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Concentration Measurement of 12 Elements in Five Herbal Plants Using Neutron Activation Analysis Approach

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ABSTRACT

Introduction: Nowadays, many people use medicinal plants to manage diseases; therefore, detailed knowledge of the type and level of elements present in these plants is of prominent importance.The present study aimed to determine the weight fraction of 12 elements in the five most common medicinal plants in Iran. The names of these plants are caraway (Carum carvi), savory (Satureja hortensis), purslane (Portulaca oleracea), fenugreek (Trigonella foenum-graecum), and milk thistle (Silybum marianum) which were purchased from herbal pharmacies.

Material and Methods: The neutron activation method was used to determine the elements. In the current study, neutrons from the research reactor core in Tehran, Iran were used and gamma spectra from radionuclides were recorded using a high purity germanium detector. The mass fractions of 12 elements were determined in the five abovementioned plants.

Results: Caraway had the maximum amounts of elements of Fe (8,789 ppm), Cr (8 ppm), and Na (517 ppm) among the selected plants. The savory contained maximum levels of Mn (95 ppm), Cl (3,702 ppm), Ca (18,328 ppm), K (21,562 ppm), and V (2.7 ppm) and the lowest amount of Fe (195 ppm), Zn (13 ppm), Ca (2,243 ppm), Al (99ppm), Mn (26 ppm), and Mg (177ppm) were observed in fenugreek.

Conclusion: The highest levels of Cr and Mg were obtained for caraway (8 ppm) and pursalne (3,915 ppm), respectively. These elements can help to decrease blood cholesterol and triglyceride levels. Furthermore, the results showed that these herbs were rich in essential nutrients for metabolic functions.

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Introduction

Currently, many people are interested in using medicinal herbs to manage diseases and their interest is growing every day. Therefore, it is important to determine the content of useful and non-profitable elements in them. There have been many studies on the benefits of using herbal medicines, including medicinal plants used to treat skin diseases and colitis, lower cholesterol and blood glucose, and control diabetes [1-5]. In contrast to chemical medicines, medicinal plants contain a large number of active substances, all of which are compatible with the nature of the human body. There are important studies on ways that herbs work on the body to manage diseases. In addition, scientists determined the concentrations of elements in medicinal plants. Some examples of concentration measurements include the application of the neutron activation analysis (NAA) method for the determination of the elements in an Indian medicinal plant, trace elements in six medicinal plants in Ethiopia, evaluation of low levels of elements in Chinese herbs, and determination of metals in Brazilian medicinal plants [6-9]. The main purpose of the mentioned study was to determine the mass containment of calcium (Ca), chromium (Cr), and magnesium (Mg), which can be very effective in the prevention and treatment of lipid disorders [10]. Among the herbs used to lower the level of blood lipids can be caraway, savory, purslane, fenugreek seed, and milk thistle. The present study analyzed the five commonly used types of popular medicinal herbs (e.g., savory, caraway, purslane, fenugreek, and milk thistle) in Arak, Iran, using the NAA method. In this method, a specific mass of 12 elements, including aluminum (Al), bromine (Br), Ca, Cr, chlorine (Cl), iron (Fe), sodium (Na), vanadium (V), *potassium* (K), Mg, *manganese* (Mn), and zinc (Zn) were determined because the therapeutic effects of these herbs largely depended on their contained elements.

Materials and Methods

Sampling and sample preparation

Five species of herbs, including caraway (Carum carvi), savory (Satureja hortensis), purslane (Portulaca oleracea), fenugreek seeds (Trigonella foenum-graecum), and milk thistle (Silybum marianum) were prepared from pharmacies of Arak, Iran. The current

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study determined a fraction of some elements by the NAA method. This method is an excellent technique because a large number of samples and many elements can be analyzed simultaneously with more accurate measurement results. In addition, this measurement method made no changes to the sample and a small sample size was sufficient for the analysis. The samples were cleaned to remove the washing dust with double-distilled water and were kept at room temperature for two days. The samples were then kept at an oven at 80° C for 6 h until they reached the constant weight. After drying, the samples were chopped, milled, and weighted. Subsequently, Samples were powdered using an agate mortar and then were passed through a 0.149 mm sieve to obtain a similar standard sample. Each sample (approximately 300-350 mg) was packaged in a polyethylene vial for neutron irradiation. Similarly, reference materials IAEA-V-10 and IAEA-336 were used as quality control and standard samples, respectively, given their similarities to the samples under study. In each series of measurements, two sets of standard materials (IAEA-336) and medicinal plants were prepared, one set for 2 min and the other for 2 h in a research reactor in Tehran, Iran, were irradiated using a pneumatic sample transfer system. To improve the accuracy of the results, the measurement was repeated 5 times. The thermal flux of neutrons at the measuring point was 3×10^{13} n.cm^{-2}.s^{-1} [11]. To determine Al, Mg, and V values, the gamma spectra of the samples and reference material were recorded immediately after the neutron irradiation. For elements with a short half-life, gamma spectra were recorded after 15 min to determine elements, such as Ca, Cl, K, Mn, and Na. To determine Br, Cr, Fe, and Zn, the samples were irradiated with neutrons for 2 h and their gamma spectra were recorded after a week. The half-life time of isotopes was obtained from references No. [12] and [13]. The radionuclides used in the analysis with their activation and counting time and gamma energies are listed in Table 1.

Gamma-ray spectrometry and analysis

Gamma-ray spectra of the samples were recorded using a high purity germanium detector as the samples were placed on its surface. Measurements were made using the detector model EGPC 5574 produced by Intertechnique Company, France, with a relative efficiency of 10% with its associated electronic equipment. The energy resolution (FWHM) for gamma radiation energy 1332.492 keV emitted during ^{60}Co nucleus decay was equal to 1.95 keV. The detector and preamplifier were shielded in a chamber consisting of three layers of lead, copper, and cadmium in 10 cm, 2 mm, and 1 mm thicknesses, respectively. This shield was used to reduce background radiation because soft cosmic rays (e.g., photons and electrons) were largely eliminated by the 100 mm-thick lead shield and did not enter the detector. X-rays (73.9 keV) emitted from the interaction of external radiation with lead are effectively absorbed by the copper layer. Cadmium also absorbs thermal neutrons in the environment and prevents them from entering the detector. [14]. Energy calibration was performed using a standard source, including ^{241}Americium, ^{137}Caesium, and ^{152}Europium. The level of elements in the samples was determined by WINSPAN 2004 gamma-ray spectrum analysis software based on Equation 1 [15]. Using the comparative method, the level of elements in the sample was determined according to values given in the reference material:

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

where C_s is the concentration of an unknown level of element in the sample, and C_{st} is the concentrations given in the standard sample. A_s and A_{st} are the activities of the produced radioisotope in the sample and standard, t_d is the decay time of the interested radioisotope in the sample and in the standard, $\left(e^{-\lambda t_d}\right)_s$ and $\left(e^{-\lambda t_d}\right)_{st}$ are the decay rates for the sample and standard sample, respectively.

To verify the accuracy and method of measuring the gamma spectrum of the reference material, IAEA-V-10 (Hey powder) was analyzed as quality control and its elements were determined. The quality of the results was evaluated using the Z-score equation [16] as follow:

$$z = \frac{x-c}{\sqrt{u_x^2+u_c^2}} \quad (2)$$

Table 1. Radionuclides, activation and counting time, and gamma-ray energies

Elements	Radioisotope	Half-life	Measured Gamma-ray energy (keV)	Description
Al	^{28}Al	2.24 m	1778.969	Activation time:
Mg	^{27}Mg	9.46 m	1014.52	2 min
V	^{52}V	3.743 m	1434.06	counted immediately after activation
				Counting time: 300 s
Ca	^{49}Ca	8.718 m	3180.317	Activation time:
Cl	^{38}Cl	37.24 m	1642.66	2 min
K	^{42}K	12.40 h	1524.67	counted15 min after activation
Mn	^{56}Mn	2.58 h	1810.757	Counting time:
Na	^{24}Na	14.997 h	1368.62	900 s
Br	^{82}Br	35.4 h	654.75	
Cr	^{51}Cr	27.69 d	320.0824	Activation time:
Fe	^{59}Fe	44.63 d	1099.245	2 h counted after one week for 80000 s
Zn	^{65}Zn	243.93 d	1115.549	

where x is the result obtained from the analysis, c is the certified value, u_x, u_c are uncertainties of measured and certified values, respectively. The measurement error of the results based on the spectral analysis was calculated as a statistical error, while the uncertainty of the reported values was obtained from the existing certificate. Moreover, the Horwitz function was used to evaluate the error value mentioned in the certificate [17]. For results to be acceptable, they must be in the range of -2<z<2; however, if z value was obtained at z<-3 or z>3, this result is unacceptable and corrective action should be taken.

Results

For the purpose of quality control, the reference material IAEA-V-10 was prepared irradiated in the same conditions and the gamma-ray spectrum was registered and analyzed. The results of this analysis are presented in Table 2. Standard deviation and Z-score calculation are shown in Figure 1 which for all samples, the Z-Score ranged within ±2. According to Figure 1, for all the elements of interest, the Z-score is in the range of ±2; therefore, the measured concentrations of the elements in the reference material were in agreement with the levels reported by the International Atomic Energy Agency. Four samples were prepared for each medicinal herb and their gamma spectrum after neutron irradiation was analyzed and the concentrations of elements were determined. The average values of the elements measured in the studied medicinal plants are demonstrated in Table 3. The specific mass of trace elements was calculated for all the herbal plant samples. For the purpose of method validation and quality assurance, quality control sample IAEA-V-10, namely Hey powder was analyzed along with the samples. The results of the measurements showed that the measured concentrations of elements in the activated reference material were in agreement with the certified values (Table 2).

Table 2. Measurement of quality control for reference material V-10 (Hey powder) and quantity of Z-score

Elements	Provided value (ppm)	95% Confidence interval (ppm)	Measured value (ppm)	Z-Score
Al	47	30-87	50±10	0.17
Br	8	7-11	6.9±0.7	-0.91
Ca	21600	21000-22200	24259±1810	1.44
Cr	6.50	5.6-7.1	5.4±0.5	-1.76
Fe	186	177-190	177±5	-1.41
K	21000	19600-22500	23450±1200	1.74
Mg	1360	1330-1450	1420±15	1.79
Mn	47	44-51	44±1	-1.49
Na	500	440-570	620±90	1.25
Zn	24	23-25	24.6±0.7	0.69

Table 3. Mean elemental concentrations and standard deviations of medicinal plants (ppm)

Common name	Caraway	Savory	Purslane	Fenugreek seed	Milk thistle
Scientific name	Carum carvi	(Satureja hortensis),	(Portulaca oleracea),	(Trigonella foenum-graecum seed)	(Silybum marianum)
Fe	8789±55	1716±36	269±14	195±8	804±43
Zn	35±2	19±1	41±2	13±1	154±7
Cr	8.0±0.1	ND	1.5±0.1	1.3±0.1	ND
Br	ND	ND	3.0±0.1	5.0±0.1	2.0±0.1
V	ND	2.7±0.3	0.6±0.1	ND	1.9±0.1
K	12060±815	21562±862	9286±527	14533±581	8142±391
Na	517 ±9	439±5	127±3	535±13	497±7
Ca	11400±1036	18378±1318	2729±447	2243±224	12342±871
Cl	1518±29	3702±43	449±12	1990±29	3062±83
Al	559±27	753±23	131±10	99±14	1197±20
Mn	35±1	95±2	77±2	26.0±0.1	64±1
Mg	3409±311	2147±121	3915±826	177±12	2992±190

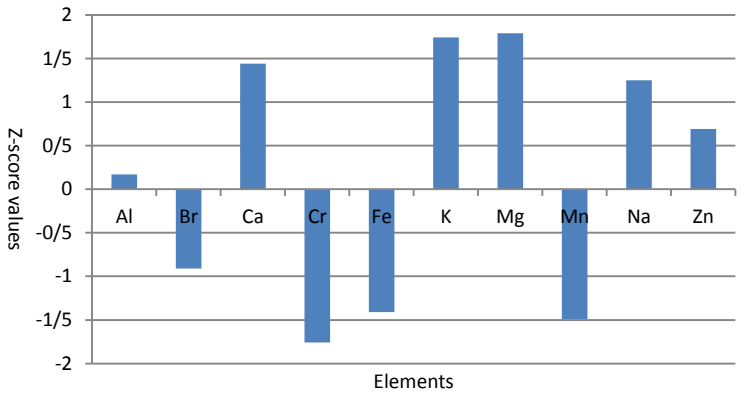

Figure 1. Control charts showing the z-scores of the analyzed reference materials IAEA-V-10

Discussion

Based on the findings of the present study, the caraway contained maximum concentrations of Cr (8 ppm), Fe (8,789 ppm), and Na (517 ppm). The maximum concentration of Zn (154 ppm) was obtained from milk thistle and the highest amount of Mg (3,915 ppm) was observed in the purslane. The savory contained the maximum concentration of Ca (18,378ppm) and Mn (95 ppm). These herbal plants may be an ample source of Cr, Zn, Mg, and Ca. The results of the current study confirmed that these herbal plants can help people to reduce their lipid and cholesterol levels because they contained elements, such as Ca, Cr, and Mg [18]. For adults, the daily intake of Ca, Cr, Mg, and Zn is 1000 mg, 120µg, 350 mg, and 15 mg, respectively. Therefore, a small amount of these herbal plants can help the intake of these useful elements. In addition, most of these medicinal plants contain useful elements, such as Fe, K, whose recommended daily intakes are 15 mg and 3,500 mg, respectively. The maximum amount of Br (5 ppm) was observed in the fenugreek seed. The acceptable Br level set by the United Nations Food Organization and the International Health Organization (FAO and WHO) for products that have not been used with disinfectants can range from 0 to 20 mg/kg [19]. The Br tolerable daily intake for daily absorption in the body by FAO/WHO ranges within 0–1 mg/kg of the bodyweight [20]. This value covers this range and is the same range for wheat crops in Iran [21]. Al is the third most abundant element in the earth's crust and it can enter the human body in different ways. According to WHO, tolerated daily aluminum intake is estimated at an average of 0.0001 bodyweights of an adult weighing 60kg, while less than 15mg is absorbed by food intakes (FAO/WHO, 1989) [20]. The level of Al in these herbal plants is limited, compared to the acceptable daily intake; therefore, no risk threats those consuming these herbs. The role of Al in the metabolism of the humans' bodies is still unknown and it is believed that increased metabolic activities can cause illness.

Conclusion

In the present research, concentrations of 12 elements were determined in five medicinal plants employing the NAA method. According to this method, the level of Al, Br, Ca, Cl, Cr, Fe, K, Mg, Mn, Na, V, and Zn in caraway, savory, purslane, fenugreek seed, and milk thistle were calculated. These medicinal plants are widely used by Iranians to prevent various diseases. The current study showed that these plants were useful in providing the necessary elements for human bodies and can compensate for their deficiency. Furthermore, unnecessary elements were lower than the allowable quantity announced by the WHO.

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