Elemental composition analysis in Sangyod rice by instrumental neutron activation analysis

S Kongsri¹ and C Kukusamude¹

¹Nuclear Research and Development Group, Thailand Institute of Nuclear Technology (Public Organization), 9/9 Moo 7, Saimoon, Ongkharak, Nakhon Nayok 26120, Thailand.
E-mail: chunyapuk@tint.or.th

Abstract. Sangyod Muang Phatthalung Rice is a traditional rice variety grown in the area of Phatthalung province for more than a hundred years. Sangyod rice is the first rice variety of Thailand that has been registered as Geographical Indication (GI). It is also good rice for anyone who is searching for good health. The concentrations of nine elements (Mg, Al, Cl, As, Br, K, Mn, Rb and Zn) in Sangyod rice, locally cultivated in four districts (Pak Phayun, Tamot, Pa Phayom and Muang) in Phatthalung province, were determined using instrumental neutron activation analysis (INAA). The method validation of INAA was verified by SRM 1568a Rice Flour. All elements were found to be in a good agreement with the certified values. The results were analyzed using analysis of variance and Tukey’s HSD test. There were no statistical differences in concentrations of Mg, Al, As, Br, K and Mn in rice from four districts. The concentrations of Cl, Rb and Zn found in rice were significantly different according to the cultivation region. Therefore, Cl, Rb and Zn were good characteristic indicators for Sangyod rice that could be applied to identify the geographical origins of rice.

1. Introduction

Rice is the staple food of Thai people and more than half of the world’s population [1]. In recently years, Sangyod rice has become one of the most popular rice in the functional food market in Thailand [2]. Sangyod rice is a very good product for those who are looking for good health. Sangyod rice is a traditional rice variety grown in Phatthalung province in the south of Thailand for more than a hundred years. It has pinkish red grain that is abundant with vitamins, minerals, especially iron which is essential for children and pregnant women. Sangyod rice is also the geographical Indication (GI) rice in Phatthalung province in Thailand [2]. Therefore, the geographical origin of rice product is an essential issue in order to prevent mislabelling and adulteration problem. Recently, characteristics of the elemental compositions have been widely used for discrimination of the geographical origin of cultivation areas such as inductively coupled plasma optical emission spectrometry (ICP-OES) [3], inductively coupled plasma mass spectrometry (ICP-MS) [4], flame atomic absorption spectroscopy (FASS), and graphite furnace atomic absorption spectrophotometry (GF-AAS) [5]. The advantages of instrument neutron activation analysis (INAA) compared with above mentioned techniques are less time-consuming sample preparation steps and less sample contamination. It is known that instrument neutron activation analysis (INAA) is a powerful technique for the determination of elements. It is also a non-destructive, versatile, sensitive, multi-element analytical technique that can be used for the investigation of various samples [1]. According to the world health organization report, Monitoring the content of essential and toxic elements is one of the most important aspects of controlling food safety, in order to establish tolerable intakes of different contaminants that exhibit thresholds of toxicity, because there is usually a small window between nutrition and toxicity [8,9].

In this study, instrumental neutron activation analysis (INAA) was applied for the measurement of elemental compositions (Mg, Al, Cl, As, Br, K, Mn, Rb and Zn) in Sangyod rice samples cultivated from different regions (Pa Phayom, Tamot, Pak Phayun and Mueang district) of Phatthalung province. The elemental compositions were tested using analysis of variance (ANOVA) and Tukey’s HSD test. In this work, we illustrated the quantification based on elemental compositions by INAA determined by comparative method. The certified reference material was also checked for the accuracy and precision of the proposed method.
2. Experimental
2.1. Sample collection and preparation
A total of 16 Sangyod rice samples were collected in paddy fields from 4 districts including Pa Phayom, Tamot, Pak Phayun and Mueang in Phatthalung province in the south of Thailand. Samples were dried and pulverized to fine powder by agate mortar. Then, the samples were dried at 60 °C for 48 h in oven and kept in desiccator prior to analysis by INAA.

2.2. Instrumental neutron activation analysis (INAA)
Rice samples (0.1 g) were separately weighed and sealed in small polyethylene bags. The bags were placed together into polyethylene rabbit prior to neutron irradiation. Rice flour SRM 1568a (NIST, USA) was purchased and used as a standard reference material. All samples and standard SRM 1568a were irradiated with thermal neutron flux of $1.8 \times 10^9$ to $2 \times 10^{12}$ n cm$^{-2}$ s$^{-1}$ at Thai Research Reactor (TRR-1/M1) [1,6]. The irradiation conditions are shown in table 1.

| Irradiation condition | Irradiation Facility | Irradiation time | Cooling time | Counting time | Radionuclide |
|-----------------------|----------------------|------------------|--------------|---------------|--------------|
| Short life radionuclide | Pneumatic system     | 25 s             | 2 m          | 300 s         | Mg Al Cl     |
| Medium life radionuclide | CA-2                | 7 h              | 12 h         | 1800 s        | As Br Mn K   |
| Long life radionuclide | Lazy Susan          | 26 h             | 14 d         | 3600 s        | Rb Zn        |

The samples were irradiated with neutron and then radioactive nuclides occurred. The radioactive nuclides emit the gamma rays with characteristic $\gamma$-energies. After the appropriate decay time, the gamma-ray energies of samples were measured by a high purity germanium detector with 1.95 keV of resolution for $^{60}$Co and 60% relative efficiency. The two radionuclide sources of Cs-137 and Co-60 were used for the calibration of the system. The quality control was evaluated according to Gilmore and Hemingway [7].

2.3 Statistical Analysis
The differences in the studied elements in rice were determined by ANOVA and post-hoc Tukey's HSD test at confidence intervals of 95%.

3. Results and discussion
SRM 1568a Rice Flour was analyzed using INAA method for quality control and method validation. The accuracy of all elements was found in a good agreement with the certified values. The precisions in term of %RSD is lower than 7%. The limit of detection (LOD) was obtained in range of 0.01 to 29 mg kg$^{-1}$. The validation results are summarized in table 2. A total of 9 elements in sixteen rice samples were analyzed using INAA. The results are presented as box plots in figure 1. Different elements found are presented by different symbols. The ranges of elements found in the samples, maximum, minimum, and median are also depicted.
Table 2. Validation results obtained through the analysis of the rice flour NIST SRM 1568a.

| Element | Certified values (mg kg\(^{-1}\)) | Experimental values (mg kg\(^{-1}\)) | % Recovery | %RSD | LOD (mg kg\(^{-1}\)) |
|---------|-----------------------------------|--------------------------------------|------------|------|----------------------|
| Mg      | 0.056 %                           | 0.055 %                              | 98.2       | 4.8  | 29                   |
| Cl      | 300                               | 305                                  | 101.7      | 1.3  | 0.3                  |
| Al      | 4.4                               | 4.2                                  | 95.5       | 7.0  | 0.06                 |
| As      | 0.29                              | 0.28                                 | 96.6       | 4.5  | 0.01                 |
| Br      | 8.0                               | 7.9                                  | 98.8       | 3.0  | 0.1                  |
| K       | 0.128 %                           | 0.127 %                              | 99.2       | 2.3  | 14                   |
| Mn      | 20.0                              | 19.7                                 | 98.5       | 3.7  | 0.6                  |
| Rb      | 6.14                              | 5.83                                 | 95.0       | 5.0  | 1.05                 |
| Zn      | 19.4                              | 19.7                                 | 101.5      | 4.9  | 0.3                  |

Figure 1. Box plots of 9 elements in Sangyod rice samples from different districts.

Data were analyzed by ANOVA and post-hoc Tukey’s HSD test. From ANOVA test at p<0.05, the significant values for Mg, Al, As, Br, Mn and K were 0.415, 0.356, 0.228, 0.782, 0.489, and 0.882, respectively. This indicates that there was no significant difference in Mg, Al, As, Br, Mn and K
concentrations whereas the mean values of Cl, Rb and Zn concentrations found in Sangyod rice were significantly different at p<0.05 in the four different cultivation area at 95% confidence interval as shown in table 3.

Table 3. Descriptive statistical analysis of elements in Sangyod rice samples.

| Element | Minimum | Maximum | Mean   | P(T<Two-tail) |
|---------|---------|---------|--------|---------------|
| Mg (%w/w) | 0.043   | 0.070   | 0.057  | 0.415         |
| Cl (mg kg⁻¹) | 115.034 | 299.804 | 206.969 | 0.001         |
| Al (mg kg⁻¹) | 77.785  | 111.479 | 93.339 | 0.356         |
| As (mg kg⁻¹) | 0.133   | 0.364   | 0.260  | 0.228         |
| Br (mg kg⁻¹) | 0.132   | 0.330   | 0.218  | 0.782         |
| Mn (mg kg⁻¹) | 8.869   | 15.993  | 12.806 | 0.489         |
| K (% w/w) | 0.096   | 0.130   | 0.109  | 0.882         |
| Rb (mg kg⁻¹) | 6.736   | 33.848  | 19.663 | 0.002         |
| Zn (mg kg⁻¹) | 15.530  | 26.763  | 20.772 | 0.016         |

Multiple comparison or post hoc was analyzed using Tukey’s HSD test. The significant different in concentration of Cl, Rb and Zn was depicted in table 4. Cl, Rb and Zn concentration in Sangyod rice cultivated in four different cultivation area was significant different at 95% confidence interval.

Table 4. Differences of Cl, Rb and Zn concentrations in (1) Pa Phayom, (2) Tamot, (3) Pak Phayun and (4) Mueang districts.

| Element | District | District | Significant |
|---------|----------|----------|-------------|
| Cl      | 1        | 2        | 0.700       |
|         | 3        |          | 0.009       |
|         | 4        |          | 0.001       |
|         | 2        | 3        | 0.063       |
|         | 4        |          | 0.006       |
|         | 3        | 4        | 0.535       |
| Rb      | 1        | 2        | 0.001       |
|         | 3        |          | 0.009       |
|         | 4        |          | 0.056       |
|         | 2        | 3        | 0.676       |
|         | 4        |          | 0.185       |
|         | 3        | 4        | 0.730       |
| Zn      | 1        | 2        | 0.228       |
|         | 3        |          | 0.542       |
|         | 4        |          | 0.010       |
|         | 2        | 3        | 0.905       |
|         | 4        |          | 0.304       |
|         | 3        | 4        | 0.109       |

4. Conclusion
Nine elements including Mg, Cl, Al, As, Br, Mn, K, Rb and Zn in Sangyod rice samples cultivated from 4 districts including Pa Phayom, Tamot, Pak Phayun and Mueang in Phatthalung province in the south of Thailand were determined by INAA. Cl, Rb and Zn concentration found in Sangyod rice were significantly different according the cultivation areas at 95% confidence interval. There was no...
significant difference in Mg, Al, As, Br, Mn and K concentration found in 4 districts at 95% confidence interval. It may be possible to trace the geographical origin of rice cultivated from different regions in Thailand for the further study. Our results provide preliminary information for Sangyod rice samples according to rice origins.

5. References

[1] Kukusamude C and Kongsri S 2018 Food Control. 91 357-64
[2] Ratanavalachai T, Thitiorul S, Tanuchit S, Jansom C, Uttama S and Itharat A 2012 J Med Assoc Thai 1 S109-14
[3] Oliveira A, Baccana N and Cadore S 2012 J. Braz. Chem. Soc. 23 838-45
[4] Cheajesadagul P, Arnaudguilhem C, Shiowatana J, Siripinyanond A and Szpunar J 2013 Food Chem. 141 3504-9
[5] Parengam M, Judprasong K, Songsak S, Jittinandana S, Laoharojanaphand S and Busamongkol A 2010 J Food Compost Anal. 23 340-5
[6] Kongsri S and Kukusamude C 2017 J. Phys.: Conf. Ser. 901, 010247
[7] Gilmore G and Hemingway J D 1995 Practical Gamma-ray Spectrometry. Chichester, UK: John Wiley & Sons
[8] BEGAA, Samir et MESSAOUDI, Mohammed. Toxicological aspect of some selected medicinal plant samples collected from Djelfa, Algeria Region. Biological trace element research, 2019, vol. 187, no 1, p. 301-306.
[9] MESSAOUDI, Mohammed et BEGAA, Samir. Dietary intake and content of some micronutrients and toxic elements in two algerian spices (Coriandrum sativum L. and Cuminum cyminum L.). Biological trace element research, 2018, p. 1-6.

Acknowledgements
Financial support from Thailand Institute of Nuclear Technology (Public Organization) is gratefully acknowledged.