Allowance, 1989; WHO/FAO, 1999).

Caraway (*Carum carvi* L.; Family Apaiaceae,) (Lim, 2013; Isidora et al., 2010), and fennel (*Foeniculum vulgare* Mill; Family Umbelliferae) (Singh and Garg, 2006; Tanira et al., 1996), are two of the oldest spices cultivated in Europe. Nowadays, it is cultivated from northern temperate to tropical climates, including countries such as India, Canada, United States and Australia, grows in many countries especially in the Mediterranean region. It has been known as a medicinal plant since the time of Hippocrates and Dioscorides. At present, widely utilized in Arabian folk medicine systems, are extensively being used in folk medicine as a carminative, found to be effective against spasmodic

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gastro-intestinal complaints, irritable stomach, indigestion, lack of appetite, diuretic, anti-inflammatory, antimicrobial and galactogogue and dyspepsia in adults, and in relieving flatulent colic of infants. Also it is given to infants in the treatment of flatulence. In addition, the volatile oils of fennel are used to control flatulent dyspepsia and colic in children (Thippeswamy et al., 2013; Mahfouz and Sharaf-Eldin, 2007).

The medicinal seeds and herbs were widely used in our country and especially in rural communities to treat various illnesses, because in the most cases to be free from adverse effects, even though they are often promoted as natural and therefore harmless (Beladel et al., 2012; Nedjimi and Beladel, 2015). To help provide higher quantities of plant-based dietary minerals, researchers have been working to enhance the mineral density of plant foods. However, mineral concentrations can differ across tissues within a single plant, across genotypes of a given species, or more broadly across species (Arzani et al., 2007; Arzani and Ashraf 2017). Therefore, more advances will be possible if attention is given to the rapid and accurate assessments of trace elements of plant materials the INAA method has been applied to determine the trace elements in fennel seeds samples used in Algeria and compared the results with reported literature data.

## 2. Materials and Methods

### 2.1. Sampling and sample preparation

Two medicinal plant seeds of caraway and fennel used in Algeria were collected in June 2014 from Ain Oussarra region (Djelfa) of Algeria. At first in a laboratory, the samples were washed several times with deionized water to remove soil particles and dust then dried for 48 h in an oven at 40 °C. The dried samples were ground to a fine powder (particle size fraction of < 200 µm) using an agate mortar and pestle. At a later stage, three samples of each collected charge weighing about 120 mg were stored in precleaned polyethylene capped bottles. In this work, the certified reference materials like GBW 07605 (National Research Center for CRM, Langfang, China) and NIST-SRM 1573a (tomato leaves) from the National Institute of Standard and Technology (NIST), was used to determine the elementals concentrations by relative techniques. On the other hand, the analytical results obtained for NIST-SRM and GBW 07605 were subjected to internal quality control procedure. All samples and the standard were placed in an aluminum irradiation capsule.

### 2.2. Irradiation and counting

The different steps of the analytical work were performed using NAA facilities at the Es-Salam research reactor. All samples of medicinal seeds and the standards were placed in an aluminum irradiation capsule which was irradiated for 6 h at a thermal neutron flux of $4.5 \times 10^{13}\,\text{ncm}^{-2}\,\text{s}^{-1}$ in a vertical experimental channel of the Algerian Es-Salam research reactor (Doumaz et al., 2016; Messaoudi et al., 2017), and were then analyzed using the instrumental neutron activation analysis to determine the concentrations of elements. After appropriate cooling, the irradiated samples together with the standard were measured at different cooling times using a coaxial HPGe detector having the following characteristics: relative efficiency: 35%, FWHM 1.8 keV for the 1332.5 keV γ-peak of $^{60}$Co. The detector is Canberra Genie 2000 gamma-spectrometric system (Genie™, 2000). The first cooling time for middle lived radionuclides was in the range of 3–5 days and counted about 7200 s for each sample and each standard. The second measurements for the long-lived radionuclides were measured after 20 days for a collection time of 14,400 s.

For this study, the gamma-ray spectrometry of the irradiated samples was carried out using the nuclear parameters listed Table 1 (Adams and Dams, 1969).

**Table 1**
Optimum experimental conditions and nuclear data employed in this study.

| Elements | Radio-nuclide | Half life | γ - peaks (keV) | Cooling time |
|---|---|---|---|---|
| Barium | $^{131}$Ba | 11.50 d | 496.3 | 20 d |
| Bromine | $^{82}$Br | 35.30 h | 554.3, 698.08, 776.5 | 3–5 d |
| Calcium | $^{47}$Ca | 4.536 d | 1297.06 | 20 d |
| Cerium | $^{141}$Ce | 32.508 d | 145.4 | 20 d |
| Cobalt | $^{60}$Co | 5.2714 y | 1173.2, 1332.5 | 20 d |
| Chromium | $^{51}$Cr | 27.7025 d | 320.1 | 20 d |
| Cesium | $^{134}$Cs | 2.0648 y | 604.7, 795.8 | 20 d |
| Iron | $^{59}$Fe | 44.5 d | 1099.3, 1291.6 | 20 d |
| Hafnium | $^{181}$Hf | 42.39 d | 133, 345.9, 482.2 | 20 d |
| Potassium | $^{42}$K | 12.360 h | 1524.7 | 3–5 d |
| Lanthanum | $^{140}$La | 40.27 h | 487.02, 815.8, 1596.21 | 3–5 d |
| Sodium | $^{24}$Na | 14.9590 h | 1368.6 | 3–5 d |
| Rubidium | $^{86}$Rb | 18.631 d | 1077 | 20 d |
| Antimony | $^{124}$Sb | 60.20 d | 169, 602.7 | 20 d |
| Scandium | $^{46}$Sc | 83.83 d | 889.3, 1120.5 | 20 d |
| Samarium | $^{153}$Sm | 46.50 h | 103.2 | 3–5 d |
| Thorium | $^{233}$Pa | 26.967 d | 300.1, 311.9 | 20 d |
| Zinc | $^{65}$Zn | 244.26 d | 1115.5 | 20 d |

### 2.3. Quality control and quality assurance (QC/QA)

The quality assurance procedures are described for individual steps in neutron activation analysis, namely, preparation of the test portion, selection of analytical protocol, calibration, instrument performance checks, irradiation, decay, measurement, spectrum analysis and interpretation, internal and external quality control, as well as for ensuring the technical competence of the personnel involved (Bode, 2010). For data validation of INAA technique, two CRMs of NIST-SRM 1573a (tomato leaves) and GBW 07605 (tea leaves) were used for quality control purposes (Table 2). In order to evaluate the laboratory performance, we determined the U-score test, Z-score and Relative Bias (RB). This parameter is calculated according to the following Eq. (1)–(3):

$$U_{score} = \frac{|X_{Lab} - X_{Ref}|}{\sqrt{\mu_{Lab}^2 + \sigma_{Ref}^2}} \tag{1}$$

$$Z_{score} = \frac{X_{Lab} - X_{Ref}}{\mu_{Lab}} \tag{2}$$

$$\text{Relative Bias(RB)} = \frac{X_{Lab} - X_{Ref}}{X_{Ref}} \times 100\% \tag{3}$$

Where $X_{Lab}$, $\mu_{Lab}$, $X_{Ref}$ and $\sigma_{Ref}$ are the laboratory results, standard deviation, the recommended and standards uncertainties respectively.

The laboratory performance is evaluated as: satisfactory if $U_{score} \leq 1$, and Satisfactory if $Z_{score} \leq 2$, questionable for $2 < Z_{score} < 3$ and unsatisfactory for $Z_{score} \geq 3$; (result and certifed value are not inagreement), (Messaoudi, 2016).

## 3. Results and Discussion

### 3.1. Concentrations of trace elements

The elemental concentrations were calculated by using instrumental neutron activation analysis techniques. In this study we used the standard reference material for the QC/QA of INAA technique.

Table 2 give a comparison of our results for the reference material to its certified values obtained in this study and the statistical parameters RB, Z-score and U-scor.

The results obtained of all elements concentrations are in good agreement with the certified values of two CRMs of NIST-SRM 1573a (tomato leaves) and GBW 07605 (tea leaves).This evaluation shows a good quality of results obtained in this investigation in the results through the statistical evaluation where the Relative bias (RB), Z-score and U-score are all accepted.