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Analysis of trace elements in various types of Iranian and imported rice using the neutron activation method

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HIGHLIGHTS

- Various varieties of rice were studied.
- Trace elements were determined using the neutron activation analysis method.
- The neuron's activation and gamma radiation spectra were used.
- Useful and harmful elements were determined.
- ICP-AES inductively coupled plasma used.

ABSTRACT

The body absorbs trace elements from food, which can have positive and negative effects depending on their type and amount. The study aimed to determine the amount of trace elements found in different varieties of Iranian rice and imported varieties. The concentration of trace elements in rice samples was measured by neutron activation analysis and inductively coupled plasma (ICP-AES). Elements concentrations (mg.kg^{-1}) were determined for aluminum (2.92-9.16), arsenic (0.064-0.156), bromine (0.24-5.20), calcium (102-981), chlorine (132-323), chromium (ND -20.4), lead (ND-0.232), cadmium (0.010-0.115), scandium (0.001-0.007), magnesium (262-519), manganese (2.97-18.50), sodium (3.99-14.30), mercury (ND- 0.002), zinc (2.62-23.60). This study found that Indian rice contains higher levels of bromine, calcium, and sodium, while Pakistani rice contains higher amounts of aluminum, chlorine, lead, and mercury. Shirodi rice is known to have higher levels of arsenic and magnesium, Tarem Hashemi rice has been found to contain higher amounts of chromium, manganese, and zinc, and cadmium is found in Sadri rice. However, the amount of toxic elements in all types of rice does not pose a significant threat to human health.

KEYWORDS
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Elements

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1 Introduction

One of the most important goals of any country's health system is to improve the health level of people in the society. Every person who wants to live a healthy and quality life in society should care about his health and the society he lives in. One of the most important effective factors for ensuring the health of people in society is healthy and nutritious nutrition. The lack or excess of nutrients in the human body can lead to various diseases, so it's important to understand the elements present in food (Shirani et al., 2019). Rice is a significant source of micronutrients and is the second most widely consumed grain after wheat, providing sustenance to over half of the world's population. Since rice is cultivated in diverse regions with varying environmental conditions, the elements present in the water and soil can be absorbed by the rice and subsequently enter the human body (Smith, 1995). According to a report by the Food and Agriculture Organization of the United Nations (FAO), world rice production is estimated at 787 million tons (Tayyib, 2023). Iran produces about 800,000. tons per year, which also imports about 400 thousand. tons for domestic needs. In this study, the concentrations of 14 elements Al, As, Br, calcium, chlorine, chromium, lead, cadmium, Sc, magnesium, manganese, sodium, mercury, and zinc were investigated by neutron activation analysis and inductively coupled plasma in different varieties of Iranian rice and some imported. All rice samples

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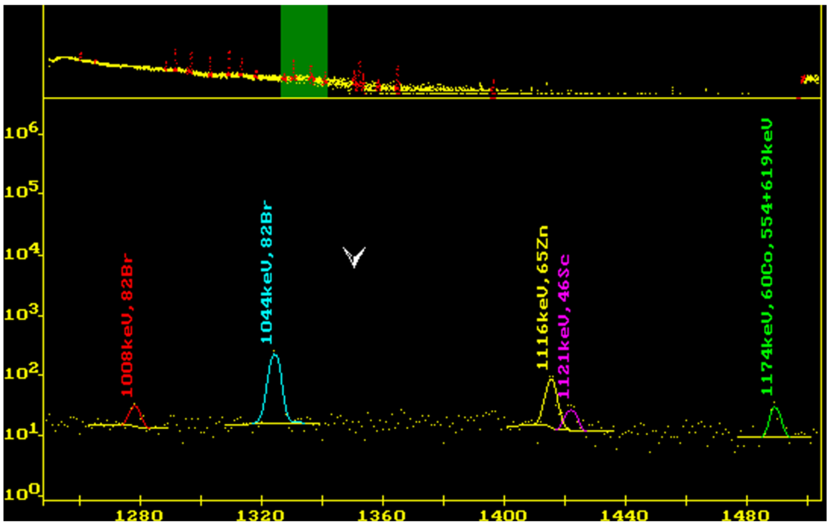

Figure 1: Gamma-ray energy spectr for Tarom Hashemi sample (keV).

were collected from a market in Arak, Iran. Neutron activation analysis is one of the most accurate techniques for measuring the concentration of trace elements (Grynpas et al., 1987). Its most important advantage is maintaining the nature of the sample, simultaneous analysis of several elements, and the need to collect samples in small quantities. Inductively coupled plasma (ICP) analysis is also one of the most accurate methods for measuring the concentration of metallic elements, which quantitatively and qualitatively analyzes over 70 elements in the ppm and ppb range (Thompson, 2012). In recent years, many efforts have been made to measure trace elements in food in Iran and other countries (Kashian et al., 2020; Reza et al., 2018).

2 Experimental method

2.1 Sampling and sample preparation in neutron activation analysis

Seven varieties of rice, including 4 varieties of Iranian Sadri, Shiroodi, Tarem Hashemi and Ramadani and 3 types of rice imported from Thailand, India and Pakistan were prepared directly from the market of Arak city. Table 1 lists sample names and codes. To analyze the concentration of elements in different varieties of rice by neutron activation method, Isfahan Miniature Reactor (MNSR) was used as a source of thermal neutrons. The core of this reactor is surrounded by beryllium reflectors.

Table 1: Coding of rice samples.

Sample	code
Thailand rice	R1
Indian rice	R2
Pakistani rice	R3
Sadri rice	R4
Shirodi rice	R5
Tarom Hashemi rice	R6
Ramazani rice	R7

The internal neutron irridiation channels are inside the beryllium and the external irrdiation channels are outside it. The neutron flux in the internal and external channels was 10^{12} cm^{-2}.s^{-1} and 5×10^{11} cm^{-2}.s^{-1}, respectively (Bode and Van Dijk, 1997). 5 mg of each sample was transferred using a pneumatic system to the radiation channel of the reactor. The neutron flux for Al, Ca, Cl, Mg, Mn and Na was 2.5×10^{11} cm^{-2}.s^{-1}, and for the remaining elements 5×10^{11} cm^{-2}.s^{-1}. After irradiation, the sample was sent to the HPGe detector chamber according to a specific schedule using a high-speed penomatic system (Norman et al., 1988). Information about the radioisotopes used, gamma line energy, irradation time, delay time, neutron flux, and gamma spectrum recording time is given in Table 2 (Norman et al., 1988). The gamma radiation spectrometer was an HPGe detector model GEM-2180-Pa from ORTEC. This detector operated at 3000 volts and its full width at half maximum (FWHM) for 1.332 MeV belonging to Co-60 was 1.2 keV and the relative efficiency was 21.5%. The detector uses the ORTEC-670 s amplifier and a 4000-channel multi-channel analyzer. Figure 1 shows the spectrum of Tarom Hashemi rice. The spectra acquired by this detector are analyzed using Span software, developed by the China Atomic Energy Initiative with the Dos operating system, for sample analysis (Pourimani et al., 2021).

These studies used a comparative method to measure the concentration of elements. The reference material contains the same elements as the unknown sample. By comparing the number of gamma photons recorded for a specific peak in both reference and unknown samples, the concentration of the desired element is determined using Eq. (1). Spectrum analysis and concentration calculations were performed using the SPAN program (Pourimani et al., 2019).

$$C_{ns} = C_{st} \frac{A_{ns}\left(\mathrm{e}^{-\lambda t_d}\right)_{st}}{A_{st}\left(\mathrm{e}^{-\lambda t_d}\right)_{ns}} \tag{1}$$

In this equation, C_{ns} and C_{st} represent the concentration

Table 2: Radionuclides, gamma-ray energies, irradiation and counting time and condition.

Element	Produced radioisotope	Half-life	Considered gamma-ray energy (keV)	Irradiation time	Description of spectra measurement
Al	Al-28	2.24 m	1778.98	1 m	Counting time of 500 s
Mg	Mg-27	9.46 m	1014.52	1 m	with a delay of
Ca	Ca-49	8.718 m	3084.40	1 m	10-15 s
Cl	Cl-38	37.24 m	1642.66	1 m	after irradiation
Mn	Mn-56	2.58 h	1810.76	1 m	Counting time of 1500 s with a
Na	na-24	14.997 h	1368.62	1 m	delay of 6 days after irradiation
As	As-76	26.24 h	559.101	5 h	Counting time of 2500 s with a
Br	Br-82	35.4 h	654.75	5 h	delay of 12 days after irradiation
Zn	Zn-65	244 d	1115.546	5 h	Counting time of 500 s
Cr	Cr-51	27.704 d	320.082	5 h	with a delay of 10-15 days
Sc	Sc-46	83.79 d	889.271	5 h	after irradiation

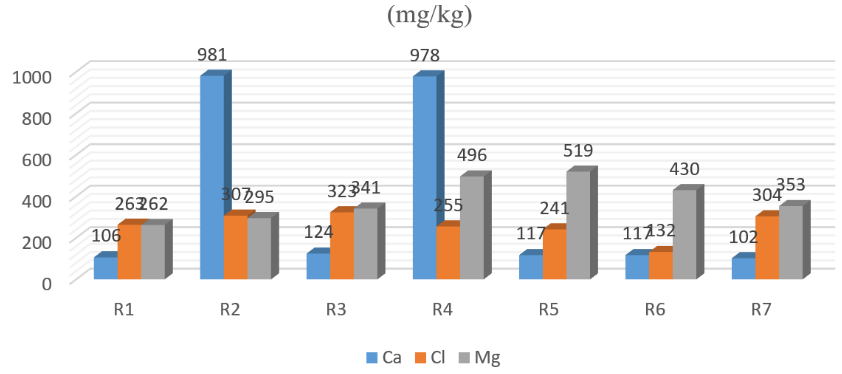

Figure 2: Histogram of Ca, Cl, and Mg value for different samples.

of an element in the unknown and standard samples, respectively. Also, A_{ns} and A_{st} are the activities of the element in the unknown sample and the standard sample, respectively. t_d is the decay time of the element in the unknown sample and the standard sample. $\left(\mathrm{e}^{-\lambda t_d}\right)_{st}$ and $\left(\mathrm{e}^{-\lambda t_d}\right)_{ns}$ respectively indicate the decay factors for the unknown sample. and are standard samples. The fractional number shows the number of photons recorded for the unknown element and the denominator shows the number of photons recorded for this element in the standard sample (Senila et al., 2014).

2.2 *Preparation of samples in ICP-AES*

To analyze the element concentration in different rice varieties by inductively coupled plasma method, the rice samples were separately powdered using an agate mortar, and 2 g of each rice sample was mixed with 2 cm^3 of 69% nitric acid and 2 cm^3 of 37% hydrochloric acid were mixed in special containers. The rice samples were digested for one hour in a microwave oven at a temperature of 140 degrees Celsius, a pressure of 40 bar, and a power of 90 W. The dilution process was carried out in a 25 cm^3 balloon, and after the rice samples were prepared, they were turned into fog using a suction device and injected into the ICP-AES device using a fogger. In order to eliminate interference and chemical disturbances, 3 appropriate emission lines were selected for each element and each analysis was repeated three times. Then, using Eq. (2), the exact concentration of the desired element was measured in $\mathrm{mg.kg^{-1}}$ (Senila et al., 2014):

$$\begin{aligned} &\text{The read value } (\mathrm{mg.L^{-1}}) \times \frac{0.025\ \mathrm{L}}{\text{weighed sample (kg)}} \\ &= \text{Element concentration } (\mathrm{mg.kg^{-1}}) \end{aligned} \tag{2}$$

3 Results and discussion

The concentrations of aluminum ranged from 2.92 to 9.16 $\mathrm{mg.kg^{-1}}$, arsenic from 0.06 to 0.15 $\mathrm{mg.kg^{-1}}$, bromine from 0.24 to 5.2 $\mathrm{mg.kg^{-1}}$, calcium from 102 to 981 $\mathrm{mg.kg^{-1}}$, chlorine from 132 to 323 $\mathrm{mg.kg^{-1}}$, chromium was not detected to 20.4 $\mathrm{mg.kg^{-1}}$, cadmium from 0.01 to 0.28 $\mathrm{mg.kg^{-1}}$, lead from not detected to 0.024 $\mathrm{mg.kg^{-1}}$, scandium from 0.001 to 0.007 $\mathrm{mg.kg^{-1}}$, magnesium from 262 to 519 $\mathrm{mg.kg^{-1}}$, manganese from 2.97 to 18.5 $\mathrm{mg.kg^{-1}}$, sodium from 3.99 to 14.30 $\mathrm{mg.kg^{-1}}$, mercury from not detected to 0.0023 $\mathrm{mg.kg^{-1}}$, and zinc from 2.62 to 20.30 $\mathrm{mg.kg^{-1}}$, as seen in Table 3. Figures 2 and 3 compare the essential elements of human organisms, which showed that samples R2 (Indian rice) and R4 (Sadri rice) were rich in Ca and Mg, and samples R6 (Tarom Hashemi) and R3 (Pakistani rice) were rich in Zn. The lowest content of the toxic element arsenic was found in R6 (Taram Hashemi) and R2 (Pakistani rice), 0.06 and 0.08 $\mathrm{mg.kg^{-1}}$, respectively, while for the rest of the samples it was almost constant and was approximately 0.14 $\mathrm{mg.kg^{-1}}$. Cr is an important element affecting the control of blood

Table 3: Concentration of elements (mg/kg) and their uncertainty in rice samples. In this table, “ND” denotes for “Not detected”.

Samples	R1	R2	R3	R4	R5	R6	R7
Al	3.23 ± 0.08	3.14 ± 0.08	9.16 ± 0.14	2.92 ± 0.08	3.14 ± 0.08	4.51 ± 0.09	3.36 ± 0.08
As	0.14 ± 0.01	0.08 ± 0.16	0.13 ± 0.01	0.15± 0.01	0.15 ± 0.01	0.06 ± 0.01	0.14 ± 0.01
Br	0.40 ± 0.03	5.2 ± 0.0	0.85 ± 0.04	0.45 ± 0.03	0.35 ± 0.03	0.24 ± 0.03	1.65
Ca	106 ± 16	981 ± 157	124 ± 17	978 ± 154	117 ± 17	117 ± 16	102 ± 15
Cl	263 ± 7	307 ± 7	323 ± 8	255 ± 7	241 ± 6	132 ± 5	304 ± 7
Cr	0.53 ± 0.11	ND	ND	0.61 ± 0.13	ND	20.4 ± 1.6	0.60 ± 0.12
Cd	0.01	0.02	0.06	0.12	0.28	0.05	0.06
Pb	0.003	0.021	0.010	0.024	0.232	0.011	ND
Sc	0.007 ± 0.001	0.003 ± 0.001	0.006 ± 0.001	0.006 ± 0.001	0.006 ± 0.001	0.002 ± 0.001	0.001 ± 0.000
Mg	262 ± 12	295 ± 11	341 ± 13	496 ± 15	519 ± 15	430 ± 15	353 ± 14
Mn	7.97 ± 0.14	2.97 ± 0.09	11	9.2 ± 0.1	9.59 ± 0.16	18.5 ± 0.2	5.82 ± 0.43
Na	5.85 ± 0.04	14.30 ± 0.80	5.66 ± 0.04	5.2 ± 0.1	5.31 ± 0.04	5.54 ± 0.04	3.99 ± 0.04
Hg	ND	ND	0.0023	0.0002	ND	ND	ND
Zn	15.10 ± 1.70	5.91 ± 1.18	20.30 ± 2.00	15.80 ± 1.70	2.62 ± 0.52	23.6 ± 2.0	19.20 ± 2.00

Table 4: Comparison of Ca, Sc, Na, Mg, Mn, Zn concentrations in rice with other countries ($mg.kg^{-1}$).

Country name	Ca	Sc	Na	Mg	Mn	Zn	References
Jamaica	117	0.001	21.3	1229	18.3	22.5	(Antoine et al., 2012)
Vietnam	-	0.02	18.43	-	11.60	17.01	(Van Tran and Teherani, 1989)
Thailand	117	-	-	550	19.7	20.7	(Parengam et al., 2010)
Italy	-	-	10.8	-	6.5	11.4	(Bode and Van Dijk, 1997)
India	290	0.346	-	-	28.6	26.1	(Norman et al., 1988)
South Korea	94.7	-	14	946	-	16.9	(Grant et al., 2013)
Brazil	118	-	-	560	20	19.4	(Barbosa et al., 2016)
Japan	-	-	12.94	-	11.86	-	(Badza and Jevremovic, 2014)
Nigeria	-	0.025	11.1	-	-	22.43	(Yamusa et al., 2013)
South Korea	94.7	-	14	946	-	16.9	(Grant et al., 2013)
Sadri	978	0.006	5.20	496	9.2	15.8	This work
Shirodi	117	0.007	5.31	519	9.59	2.62	This work
Tarom Hashemi	117	0.002	5.50	430	18.5	23.6	This work
Ramazani	112	0.001	3.99	353	5.82	19.2	This work

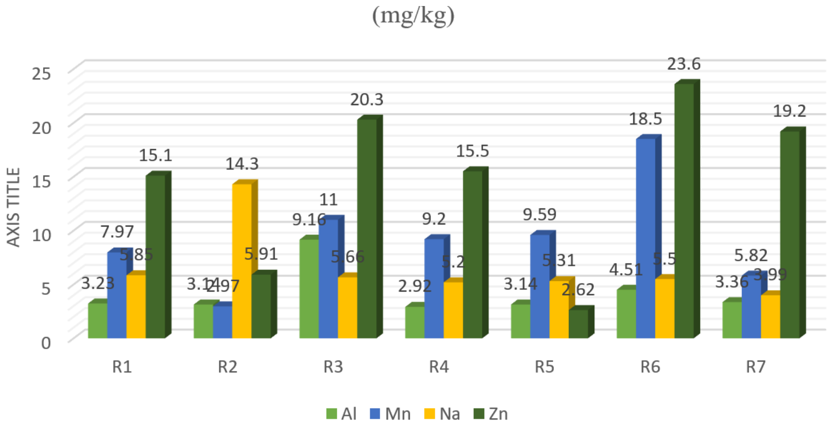

Figure 3: Histogram of Al, Mn, Na, and Zn value for different samples.

pressure and is useful for human health (Kashian et al., 2018). The results of the conducted research showed that the Tarom Hashemi variety was very rich in this element (20.4 $mg.kg^{-1}$) compared to other samples. Lead and cadmium are toxic and harmful elements. The maximum values observed for the Shiroudi variety were 0.23 and 0.28 $mg.kg^{-1}$, which were an order of magnitude higher than most other samples. Mercury is also a harmful element, which fortunately was not detected for most varieties, only for two varieties R3 and R4, which obtained amounts of 0.0023 and 0.0002 $mg.kg^{-1}$. The permissible limit for lead, cadmium and mercury in rice is estimated at 0.2, 0.2 and 0.5 $mg.kg^{-1}$ net weight, respectively, which is slowly being exceeded in the case of the Shiroudi variety (Canady et al., 2013). For arsenic, the value of the tolerable daily intake for one person with a body weight of 70 kg is estimated at 0.14 mg, which in the case of R4 and R5 varieties with the maximum arsenic content consumption 150 g per day, the value delivered to the body is 0.023 mg, which is a distant value from the tolerated value.

Table 4 compares the content of trace elements: calcium, scandium, sodium, magnesium, manganese, and zinc in rice from different countries. As the table shows, the calcium element content in Sadri rice was higher than that in rice from Jamaica, Thailand, India, Hungary, South Korea, and Brazil. The amount of trace element sodium in Iranian rice samples was lower than in the samples of other countries. The amount of useful element magnesium in the tested Iranian rice was average and less than some countries and more than some countries and obtained about 500 mg.kg^{-1}. The manganese content of Iranian Tarom Hashemi rice was higher than other samples from other countries and was on par with Jamaican rice. The important trace element zinc in Iranian Tarom Hashemi rice with a concentration of 23.6 mg.kg^{-1} was lower than in Indian rice and higher than in other countries. The concentration of the constituent elements ranged around several μg.kg^{-1}, which is not a toxic or useful element.

4 Conclusions

The results of this study show that Iranian rice is a good source of useful elements such as calcium, magnesium, zinc, and chromium for consumers, and there are very few toxic and harmful elements in them. The level of toxic elements was below the permissible limit and did not pose a threat to humans. Compared to other countries, Iranian rice has good quality.

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Conflict of Interest

The authors declare no potential conflict of interest regarding the publication of this work.

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