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Determination of trace elements in the seeds of fruits using instrumental neutron activation analysis (INAA) in Arak, I.R. Iran

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Abstract In this study, four fruit's seed samples as *Punica granatum* L., Citrus medica var. limonum, *Malus domestica* L. and Citrus vulgaris Risso were prepared from Arak's markets. They were analyzed using instrumental neutron activation method (INAA). In this method, Tehran research reactor as a neutron source and relative INAA method has been used as the analysis method and to record gamma ray spectrum, the high purity germanium detector was used. Pomegranate seeds had the highest number of essential elements. Apple seeds and sour orange seeds contain the highest levels of Mg and K, Respectively.

Keywords Fruit · Trace element · Neutron activation · Seed · Arak · Iran

Introduction

Determination of trace elements including also toxic elements is necessary in human foods. Decrease of useful elements or increase of toxic elements brings up some short comings or serious diseases, respectively. In each area, the absorbed elements in foods is different, as foods might be produced in area which is contaminated by industrial material or these materials are exceptionally abundant in soil [1]. One of the most importance mineral compounds storage in seeds is phytate, a mixed cation salt of phytic acid. Phosphorus, phytic acid and phytate in seeds and fruits are found to be significant. Phytic acid has 12 hydrogen (on the 6 phosphate groups) Which are dissolved in water. These negatively charged bind mainly K^+ and Mg^{2+} but may also form salts with other compound including Ca^{2+}, Mn^{2+}, Zn^{2+}, Ba^{2+} or Fe^{3+} [2]. Fruit has been recognized as a good source of vitamins and minerals. The nutrients in fruit are vital for health and maintenance of our body. People who eat fruit as part of an overall healthy diet generally have a reduced risk of chronic diseases. In Iran, the seeds of some fruits are used as drugs. The potassium in fruit can reduce risk of heart disease and stroke for human. Folate (folic acid) helps the body form red blood cells and also helps prevent neural tube birth defects, such as spina bifida [3].

An ultrasensitive nuclear analytical technique, analysis by neutron activation method is applied for determination of halogens. This technique is an appropriate method because samples can be analyzed simultaneously for large number of elements with more precise measurement results. INAA is nondestructive measurement method and there is no need for sample digestion and only a few amounts of samples are needed. In this paper the Fe, Zn, Sc, Sb, Cr, Br, La, K, Na, Al, Mn and Mg values of four kind of fruit seeds from Iran have been measured using instrumental neutron activation analysis (INAA) method. These seeds are often used in Iran as herbal Medicine. Lastly, a comparison between this results and some other reported results, were done.

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Experimental

Sampling and sample preparation

In this work, 50 fruits of each kind of fruits were randomly collected from the local market of Arak city in Iran which included golden apple (*Malus domestica* L.), lemon (Citrus medica var. limonum), sour orange (Citrus vulgaris Risso) and pomegranate (*Punica granatum* L.). Then, seeds of each kind of the fruits were separated and mixed. Four samples of each kind of seeds were analyzed and the mean and standard deviation were determined. After sampling, samples were changed into powders using an agate mortar. In order to make them homogenous, sieved to pass through mesh with 0.149 mm diameter and dried at 80 °C in an oven for 4 h. Samples (about 300–350 mg) were sealed in polyethylene vial prior to neutron irradiation. Similarly, for quality control purpose reference materials IAEA-336 (about 50–60 mg) was prepared and was analyzed together with samples.

Using the pneumatic sample transfer system, the sample and standard reference material (IAEA-V 10) were irradiated for 2 min at Tehran Research Reactor. The thermal neutron flux was about 3×10^{13} n·cm^{-2}·s^{-1} [4]. The sample and standard reference material were counted immediately after irradiation to determine Al and were counted 15 min after irradiation to determine the amount of elements with short half-life of radionuclides such as Mn, Na, Mg and K. For measurement amount of Fe, Zn, Sc, Sb, Cr, Br, La and As the samples were irradiated for 2 h and counted after 1 week [5]. The radionuclides used in the analysis with their gamma energies, irradiation time, and counting time and conditions are listed in Table 1.

Spectrometry and spectrum analysis

After irradiation, samples were placed for gamma ray spectrometry in face to face of high purity germanium (HPGe) detector. Detection was performed using (EGPC 5574 model, manufactured by Intertechnique, France) with 10% relative efficiency coupled with multi-channel analyzer. The energy resolution (FWHM) for gamma-ray (^{60}Co) with 1332 keV energy was 1.95 keV. The detector and preamplifier are shielded in a chamber of three layers composed of 10 cm thick lead, 1 mm thick cadmium, and 2 mm thick by copper. This shield serves to reduce background radiation. The soft components of cosmic ray, consisting of photons and electrons, are reduced to a very low level by 100 mm of lead shielding. The X-ray (73.9 keV) emitted from lead by its interaction with external radiation is suppressed by copper layer and cadmium layer successively, absorbing thermal neutrons produced by cosmic ray [6].

The concentration of the elements in the activated samples were calculated quantitatively using the gamma-ray spectrum analysis software packages known as Winspan 2004 that uses Eq. (1) to determine the concentrations of the elements in a sample in comparison with the known masses of the elements in 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 and C_{st} are concentrations of unknown analyte (interested element) in the sample and standard; A_s and A_{st} are the activity rates of unknown analyte in the sample and standard, t_d is the decay time of the unknown element in the sample and in the standard, $\left(e^{-\lambda t_d}\right)_s$ and $\left(e^{-\lambda t_d}\right)_{st}$ are the decaying factors for seed sample and standard sample respectively.

Figure 1 shows an example of spectra of pomegranate seed for Fe.

Table 1 Radionuclides, gamma ray energies, irradiation and counting time and conditions

Element	Reaction	Half life	Energy (keV)	Irradiation and counting conditions
Al	^{27}Al(n,γ) ^{28}Al	2.24 months	1779	2 min irradiation, counted immediately after irradiation for 300 s
Mn	^{55}Mn(n,γ) ^{56}Mn	2.58 h	1810	2 min irradiation, counted 15 min after irradiation for 900 s
Na	^{23}Na(n,γ) ^{24}Na	15.00 h	1368	
Mg	^{26}Mg(n,γ) ^{27}Mg	9.46 months	1014	
K	^{41}K(n,γ) ^{42}K	12.40 h	1525	
Fe	^{58}Fe(n,γ) ^{59}Fe	44.63 days	1099	2 h irradiation, counted 1 week after irradiation for 60,000 s
Zn	^{64}Zn(n,γ) ^{65}Zn	244 days	1115	
Sc	^{45}Sc(n,γ) ^{46}Sc	83.82 days	889	
Sb	^{121}Sb(n,γ) ^{122}Sb	2.7 days	564	
Cr	^{50}Cr(n,γ) ^{51}Cr	27.69 days	320	
Br	^{81}Br(n,γ) ^{82}Br	35.4 h	554	
La	^{139}La(n,γ) ^{140}La	40.22 h	1596	

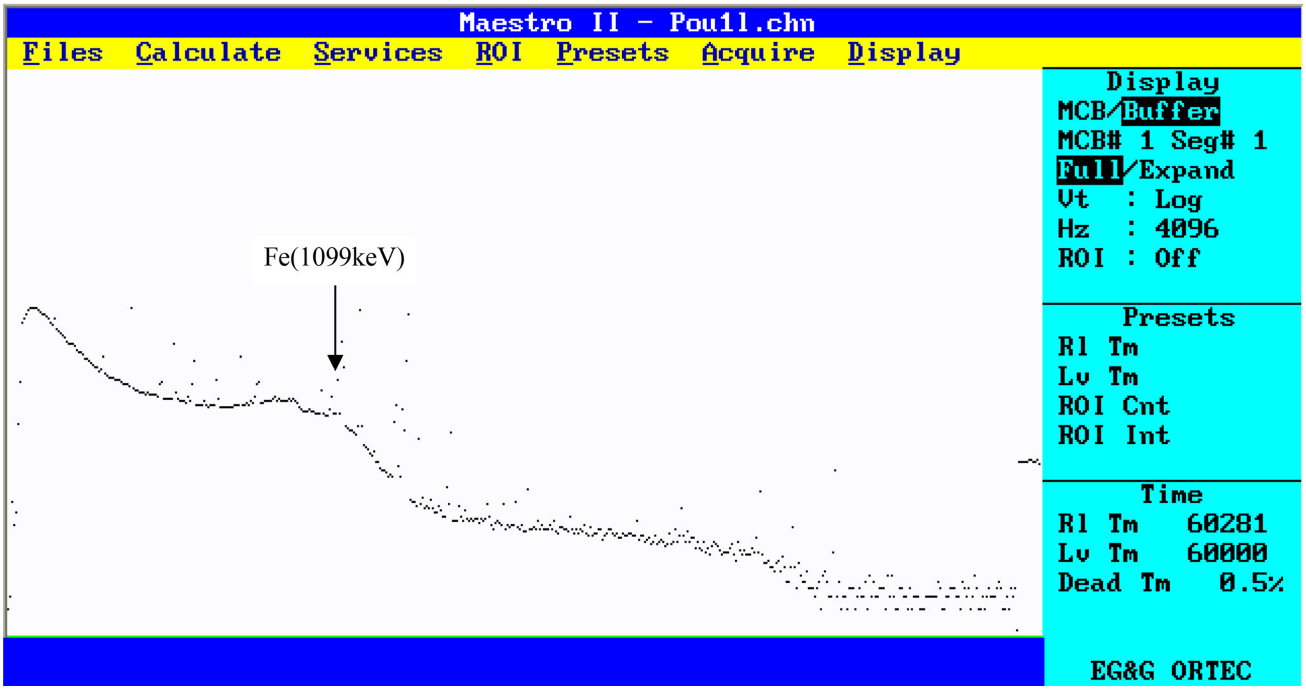

Fig. 1 Gamma-ray spectrum of POU sample

Table 2 Concentrations of elements in IAEA-336 reference materials

Elements	Recommended value (ppm) (probability level 0.05)	Standard deviation (ppm)	Measured value(ppm) (probability level 0.05)	*Z* score
K	1840 (1640–2040)	100	1890 (1758–2022)	0.50
Na	320 (280–360)	20	345 (321–369)	1.25
Mn	63 (56–70)	3.5	65 (60–69)	0.57
Al	680 (570–790)	55	726 (661–791)	0.84
Fe	430 (380–480)	25	464 (436–491)	1.36
Zn	30.4 (27.0–33.8)	1.7	32 (30–34)	0.94
Cr	1.06 (0.89–1.23)	0.085	1.21 (1.11–1.31)	1.76
Sb	0.073 (0.063–0.083)	0.005	0.071 (0.066–0.079)	− 0.40
Sc	0.17 (0.15–0.19)	0.01	0.16 (0.15–0.17)	− 1.0
La	0.66 (0.56–0.76)	0.05	0.65 (0.57–0.73)	− 0.20
Br	12.9 (11.2–14.6)	0.85	13.1 (12.2–13.8)	0.24

Result

For Quality control purpose, gamma ray spectrum of reference material IAEA-336 was collected and was analyzed. Results of this analysis are listed in Table 2. Standard deviation and *Z* score model calculation given in Table 2 which for all samples the *Z* score ranges within ± 3. The concentrations of trace elements were calculated for fruit's seeds samples. Result for average trace concentrations for all fruit seeds included common and scientific name are given in Table 3. Our result indicated that pomegranate seeds contain maximum concentrations of Fe (74 ppm), Zn (24 ppm) and Na (268 ppm) and may be use an ample source of Mn, Mg and K for human.

Golden apple seeds contain the highest levels of Mg (1976) with sufficiently high levels of Fe, Na and K. They were included the least content of Cr, Al, Mn. Highest Cr (1.8 ppm) and Al (5.1 ppm) concentrations were obtained for lemon seeds while their Zn, Mg contents are lower than other seeds. For lemon Sb was below detection limits

Table 3 Mean elemental concentrations and standard deviations of the fruit seeds (ppm)

Sample code	POU	LIG	GAS	SOG
Common name	Pomegranate	Lemon	Golden Apple	Sour orange
Scientific name	*Punica granatum* L	Citrus medica var. limonum	*Malus domestica* L	Citrus vulgaris Risso
Fe	74 ± 3	41 ± 3	47 ± 2	30 ± 2
Zn	24 ± 2	5.1 ± 0.3	8.9 ± 0.5	11.2 ± 0.5
Sc	ND	0.011 ± 0.001	0.0022 ± 0.0003	0.0127 ± 0.0019
Sb	0.025 ± 0.003	ND	ND	ND
Cr	0.11 ± 0.02	1.8 ± 0.2	0.045 ± 0.005	0.89 ± 0.07
Br	1.3 ± 0.1	0.13 ± 0.01	ND	ND
La	0.0041 ± 0.0007	0.0024 ± 0.0005	ND	ND
K	4084 ± 245	5496 ± 329	4995 ± 300	6700 ± 400
Na	268 ± 16	76 ± 5	91 ± 6	48 ± 3
Al	3.8 ± 0.3	5.1 ± 0.5	3.2 ± 0.3	3.4 ± 0.3
Mn	9.7 ± 0.9	5.2 ± 0.5	3.6 ± 0.3	3.9 ± 0.4
Mg	1126 ± 101	798 ± 72	1976 ± 177	1214 ± 110

Table 4 Comparison of trace elements (ppm) in fruits in this work with results of some countries

Fruit and seeds	Cr	Fe	Mg	Mn	Na	Zn	Sc	Reference
Apple (Pakistan)	0.39	172	1232	6.5	587	35.7	0.027	[7]
Apple (USA)	0.43	9.3	297	4.3	15	1.4	–	[10]
Apple seeds	0.045	47	1976	3.6	91	8.9	0.022	This work
Pomegranate (Pakistan)	0.47	145	1350	4.2	222	9.8	0.016	[7]
Pomegranate (Bangladesh)*	–	0.03	1.2	–	0.4	0.025	–	[9]
Pomegranate seeds	0.11	74	1126	9.7	268	24	ND	This work
Orange (Pakistan)	0.11	85	630	4.1	347	16	0.019	[7]
Orange (USA)	0.06	8.9	704	1.5	1.42	0.04	–	[10]
Orange (Bangladesh)*	–	0.04	1.62	–	2.8	0.048	–	[9]
Sour orange seeds	0.89	30	1214	3.9	48	11.2	0.013	This work
Lemon (Bangladesh)*	–	0.023	1.2	–	0.15	0.012	–	[9]
Lemon (Iran\Iranshahr)	–	1.6	55.2	–	167.1	0.09	–	[8]
Lemon (Iran\Gorgan)	–	3.7	401.6	–	27.9	1.5	–	[8]
Lemon seeds	1.8	41	798	5.2	76	5.1	0.011	This work

* Basis on fresh weight of edible part

(ND). Sour orange seeds had high Sc (12.7×10^{-3} ppm) and K (6700 ppm) levels while they were contained low amount of Na. In sour orang sample the Sb, Br and La were below detection limits. The As concentration was below detection limits for all analyzed samples.The results showed that levels of Sc, Cr and K in citrus family seeds were more than the rest. In Table 4, the determined mean concentrations of various elements in fruit seeds were compared with the reported values from other countries [7–10]. Concentration levels of Fe, Cr and Sc in apple and pomegranate from Pakistan were more than apple seeds. Mg in pomegranate was more than pomegranate' seeds while this element had stored in apple seeds more than apple. Apple from Pakistan had more Zn, Na and Mn than apple's seeds but concentration of these elements in pomegranate seeds were more than pomegranate.

According to reported values from Pakistan, most of elements in apple and pomegranate are more or the same range of the seeds measured in this work [7]. Lemon and sour orange belongs to the citrus family with more concentration Mg in seeds than fruits and similarly Fe in lemon seeds is higher. The Iranian lemon was richer than

Bangladesh in terms of mineral such as Fe, Mg and Zn [8, 9]. Amount of sodium concentration for one kind of Iranian lemon (Iranshahr) in compare with other is so much. Differences of trace elements for most of elements in apple originated from Pakistan and United State is so much [10]. For most of fruits undertaken study in this work, trace elements concentrations in seeds are more than edible part.

Conclusion and discussions

In this study concentrations of 13 elements were determined in four fruit' seeds employing instrumental neutron activation analysis method. According to this method were calculated amount of Fe, Zn, Sc, Sb, Cr, Br, La, K, Na, Al, Mn, Mg and As in seeds of *punica granatum* L, citrus medica var. limonum, *malus domestica* L and citrus vulgaris risso. Results of this research shows enrich of useful nutrients such Zn, Fe and Na in pomegranate seeds and Mg in apple seeds, which can be used their powders as edible part or can be added to another foodstuff. The Recommended Dietary Allowances (RDAs) of Zn, Mn and Fe are 15, 2.5–5 mg/day and depend on age and gender 8–18 mg/day respectively [11]. For Mg at least intake is 100 mg/day. According to these criteria 100 g of pomegranate seeds can be supply adequate nutrients consumption. Also Sour orange seeds and apple seeds are rich in K and Mg, respectively.

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