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Original Article

Instrumental Neutron Activation Analysis of Trace Elements in Some Food Spices Consumed In Tehran, Iran

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Abstract

Introduction
There is a growing interest in determining the concentration of various elements in food spices. In the present study, the instrumental neutron activation analysis (INAA) was employed to measure the trace elements in 11 commonly food spices consumed in Tehran, Iran.

Materials and Methods
The levels of K, Mn, Na, Cl, V, Br, Al, and As were determined and their effects on human health were discussed. The results were compared with the values reported in the literature. The accuracy and precision of the analytical procedure was estimated by analyzing the Lichen (IAEA-336) reference material.

Results
The concentrations of the measured elements in the spices were 3850-29157, 10-335, 153-2849, 186-3063, 0.2-2.8, 2.1-58.7, and 72-2102 ppm for K, Mn, Na, Cl, V, Br, and Al, respectively. As was only detected in thyme (0.8 ppm) and plantain (0.42 ppm).

Conclusion
As the findings of the present study indicated, the concentrations of K and Na in the black pepper, garlic, and ginger were significantly higher than the values reported in other countries. The Mn levels in the black pepper and garlic consumed in Tehran were comparable with those in Poland. Furthermore, the concentration of As in these spices were lower than the maximum permissible limit.

Keywords: Element, Neutron Activation Analysis, Spices, Toxic

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1. Introduction

Spices can be defined as the dry parts of a plant, such as root, leaves, and seeds [1]. A notable use of spices and herbs in very early times were in medicine, making holy oils and unguents, as well as aphrodisiacs [2]. In the last three decades, the uses of spices have markedly increased in most of the regions around the world, including Europe and North America [3]. The specific uses of spices tend to considerably vary across cultures and countries in the medicine, religious rituals, cosmetic, perfumery and foods. Food spices, which are partially considered as sources of nutrients, were shown to play an important role in the health [4].

In addition, the spices have been recognized to have some medical applications due to having antioxidant and antimicrobial properties. Many spices have been found to possess anti-diabetic, anti-inflammatory, and anti-hypersensitive capacity [5,6]. On the other hand, the process of preparation and handling of the spices can make them a source of food poisoning [7].

Considering the importance of essential and toxic elements in various human metabolic processes, there is an increased interest to measure the concentration of different elements in food spices. The habitual addition of the spices contaminated with trace and heavy metals to the food may result in the accumulation of these chemical contaminants in the human organs and lead to different health problems.

The aim of the present study was to estimate the levels of some essential elements (i.e., K, Mn, Na, Cl, Br, and Al) as well as a toxic element (As) that may be present in the popular food spices used in Tehran (with a population of nine million), Iran. To this aim, the instrumental neutron activation analysis (INAA) was employed. The most important attribute of this technique is that it is non-destructive; therefore, it eliminates a significant source of potential error due to the incomplete dissolution of the samples and foreign contaminants introduced during the analysis. Additional important advantage of the INNA is its capability for simultaneous multi-element determination over a wide range of concentrations. However, care is required regarding the interfering nuclear reactions producing the same products from different elements.

2. Materials and Methods

This study was conducted on eleven popular spices, including turmeric, thyme, sumac, black pepper, red papper, cumin, garlic, limon, ginger, cinnamon, and plantain. All samples were in the powder form and were purchased from the major markets in Tehran. These spices are directly used for flavoring and coloring the foods. The comparative method of INAA was used to determine the composition of elements in the selected spices. Since the samples and standard refrence materials are irradiated and counted under the same conditions and geometries, such nuclear parameters as cross section, neutron flux, decaying scheme, and detector efficiency are eliminated in both sample and standard.

For elemental analysis, the package of the studied samples were opened prior to performing the analysis and homogenized in an agate mortar. Subsequently, the samples were passed through a 100-mesh sieve to get a fine powder and dried at 80°C in an oven for 4 h to avoid any moisture content. A small mass in the range of 40-70 mg was weighed from each sample and sealed in a polyethylene vial. Similarly, a sediment standard reference material SDN-N-1/2 with equal mass to that of the sample was prepared. The concentrations of the elements in this standard reference material is presented in Table 1.

Using the pneumatic sample transfer system, the sample was irradiated along with the standard reference material for 3 min at Tehran Research Reactor. The thermal neutron flux was about 3×10^{13} n cm^{-2} s^{-1} [8]. The sample and standard reference material were counted immediately after irradiation to determine V and Al. After 15 min of decay time (for decay of short half-life of radionuclides), the same sample and standard were measured again to determine K, Mn, Na, and Cl. Furthemore, to measure Br and As, the sample and standard were irradiated for 1 h and counted after 15 h decay time.

Table 1. Concentrations of elements in SD-N-1/2 and Lichen reference materials.

Element	Recommended value mg/kg in Lichen (IAEA-336)	95% Confidence Interval mg/kg in Lichen (IAEA-336)	Certified value mg/kg in SD-N-1/2	95% Confidence Interval mg/kg in SD-N-1/2
AL	680	570-790	3.75(%)	3.58-3.85 (%)
As	0.63	0.55-0.71	50.0	42.4-60.0
Br	12.9	11.2-14.6	52.0	39.0-64.6
Cl	1900	1600-2200	9040	9000-9600
K	1840	1640-2040	1.54 (%)	1.46-1.66 (%)
Mn	63	56-70	777	728-801
Na	320	280-360	1.04 (%)	1.03-1.07 (%)
V	1.47	1.25-1.69	77.7	65.0-80.7

Table 2.Radionuclides, main gamma energies, irradiation and counting conditions

Element	Radionuclide	Half life	Energy (keV)	Irradiation and counting conditions
Al	^{28}Al	2.24 m	1779	3 minutes irradiation and counted immediately after irradiation for 300s
V	^{52}V	3.75 m	1434	
K	^{42}K	12.40 h	1525	3 minutes irradiation and counted 15 minutes after irradiation for 1500s
Mn	^{56}Mn	2.58 h	1810	
Na	^{24}Na	15.00h	1368	
Cl	^{38}Cl	37.20 m	2167	
Br	^{82}Br	35.4 h	554	1 hr irradiation and counted 15 hrs after irradiation for 5000s
As	^{76}As	26.3 h	559	

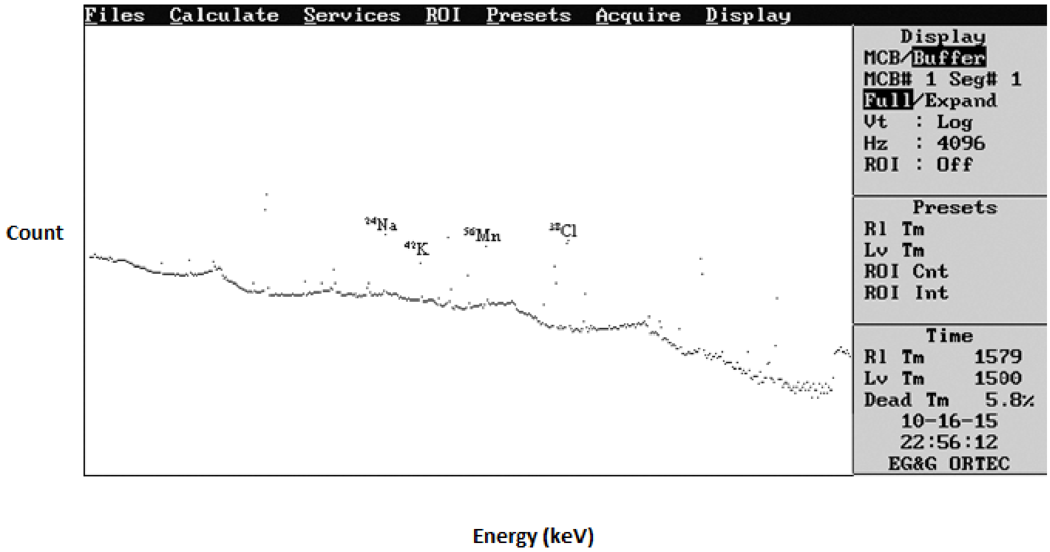

Figure 1. A typical gamma ray spectrum of Thyme

The radionuclides used in the analysis along with their gamma energies, irradiation, and counting conditions are listed in Table 2.

The measurements were carried out by gamma-ray spectrometer system using HPGe detector (EGPC 5574 model, manufactured by Intertechnique, France) with 10% relative efficiency coupled with multi-channel analyzer. The energy resolution was 1.9 keV for the 1332 keV gamma ray of ^{60}Co. The gamma ray spectra were registred using the Meastro II software. Figure1 illustrates a typical gamma ray spectrum obtained for the thyme. The concentration of the elements in the activated samples were calculated quantitatively using the gamma-ray spectrum analysis software packages known as Winspan 2004. This software uses equation (1) to determine the concentrations of the elements in a sample in comparison with the known masses of the elements in reference material.

Table 3. Mean elemental concentrations and standard deviations of the popular spices consumed in Tehran.

Spice	Brand	No of sample	Element (ppm)							
			K	Mn	Na	Cl	V	Br	Al	As
Turmeric	A	5	28949 ± 650	48 ± 3	331 ± 15	2504± 100	2.1± 2.0	38.3± 2.4	477± 25	ND*
Thyme	B	5	11401 ± 342	68 ± 4	818 ± 35	2517± 95	0.70± 0.07	11.4± 0.7	2102± 118	0.80± 0.07
Sumac	B	5	9343 ± 280	24 ± 2	290 ± 13	597± 30	1.3± 0.1	2.8± 0.3	678± 38	ND
Black pepper	A	5	18447 ± 435	224 ± 14	208 ± 10	3063± 110	2.80± 0.24	58.7± 4.0	1275± 67	ND
Red pepper	A	5	29157 ± 580	19 ± 2	446 ± 21	3031± 115	1.10± 0.09	4.0± 0.3	531± 29	ND
Cumin	A	5	18256 ± 450	20 ± 2	1095 ± 57	2573± 123	0.600± 0.067	5.8± 0.4	348± 19	ND
Garlic	B	5	9202 ± 276	10 ± 1	391 ± 19	804± 38	0.300± 0.04	2.1± 0.2	72± 5	ND
Limon	B	5	13177 ± 329	13 ± 1	1123 ± 56	1260± 58	0.80± 0.08	4.1± 0.3	470± 29	ND
Ginger	A	5	15259 ± 981	157 ± 9	2849 ± 130	661± 30	0.20± 0.03	5± 0.4	131± 9	ND
Cinnamon	A	5	3850 ± 134	335 ± 20	153 ± 7	186± 10	0.400± 0.039	7.5± 0.6	241± 13	ND
Plantain	B	5	22345 ± 447	33 ± 2	485 ± 23	2328± 84	1.90± 0.17	8.1± 0.6	836± 45	0.417± 0.048

*ND= Not detected

$$C_s = C_{st}\frac{A_s(e^{-\lambda t_d})_{st}}{A_{st}(e^{-\lambda t_d})_s} \quad (1)$$

Where, C_s and C_{st} are the concentrations of the unknown analyte (interested element) in the sample and standard, respectively; A_s and A_{st} are the activity rates of the unknown analyte in the sample and standard, respectively; t_d is the decay time of the unknown element in the sample and standard, respectively; $(e^{-\lambda t_d})_s$ and $(e^{-\lambda t_d})_{st}$ are the decaying factors for the analyte and the standard, respectively.

The accuracy of the analytical method was evaluated by analyzing the reference material known as Lichen (IAEA-336), which was irradiated along with the sample.

3. Results

Table 3 shows the mean concentrations of eight elements analyzed in the selected popular food spices, using the INAA. The concentrations were reported with standard deviations. The evaluation of the data demonstrated that different spices contained K, Mn, Na, Cl, V, Br, Al, and As in various proportions. The variations in the elemental concentration are mainly attributed to the composition of the soil in which the plants are cultivated and the differences in botanical structure. Other factors responsible for these variations in the elemental content include preferential absorbability of the plant, use of fertilizers, irrigation water, climatological conditions, and industrial activities [9].

The turmeric and cinnamon had the highest (28949 ppm) and lowest (3850 ppm) K concentrations among the other tested spices. The Na concentration was significantly high in the ginger (2849 ppm), which was about 19 times higher than that in the cinnamon (153 ppm). The concentrations of Cl were between 186 and 3033 ppm in the cinnamon and black pepper, respectively. Except for the ginger, all spices had concentration of K > Cl > Na. K, Cl, and Na as electrolytes are important for the normal distribution of fluid balance in the intracellular and extracellular cells of the human body [10].

These elements are also actively involved in inducing the proper balance of acid-base in the body. Low level of K in human body causes heart stroke, diabetes, and hypertension [11]. High doses of Cl intake results in the malfunction of the nervous system and such organs as liver and lungs [12]. Furthermore, high or low Na level in human body can cause seizures, coma, and death. The results of Mn obtained in this study revealed that Mn had the highest (335 ppm) and lowest (10 ppm) accumulation in the cinnamon. Mg is an essential micronutrient, which is used for the normal bone structure, reproduction, normal functioning of the central nervous system, and the elimination of tiredness, fatigue, and nervous irritability [13].

According to the Food and Agriculture Organization of the United Nations (FAO) and World Health Organization (WHO) (1984), the permissible limit of Mn in edible plants is 2 ppm [14, 15]. The concentration range of V varied between 0.2 and 2.8 ppm as observed in the ginger and black pepper, respectively. V is useful in the treatment of diabetes mellitus [12]. It works in place of insulin to reduce the glucose levels in blood [10]. As revealed by the analytical data, the black pepper and turmeric had high Br concentrations, which were estimated to be 58.7 and 38.3 ppm, respectively. However, the functional role of this element has not been known yet [12, 16].

Furthermore, the concentrations of Al ranged between 72 and 2102 ppm as observed in the garlic and thyme. Al has no known physiological importance in the human body [17]. The excessive intake of Al causes such diseases as neurological dementia or dialysis dementia, Parkinson's, and Alzheimer's. The daily average intake of Al by adults is about 7-10 mg d^{-1} [18]. The concentrations of As in the thyme and plantain samples were 0.8 and 0.4 ppm, respectively, while it was below the detection limit in other samples. Based on the FAO/WHO (1984), the maximum permissible limit (MPL) of As in plants is 1 ppm.

Table 4. Comparison of essential elements concentrations in spices consumed in Tehran with those in other countries.

Spice $\left(\frac{\text{Country}}{\text{region}}\right)$	Element (ppm) K	Mn	Na	Reference
Black Pepper $\left(\frac{\text{Poland}}{\text{Galeo}}\right)$		189 ± 3		[20]
Black Pepper $\left(\frac{\text{Poland}}{\text{Prymat}}\right)$		190 ± 2		[20]
Black Pepper $\left(\frac{\text{Poland}}{\text{Kamis}}\right)$		197 ± 3		[20]
Black Pepper (Nigeria)	2290	0.02	45	[21]
Black Pepper $\left(\frac{\text{Iran}}{\text{Tehran}}\right)$	18447 ± 435	224 ± 14	208 ± 10	Present data
Red Pepper $\left(\frac{\text{India}}{\text{Haryana}}\right)$		20.4 ± 1.05		[22]
Red Pepper $\left(\frac{\text{Iran}}{\text{Tehran}}\right)$	29157 ± 580	19 ± 2	446 ± 21	Present data
Garlic $\left(\frac{\text{Poland}}{\text{Galeo}}\right)$		11.0 ± 0.07		[20]
Garlic $\left(\frac{\text{Poland}}{\text{Prymat}}\right)$		9.41 ± 0.03		[20]
Garlic $\left(\frac{\text{Poland}}{\text{Kamis}}\right)$		10.1 ± 0.2		[20]
Garlic (Nigeria)	540.0	0.01	41.0	[21]
Garlic $\left(\frac{\text{India}}{\text{Haryana}}\right)$		20.4 ± 1.05		[22]
Garlic $\left(\frac{\text{Iran}}{\text{Tehran}}\right)$	9202 ± 276	10 ± 1	391 ± 19	Present data
Ginger (Nigeria)	21.50	0.02	50	[21]
Ginger (Ethiopia)		184-401		[23]
Ginger $\left(\frac{\text{Iran}}{\text{Tehran}}\right)$	15259 ± 981	157 ± 9	2849 ± 130	Present data
Cinnamon $\left(\frac{\text{Poland}}{\text{Galeo}}\right)$		19.1 ± 0.1		[20]
Cinnamon $\left(\frac{\text{Poland}}{\text{Prymat}}\right)$		18.7 ± 0.1		[20]
Cinnamon $\left(\frac{\text{Poland}}{\text{Kamis}}\right)$		5.50 ± 0.12		[20]
Cinnamon $\left(\frac{\text{Iran}}{\text{Tehran}}\right)$	3850 ± 134	335 ± 20	153 ± 7	Present data

Table 5. INAA results of LICHEN (IAEA-336)

Element	Measured value (ppm) Mean (min – max)	Recommended value (ppm) (min – max)
Al	695 (650 – 730)	680 (570 – 790)
V	1.54 (1.32 – 1.61)	1.47 (1.25 – 1.69)
K	1850 (1780 – 1950)	1840 (1640 – 2040)
Mn	67 (64 – 71)	63 (56 – 70)
Na	315 (295 – 330)	320 (280 – 360)
Cl	1960 (1850 – 2030)	1900 (1600 – 2200)
Br	12 (10.8 – 13.9)	12.9 (11.2 – 14.6)
As	0.67 (0.60 – 0.76)	0.639 (0.55 – 0.71)

The concentrations of As in the thyme and plantain were within the MPL. This element is supposed to be toxic in nature. The high level of As can lead to harmful effects on the skin, lungs, liver, and bladder. Its minor effects can cause nausea, vomiting, and even damage to the blood vessels [19].

For the purpose of quality assurance, a standard reference material of biological origin, known as IAEA-336 (Lichen) was employed. The measured concentrations of the elements in Lichen were in good agreement with the recommended values of the same reference material.

4. Discussion

The measured concentrations of K, Mn, and Na in the black pepper, red pepper, and cinnamon were compared with those reported in other countries (e.g., Poland, Nigeria, India, and Ethiopia) (Table 4). As the findings of the present study indicated, the measured concentrations of K and Na in the black pepper, garlic, and ginger were significantly higher in this study than the values reported in Nigeria.

In addition, the Mn levels in the black pepper and garlic consumed in Tehran were comparable with those used in Poland; nevertheless, they were markedly higher than those in Nigeria. The quality control of the measurements was established from the results of analyzing IAEA-336 (Lichen). As shown in Table 5, the measured concentrations of the elements in Lichen, which are based on the averages of five measurements, were in good agreement with the recommended values of the same reference material.

5. Conclusion

The present study generated data regarding the essential and toxic elements in 11 popular spices used in Tehran. The elemental analysis of these spices indicated their richness in K, Na, Cl, and Al. In general, the data obtained in this study demonstrated that the investigated spices are additional sources of essential element intake. Furthermore, the results of some measurements indicated that the spices might also contain some toxic elements. The levels of As determined in this study were below the MPL. Therefore, the daily use of the spices will have no risk if taken in a limited quantity; however, they should be under continuous monitoring.

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