

Neutron activation analysis of Californian and Japanese rice

Stefan Badza · Tatjana Jevremovic

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Abstract The main motivation in studying different types of rice was to determine how processing of rice affects its mineral composition, and to compare how it affects rice dietary intake. Specifically the estimated difference in between the brown and white rice produced in Japan and California are studied. These various rice samples were analyzed using neutron activation analysis technique available at the Utah Nuclear Engineering Program (UNEP). Samples were prepared using novel technique developed at UNEP and submitted for short and long irradiation. The detected elements were As, Br, Cl, Cd, Mn, Na, K. The concentrations of Mn, K and Na are significantly higher in the brown than in the white rice, while As, Br and Cl have more homogeneous presence and therefore smaller difference in concentration. Elemental concentration was compared with The Institute of Medicine (IOM) in the United States values of recommended dietary allowance and Food and Drug Administration (FDA) limits for harmful elements. From these measurements, only the concentration of Mn in rice satisfies daily needs in the range set as defined by IOM. The concentrations of potentially harmful elements are lower than FDA limits.

Keywords White rice · Brown rice · Neutron activation analysis · Rice processing · Rice dietary intake levels

Introduction

Rice has a significant role in diet of more than two-thirds of world population. The consumption of rice in Japan is 59 kg per year per capita [1], while in the United States is 9.52 kg per year per capita consumed by 20 % of population [2]. Brown rice has unrefined grains and therefore contains dietary fiber, and traces of various minerals. White rice has refined grains and it lacks some of the minerals found in brown rice. Brown rice is produced when the husk of grain of rice is removed. White rice is produced when the next bran and germ layer of grain are removed.

Sampling and sample preparation technique

Brown and white rice samples were randomly collected from the bags of Californian and Japanese rice purchased in local stores in Salt Lake City, Utah. Analyzed samples of Californian and Japanese rice are of the same varietal. The lab procedure for preparing the rice samples for neutron activation analysis (NAA) is very important. The main aspect of samples preparation is to keep it as less contaminated as possible (for example from hand direct touches) and as much as possible homogenized to assure a uniform irradiation. The procedure for NAA rice samples included the following steps:

- (1) Rice grains were dried at room temperature for at least two days.
- (2) Sampled grains were cleaned with dry paper napkins.
- (3) To ensure homogeneity of a sample, grains were compactly packed into small polyvinyl plastic bags.
- (4) Representative metals in soil standard reference materials (Lot number: 014651; RTC chemicals) with

S. Badza (✉)
Faculty of Physics, The University of Belgrade, Belgrade, Serbia
e-mail: badza.stefan@gmail.com

T. Jevremovic
Nuclear Engineering Program, The University of Utah, Salt Lake City, UT, USA

known element composition are prepared in the same way.

- (5) One sample of each type of rice and one SRM are placed into polyethylene tube for irradiation in the reactor.
- (6) Mass of the samples and standard reference material (SRM) were between 50 and 100 mg.

Neutron activation analysis

Utah Nuclear Engineering Program houses numerous advanced laboratories with the state-of-the-art equipment for radiation measurements and detection, as well as the Training, Research, Isotopes, General Atomics (TRIGA) reactor; The University of Utah TRIGA Reactor (UUTR). A special thermal irradiation port (TI) is designated among other uses for NAA. The rice samples are irradiated in the TI at neutron flux of 3.76×10^{11} neutrons/cm² sec corresponding to 90 kW of the UUTR power. Samples were not counted before the activation because the producer guarantees that there is no radioactive contamination. For the first group of samples irradiation time varied from 1 min to 2 h. The optimal times for determining elemental composition were determined to be 5 min for short half-life isotopes and 90 min for longer half-life isotopes. The first group of samples that was exposed to a short irradiation time of 5 min; after irradiation the samples were left in the reactor pool to decay for 45 min before they were measured. The second group of samples that was exposed to a longer irradiation of 90 min and these samples were left to decay for 48 h before counting. The SRM samples were irradiated for the same time as respective rice samples. The short irradiation time was used to detect short half-life radionuclides (such as for example, Cl, Mn) [3], while the long irradiation time was used to detect radionuclides with longer half-lives (for example, As, Br, Cd, Na, K).

After samples decayed for a given time, they were placed into high purity germanium (HpGe) detector. All the samples were placed in the same fixed position above the HpGe detector. The geometry of the sample was the same as the geometry of the calibration. Sample size is negligible and is treated as a point source. No blanks were used. Background is subtracted by performing a 24 h background count. This background is then included as part of the algorithm GENIE uses that subtracts out the background automatically before giving an interference report. Measuring time varied from 10 to 30 min, depending on the activity of the samples. Activity data was turned into spectra and peaks were detected using the Genie 2K™ software. Generated interference reports were used for further analyses based on the in-house Microsoft Excel NAA calculator. The analysis included the following:

- Using SRM to determine the concentration of As, Mn, Na and K;
- Using data analysis of Microsoft Office Excel 2003 and known parameters of irradiation to determine concentrations of the elements that were not included in the SRM, such as Cd, Br and Cl.

Results

The NAA can detect only inorganic elements present in samples. Seven elements were detected in the brown and white rice samples as summarized in Table 1. In the white Japanese and white Californian rice, elements such as As, Br, Cd, Cl, Mn, Na, K were found. In brown Japanese and brown Californian rice all of those elements, except Cd, were found as well. Mean values and standard deviation (SD) of concentrations of elements are provided as well in Table 1. Relative error was calculated as percentage of SD at mean value; relative errors for most of found elements are within 10 %. Only a potassium concentration shows greater error of around 25 %. Potassium has the highest measured activity and that contributes to a higher relative error. Polyvinyl plastic bags were handled with gloves to limit any contamination and possible errors in measurements that it can produce. The error depends on the activity of the sample while it is counted. The samples were irradiated and let to decay for various times. Therefore error varied with different measurements.

Understanding the rice inorganic element composition

Rice can be cultivated in different environments. Most of the cultivation is in portions of flooded soil used for rice cultivation known as paddy fields. Some rice types can withstand dry conditions. The elements that were detected come from minerals in soil and water from paddy soil. Some producers enrich rice with vitamins and elements beneficial for diet. In the presented study, the elements that are usually reported to be found in rice are also detected with the NAA in Californian and Japanese white and brown rice. The summary of results is shown in Table 1 and discussed as follows:

- The most dominant trace element found in rice was potassium (K), ranging from 491 µg/g in the white Californian rice to 2,308 µg/g in the brown Japanese rice. The concentration of potassium in white rice corresponds within SD of the Asian white rice as reported in Ref. [4]. Potassium is the essential plant nutrient that improves root growth and plant vigor [5]. The plant takes the potassium from soil and water; as it

Table 1 Elemental Composition of Rice Grains

Element	Brown Japanese $\mu\text{g/g}$	White Japanese $\mu\text{g/g}$	Brown Californian $\mu\text{g/g}$	White Californian $\mu\text{g/g}$
As	0.079 ± 0.015	0.055 ± 0.012	0.049 ± 0.009	0.050 ± 0.011
Br	0.423 ± 0.029	0.34 ± 0.04	0.118 ± 0.011	0.25 ± 0.01
Cd	ND ^a	3.975 ± 0.91	ND ^a	2.47 ± 0.62
Cl	256.13 ± 23.35	241.99 ± 20.34	232.12 ± 17.68	225.49 ± 25.42
Mn	28.47 ± 3.89	11.16 ± 0.75	43.71 ± 16.69	16.66 ± 0.67
Na	15.16 ± 0.90	12.94 ± 3.53	14.64 ± 3.53	12.39 ± 2.27
K	2308.68 ± 558.91	618.13 ± 155.58	1588.71 ± 338.71	491.26 ± 123.08

^a detection limit 0.01 $\mu\text{g/g}$

develops potassium concentrates in the grains [6]. Food with concentration of potassium under 3,000 $\mu\text{g/g}$ [4] is considered to have its low abundance.

- The concentration of chlorine (Cl) is significantly higher than the one found in jasmine rice and close to concentration found in Asian rice as reported in [3, 7–9]. The difference between the concentration of chlorine in the Japanese rice and in the Californian rice is less than 10 %. Concentration of chlorine in rice is within results of research of Asian rice, 193 to 264 $\mu\text{g/g}$, as described in [7].
- Manganese (Mn) concentration in rice is related to its concentration in soil and water [8]. Concentration in the Californian rice is higher than in the Japanese rice. Concentration of this element found in white Asian rice is between 7.66 and 9.95 $\mu\text{g/g}$ according to [3] and [7]. As shown in Table 1, Mn in the Japanese rice is found to be in excess of 1.2 $\mu\text{g/g}$ when compared to reported data in literature.
- Sodium (Na) presence in rice comes primarily from soil and water. The differences between concentrations in the Japanese rice and the Californian rice are less than the SD of respective results reported in [7]. The concentration is considered to be low if it is below 140 mg per serving [10].
- Cadmium (Cd) is a toxic heavy metal that can be found in soil. Its concentration in soil is related to presence of ZnS caused by the geochemical similarity between Cd and Zn. In analyzed rice the Cd was discovered only in white rice. Cadmium comes from soil accumulates in rice grains [11]. Therefore, more concentration of Cd in soil contributes to more concentration of Cd in rice grains. Concentration of Cd found in the Japanese rice is higher than that found in the Californian rice. That corresponds to the fact that soil in Japan has somewhat higher concentration of Cd in soil than USA agricultural soils [12], [13]. The concentration of Cd in brown rice was significantly lower than in white rice because it is not processed in the same way as white rice. Therefore the concentration is too low to be detected by our experiment [3].

- The bromine (Br) concentration in rice is considered to be low. Most of the areas in which rice is cultivated have seasonal flooding. Flooding results in dissolution of Br in soil. Higher concentration of Br in soil contributes to higher concentration of Br in rice, [14]. This low concentration corresponds to reported concentrations in jasmine rice, [3].
- Arsenic (As) concentration in the analyzed rice samples is found to be low. Most of the rice is cultivated in paddy fields. Water used for irrigation of paddy fields can contain As [15, 16]. If it contains it, the concentration of As in paddy field will significantly increase. The transfer of As to rice is ten times faster than for the other grain crops [17]. Rice plant absorbs As from water. Both, the Japanese and the Californian rice, have low concentrations of As. Therefore it can be stated that there was no significant pollution of water by As.

Understanding the difference in elemental compositions of brown and white rice

The concentration of detected elements as shown in Table 1 is different between brown and white rice. Raw rice seeds are milled to remove the chaff (outer husk) to produce brown rice. After removing the germ, bran and rest of the husk, white rice is produced. The rice bran makes about 7 % of the mass of commercially produced brown rice [18]. It can be seen from Table 1 that the larger difference in elemental composition concentrations is found to be for K. Decrease in mean value of concentration from brown to white rice is 73.2 %. The concentration of K in rice grain bran is expected to be between 1 and 1.5 mg/g according to [19]. Difference in concentration of Mn between brown and white rice is 60.8 %. Manganese is also one of the elements that concentrate in rice bran [20]. Sodium shows to be for 14.6 % less present in the white Japanese rice. That change confirms the result of study done on rice bran. Difference in concentration of Br are 21.3 %. That confirms concentration of Br is higher in rice bran than in endosperm of rice grain. The difference of Cl

presence is less than 5 %, therefore it is homogeneously present over the whole rice grain. Figure 1 shows the graphical representation of elemental composition of As, Br, Cl, Mn, Na and K in the Japanese rice. For example, the larger difference between the white and the brown Japanese rice is found for K and Na. From Fig. 2, however, we see that significant difference in Californian rice is for K and Mn. Percentage-wise, concentration of K decreases after rice processing by 69 % [19]. On the other side, we can see that the concentration of Br is more than double in the white when compared to the brown Californian rice. That can be contributed to higher abundance of it in endosperm of rice grain and artificial additions of Br in the production process. The change of concentration in Cl is less than 3 % that shows it is homogeneously concentrated over the whole rice grain.

Analysis of rice dietary intake for essential and harmful elements

The consumption of rice in the United States is lower than in Japan, since in the United States most of the population does not consume rice on daily basis. Hence, for analysis of daily intake per person it is assumed that a person in the US consumes 160 g of rice in average. One of potentially harmful elements that we found in examined samples is arsenic. Joint Food and Agriculture Organization of the United Nations and World Food Organization Expert Committee of Food Additives have set a recommended weekly exposure limit for inorganic arsenic of 15 μg per one kilogram of body weight [19, 20]. An average person, assuming to weight 75 kg, has the daily exposure limit to As equal to 150 μg . From Table 1 and Figs. 1 and 2, we conclude that there is no significant exposure from tested daily consumption of Japanese and Californian rice. Another potentially harmful element is cadmium. Recommended safe intake limit of Cd is 1 mg per kilogram of body mass [21]. Therefore for an average person weighting 75 kg, daily intake limit is 75 mg.

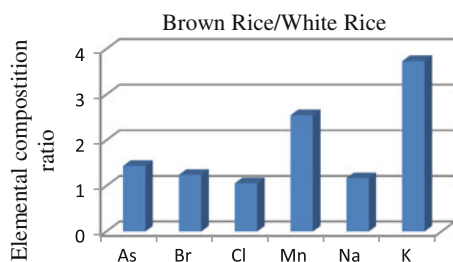


Fig. 1 Ratio of elemental compositions of brown and white Japanese rice

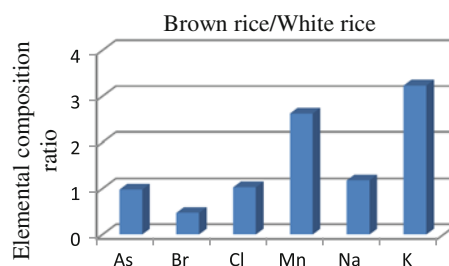


Fig. 2 Ratio of elemental compositions of brown and white Californian rice

Concentration of Cd found in the white rice will deposit 0.5 mg of Cd from daily intake of such rice; therefore there is no significant contamination by heavy elements from rice.

The Institute of Medicine (IOM) in the United States has set the values of recommended dietary allowance (RDA) intake for essential elements [7, 22–24]. RDA for sodium and potassium set by IOM are 4.7 g per day for adults and 1.5 g per day for young people, respectively. RDA for manganese is set by IOM as 330 mg per day for adult man. Daily recommended intake for chlorine is 3,400 mg. The percentage of necessary daily intake that is contributed by white and brown Californian and Japanese rice from our study is shown in Fig. 3.

The contribution of potassium from rice to daily dietary intake is lower for the white Californian rice, only 1.5 %. The largest contribution to daily intake of this element is from the brown Japanese rice, around 6.2 %. The daily intake of sodium is less than 1 %. The intake of manganese while consuming the rice is 21.2 % for brown Californian rice that means brown rice is Mn rich food [25]. Rice satisfies less than 1 % of daily need for Cl of an average adult person. Overall, brown rice contributes more to the recommended daily intake of these elements.

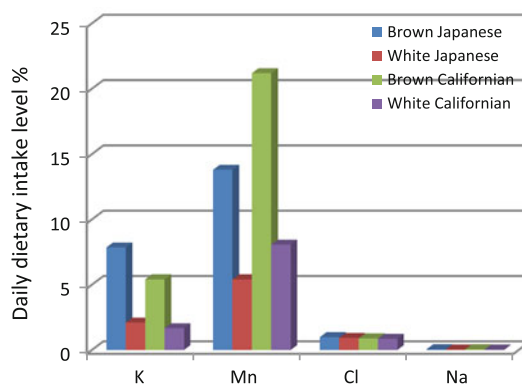


Fig. 3 Evaluation of daily white and brown rice dietary intake level

Conclusion

Using neutron activation analysis at the University of Utah Nuclear Engineering Program, a study of elemental composition of different types of rice is developed. There is extensive literature showing studies on rice composition especially tailored toward finding harmful elements. The analyses are either based on neutron activation or some other chemical or nuclear engineering techniques. The neutron activation analysis is a non-destructive test of the sample elemental composition.

Japanese and Californian brown and white rice are studied for finding and identifying elemental compositions. The detected elements were As, Br, Cl, Cd, Mn, Na, K. The presence of these elements is compared between brown and white rice from Japan and California to find that there is significantly more Mn, K and Na in the brown than in the white rice. From our measurements we found that the concentrations of potentially harmful elements such as As or Cd are lower than the FDA limits in all analyzed rice samples. In addition we have studied what is the dietary value of brown and white rice. From our summary it follows that daily dietary recommended levels of the basic elements in rice (Mn, Br, Na, K for example) are satisfied for Mn, following the IOM standards.

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