# A preliminary study on identification of Thai rice samples by INAA and statistical analysis

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**Abstract**. This study aims to investigate the elemental compositions in 93 Thai rice samples using instrumental neutron activation analysis (INAA) and to identify rice according to their types and rice cultivars using statistical analysis. As, Mg, Cl, Al, Br, Mn, K, Rb and Zn in Thai jasmine rice and Sung Yod rice samples were successfully determined by INAA. The accuracy and precision of the INAA method were verified by SRM 1568a Rice Flour. All elements were found to be in a good agreement with the certified values. The precisions in term of %RSD were lower than 7%. The LODs were obtained in range of 0.01 to 29 mg $kg^{-1}$. The concentration of 9 elements distributed in Thai rice samples was evaluated and used as chemical indicators to identify the type of rice samples. The result found that Mg, Cl, As, Br, Mn, K, Rb, and Zn concentrations in Thai jasmine rice samples are significantly different but there was no evidence that Al is significantly different from concentration in Sung Yod rice samples at 95% confidence interval. Our results may provide preliminary information for discrimination of rice samples and may be useful database of Thai rice.

## 1. Introduction

Thai Jasmine Rice (Khao Dawk Mali 105) is one of the most important consuming products in Thailand. Khao Dawk Mali 105 is originated from Thailand, mostly grown in Thung Kula Rong Hai area in the northeast of Thailand [1]. Thung Kula Rong Hai area covers five provinces including Roi-Et, Mahasarakham, Sisaket, Yasothon, and Surin. It is not only for the local consumption but also the one of the main export products to all over the world. Thai jasmine rice cultivated in Thung Kula Rong Hai area in the northeastern region is the most famous premium rice which has a unique sweet-scented aroma, softness, and tender texture [2]. Sungyod rice is originated from Phatthalung province and recognized as Geographical Indication (GI) rice. Therefore, adulteration of Thai Jasmine Rice and Sungyod rice with other cultivation area leads to rice authenticity problems by mislabeled addition of inferior rice to premium rice. However, the geographical origin of rice cannot be distinguished by image analysis [3]. Thus, it is important to resolve these rice authenticity problems. Recently, elemental compositions have been used as a chemical indicator for discrimination of cultivation areas [4].

Several analytical techniques that have been published for the detection of elemental compositions are inductively coupled plasma optical emission spectrometry (ICP-OES) [5], inductively coupled plasma mass spectrometry (ICP-MS) [1], flame atomic absorption spectroscopy (FASS), graphite furnace atomic absorption spectrophotometry (GF-AAS) [6] and so on. However, these methods require many time-consuming sample preparation steps prior to analysis. Moreover, the risk of samples contamination and loss of analytes can be occurred in the sample preparation procedures. Neutron activation analysis (NAA) is non-destructive method [7] suiting for solid samples that are difficult to dissolve. The sample preparation for NAA is not necessary, thus it can reduce the risk of contamination and analysis time [8].

In this work, we illustrated the preliminary study on identification the origin of Thai jasmine rice and Sungyod rice cultivated from different regions of Thailand, Thung Kula Rong Hai area and Phatthalung province using INAA and statistics. The quantification based on elemental composition by INAA was determined by comparative method. Certified reference material was also checked.

## 2. Experimental

### *2.1. Rice samples*

Samples of two kinds of Thai rice were collected from paddy fields from different regions (the Northeast and the South) in Thailand. The samples (n=45) of Thai jasmine rice (Khao Dawk Mali 105) from Thung Kula Rong Hai area in the Northeast of Thailand were collected. The samples (n=48) of Sungyod rice were collected from 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.

### *2.2. Instrumental neutron activation analysis*

The samples and reference material (approximately 100 mg) were weighed and sealed in polyethylene bags prior to neutron irradiation. These containers were packed into rabbit for irradiation. The irradiation condition and other details of the elemental analysis are presented in Table 1. After the appropriate decay time, the gamma-ray activities of the radioisotopes were counted using a high purity germanium HPGe detector operated by the Gamma Vision computer program (EG & ORTEC, USA). In this study, Magnesium (Mg), Aluminium (Al), Chlorine (Cl), Arsenic (As), Bromine (Br), Manganese (Mn), (K), Rubidium (Rb), and Zinc (Zn) in rice samples were quantified by INAA.

**Table 1** The irradiation conditions for the analysis of elements in Thai rice samples

| 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 |

## 3. Results and discussion

In order to identify Thai rice samples according to the geographical origins, rice samples cultivated from Thung Kula Rong Hai area and Phatthalung province were collected. Thung Kula Rong Hai covers 5 provinces including Sisaket, Yasothon, Roi Et, Surin, and Mahasarakham provices. The multi-elemental compositions of rice were analyzed by INAA. The accuracy and precision of the INAA method were verified by SRM 1568a Rice Flour. All concentration values were found to be in a good agreement with the certified values. The precisions in term of %RSD were lower than 7%. The LODs were obtained in range of 0.01 to 29 mg $kg^{-1}$.

The results of Mg, K, As, Br, Cl, Al, Mn, Rb, and Zn concentration of Thai jasmine and Sungyod rice obtained from Thung Kula Rong Hai area and Phatthalung province are summarized in Fig. 1. Fig. 1A shows box plots of Mg and K concentrations in Thai jasmine rice and Sungyod rice. Mg found in Thai jasmine rice and Sungyod rice were in the ranges of 0.048-0.083 and 0.034-0.088 %(w/w), respectively, while K was found in the ranges of 0.089-0.178 and 0.072-0.130 %(w/w), correspondingly. As and Br (Fig. 1B) found in Thai jasmine rice were 0.043-0.405 ppm and 0.015-0.302 ppm and those in Sungyod rice were 0.067-0.400 ppm and 0.080-0.403 ppm, respectively. Cl found in Thai jasmine rice and Sungyod rice were in the ranges of 149.476-617.284 and 99.129-316.656 ppm, respectively, while Al was found in the ranges of 76.375-122.785 and 71.946-125.526 ppm, correspondingly, as shown in Fig. 1C. Mn, Rb, and Zn in Thai jasmine rice and Sungyod rice are shown in Fig. 1D. Mn and Rb found in Thai jasmine rice were 8.222-21.450 ppm and 2.077-10.080 ppm and those in Sungyod rice were 7.822-16.215 ppm and 6.197-50.544 ppm, respectively. Zn found in the ranges of 13.930-28.870 and 7.971-28.524 ppm for Thai jasmine rice and Sungyod rice samples, respectively.

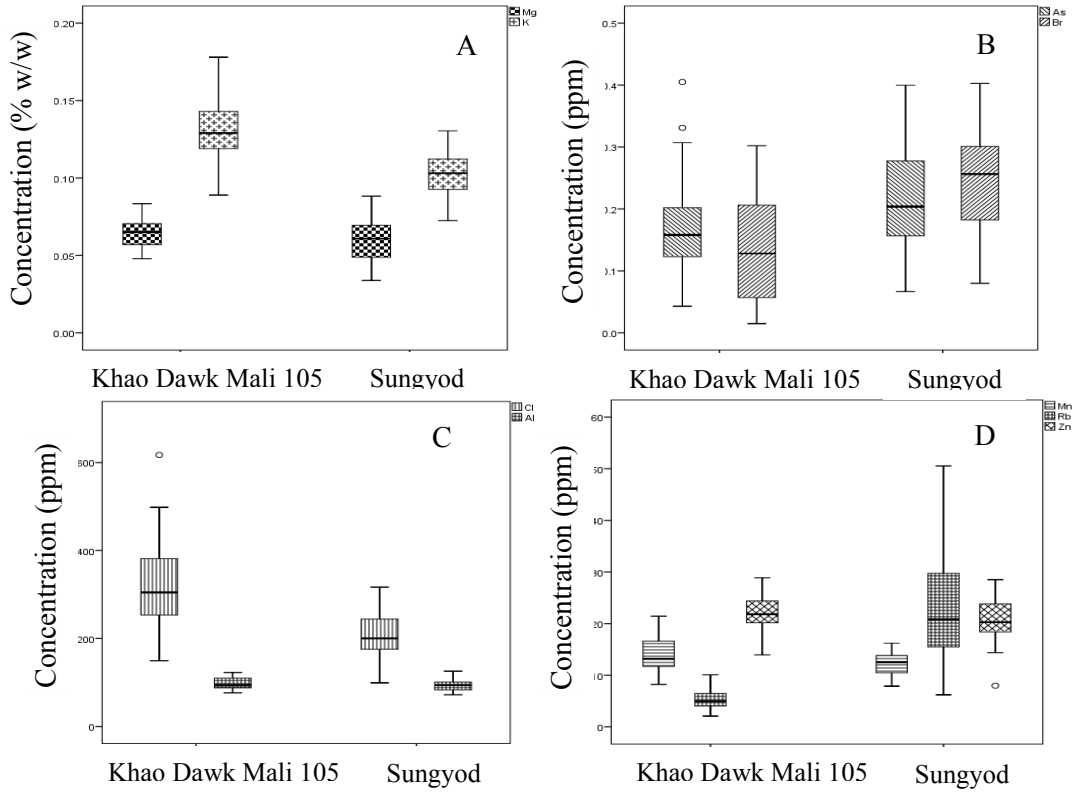


Fig. 1 Box plots of the concentration of 9 elements in Thai jasmine rice and Sungyod rice samples

The average and RSD of the interested elements found in Thai jasmine rice and Sungyod rice are illustrated in the Table 2. T-test was evaluated for testing the difference of elemental composition between Thai jasmine rice and Sungyod rice grown in different regions of Thailand. The p-values of Mg, Cl, Al, As, Br, Mn, K, Rb, and Zn were 0.043, <0.0001, 0.067, 0.003, <0.0001, 0.007, <0.0001, <0.0001, and 0.045, respectively. It indicates that Mg, Cl, As, Br, Mn, K, Rb and Zn concentrations were significantly different but there was no significant difference in Al concentration between Thai jasmine rice and Sungyod rice samples at 95% confidence interval. This was implied that the elemental composition could be good indicators and possible to identify rice samples.

**Table 2** Descriptive statistical analysis of elements in Thai jasmine rice and Sungyod rice samples.

| Element | Average (Thai jasmine) | Average (Sung Yod ) | RSD (Thai jasmine) | RSD (Sung Yod) | P(T≤Two-tail) |
|---|---|---|---|---|---|
| Mg(%) | 0.065 | 0.060 | 0.154 | 0.217 | 0.043 |
| Cl (mg $kg^{-1}$) | 319.696 | 205.783 | 0.295 | 0.244 | <0.0001 |
| Al (mg $kg^{-1}$) | 97.472 | 92.899 | 0.124 | 0.126 | 0.067 |
| As (mg $kg^{-1}$) | 0.166 | 0.217 | 0.476 | 0.364 | 0.003 |
| Br (mg $kg^{-1}$) | 0.132 | 0.246 | 0.606 | 0.337 | <0.0001 |
| Mn(mg $kg^{-1}$) | 13.880 | 12.300 | 0.228 | 0.175 | 0.007 |
| K (%) | 0.131 | 0.102 | 0.153 | 0.137 | <0.0001 |
| Rb (mg $kg^{-1}$) | 5.406 | 22.794 | 0.374 | 0.443 | <0.0001 |
| Zn (mg $kg^{-1}$) | 22.057 | 20.541 | 0.152 | 0.185 | 0.045 |

## 4. Conclusion

Nine variables including Mg, Cl, Al, As, Br, Mn, K, Rb, and Zn in Thai jasmine and Sungyod rice samples cultivated from Thung Kula Rong Hai area and Phatthalung province were determined by INAA. Mg, Cl, Al, As, Br, Mn, K, Rb, and Zn found were significantly different between Thai jasmine rice and Sungyod rice samples at 95% confidence interval. There was no significant difference in Al concentration found between Thai jasmine rice and Sungyod rice samples 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 Thai rice samples according to rice origins.

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