Discrimination of geographical origin of rice based on multi-element fingerprinting by high resolution inductively coupled plasma mass spectrometry

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ABSTRACT

Rice is a staple food for nearly half the world’s population. The discrimination of geographical origin of rice in order to its authenticity is essential to prevent mislabeling and adulteration problems. The multi-element fingerprinting has a great potential for the differentiation of rice grains. A study of the capability of the high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) methodology for multi-element fingerprinting of rice has been carried out. A total of 31 Thai jasmine rice and 5 foreign (France, India, Italy, Japan and Pakistan) rice samples were analysed by high resolution ICP-MS after acid digestion. Accuracy of the whole procedure was verified by the analysis of rice flour standard reference material (NIST SRM 1568a). The concentrations of 21 elements were evaluated and used as chemical indicator to discriminate the origin of rice samples. The classification of rice samples was carried out based on elemental composition by a radar plot and multivariate data analysis, including principal component analysis (PCA) and discriminant analysis (DA). Thai jasmine rice can be differentiated from foreign rice samples by radar plots and multivariate data analysis. Furthermore, the DA can differentiate Thai jasmine rice samples according to each region of origin (northern, northeastern or central regions of Thailand). Therefore, multi-element fingerprinting combined with the use of multivariate statistical techniques can be considered as a powerful tool for rice authentication.

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1. Introduction

Rice is the seed of the monocarpic annual plant “Oryza sativa L.” and is one of the most important staple food crops, providing a staple diet for almost half of the world’s population (Vlachos & Arvanitoyannis, 2008). It also possesses the main source of calories and protein for human being, particularly in Asia, America and some European countries. According to the Food and Agriculture Organization (FAO), developing countries are the main player in the world rice trade. The world’s leading producers of rice include China, India, Indonesia and Bangladesh (FAOSTAT, 2012). Thailand has been the world’s largest rice-exporting country of rice over the past decade (USDA, 2012).

Jasmine rice (Thai Hom Mali rice or Thai fragrant rice) is originally from Thailand, mostly grown under the rain-fed conditions, especially in the northeast region of the country. It considerably commands a premium price in the world market and is vulnerable to economic adulteration. For this reason, rice cultivar and cultivation area are crucial factors in market prices (Suzuki, Chikaraishi, Ogawa, Okkouchi, & Korenaga, 2008). The determination of rice authenticity is indeed essential to resolve problems of mislabelling and misleading about origin and adulteration, which is defined as a process of adding inferior rice to premium rice, affecting the credibility of producers and traders and the right of consumers (Gonzalez, Armenta, & de la Guardia, 2009).

In recent years, research efforts have focused on the potential of analytical techniques for the determination of the source or geographical origin of agricultural products (Karoui & De Baerdemaecker, 2007; Luykx & van Ruth, 2008). For most of the food products, the authenticity is determined by geographical origin, botanical/cultivar type or the absence of adulterants (Kelly et al., 2002). Regarding rice, source identification is a more complex issue because it can depend on both geographical origin and cultivar type. It is recognised that the mineral and trace elemental composition of rice reflects both the cultivar and soil where rice grows (Kelly, Heaton, & Hoogwerff, 2005). Nonetheless, multi-element and multi-isotope analysis have been applied for differentiation of rice origins such as Vietnamese rice (Kokot & Phuong, 1999), USA, Europe and India/Pakistan rice (Kelly et al., 2002), Japanese rice (Suzu-
ki et al., 2008; Yasui & Shindoh, 2000) and Spanish rice (González, Armenta, & de la Guardia, 2011). However, it has to be noted that the isotopic fractionation can occur depending on the planting date and variable climatic conditions (Schmitt et al., 2012).

Multi-element fingerprinting has traditionally been based on quadrupole based ICP-MS analysis which is the most powerful technique for rapid, precise and accurate detection of most elements in the periodic table (Husted et al., 2011). However, spectral interferences, e.g. isobaric, doubly charged, and polyatomic interferences, observed for some elements are still major limitations in ICP-MS which result in complicated or even incorrect measurements (Pick, Leiterer, & Einax, 2010). Alternatively, high-resolution ICP-MS is capable of providing higher sensitivities along with higher mass resolutions (up to 10,000) which are especially useful for resolving troublesome interferences commonly encountered in traditional ICP-MS.

The aim of this study is to discriminate the geographical origin of rice based on multi-element fingerprinting by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) followed by a radar plot and multivariate statistical analysis.

2. Experimental

2.1. Samples

A total of 36 polished rice samples were analysed. Thirty Thai jasmine white rice samples with known origin were collected in Thailand over a period of several months (sampling locations are shown in Fig. S1) and six samples were purchased from supermarket in France, including one Thai rice from unknown region origin and five foreign white rice samples from different countries chosen for their popularity in the world market; Camargue rice (France), japonica rice (Japan), arborio rice (Italy), Sundari rice (India) and basmati rice (Pakistan). All rice samples with location and labelling were listed in Table 1.

2.2. Reagents

Nitric acid (HNO₃, 69%) for trace metal analysis and hydrogen peroxide (H₂O₂, 30%, Instra-analysed) were purchased from Baker (Deventer, The Netherlands). Standard solutions used for element concentration determination were prepared from 1000 µg mL⁻¹ single-element solutions (in 4% HNO₃) from PlasmaCAL (SCP Science, Canada). Deionised water (18.3 MΩ cm) was obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

2.3. Instrumentation and methods

The HR-ICP-MS instrument Element XR (Thermo Fisher Scientific, Bremen, Germany) was utilised. The instrument was equipped with a cyclonic spray chamber and a MicroMist quartz concentric nebulizer (Glass Expansion, Hawthorn, Australia) for sample introduction. In brief, the operating conditions of the instrument were a RF power of 1200 W with Ar flow rates of 16, 0.8 and 0.961 L min⁻¹ for cool, auxiliary and sample gas, respectively. For the measurement, the following isotopes with their corresponding resolution were monitored: low resolution applied for ¹⁰B, ¹¹B, ¹³C, ¹⁴N, ¹⁵N, ¹⁶O, ¹⁷O, ¹⁸O, ¹⁹F, ²⁰Ne, ²¹Ne, ²²Na, ²³Na, ³⁵Cl, ³⁶Cl, ³⁷Cl, ³⁸Cl, ³⁹K, ⁴⁰K, ⁴⁴Ti, ⁴⁷Ti, ⁵₁V, ⁵²Cr, ⁵₃Mn, ⁵₄Fe, ⁵₅Fe, ⁵₆Fe, ⁵₇Fe, ⁵₈Ni, ⁶⁰Ni and ⁶²Zn; high resolution applied for ²⁷Al, ⁵⁷Fe, ⁶³Cu, ⁸⁶Sr, ¹³⁷Ba, ¹⁰⁹Pd, ¹ⁱ¹Cd, ¹³³Cs, ¹⁴⁸Nd, ¹⁷⁶Lu, ¹⁸⁷Os, ¹⁹⁵Ir, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb; medium resolution applied for ²⁶Mg, ⁴⁷Ti, ⁵¹V, ⁵₂Cr, ⁵₃Mn, ⁵₄Fe, ⁵₅Fe, ⁵₆Fe, ⁶⁰Ni and ⁶²Zn; high resolution applied for ¹⁸⁷As and ⁸²Se, respectively.

Calibration standards were prepared by mixing and diluting single-element standard solutions. Accuracy of the whole procedure was verified by employing the certified reference material of rice flour, NIST 1568a, from the National Institute of Standards and Technology (Gaithersburg, MD, USA).

2.4. Total concentration of elements

Rice samples were ground in a mortar to obtain fine powder before sample digestion. Then, 0.2 g of powdered samples was digested in 50-mL polyethylene tube (DigiTubes, SCP Science, Canada) with 2.5 mL of concentrated HNO₃ at 90 °C for 2 h using a

<table>
<thead>
<tr>
<th>Table 1</th>
<th>List of rice samples labels for discrimination of geographical origin.</th>
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<tr>
<td>Types of rices</td>
<td>Country</td>
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<tr>
<td>Thai jasmine white rice</td>
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<td></td>
<td>Thailand</td>
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<td>Foreign rices</td>
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<td>Camargue rice</td>
<td>France</td>
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<td>Japonica rice</td>
<td>Japan</td>
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<td>Sundari rice</td>
<td>India</td>
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<tr>
<td>Arborio rice</td>
<td>Italy</td>
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<tr>
<td>Basmati rice</td>
<td>Pakistan</td>
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</tbody>
</table>

* 3 different samples were collected.
** 2 different samples were collected.
SPC Science DigiPrep MS heating block with time and temperature controller. After cooling to room temperature, 1.0 mL of 30% (w/v) H₂O₂ was added and the samples were heated again at 90 °C for 2 h with the heating block till a transparent solution was obtained. Then, the digests were diluted to 10 mL with deionised water and analysed on the total content of elements by HR-ICP-MS. Three independent replicates were made; respective blanks were considered in final results. Calibration was done using matrix-matched calibration method. This matrix-matched calibration can be made by analysing selected rice sample by standard addition and using the obtained calibration curve as external calibration for the other samples.

2.5. Data processing and statistical analysis

The analytical data were manipulated using Excel 2010 spreadsheet. Data in term of elemental concentrations were processed by radar plot analysis whereas statistical analysis was performed by using XLSTAT 2012 from Addinsoft (a set of data-analysis and statistical functions for Microsoft Office Excel). The discrimination of rice samples was carried out by the multivariate data analysis (chemometrics), including principal component analysis (PCA) and discriminant analysis (DA) which are commonly used in pattern recognition problems. Principal component analysis (PCA) is statistical data reduction technique which is used for exploratory and unsupervised pattern recognition, whereas discriminant analysis (DA) is a method for classifying that maximises the variance between groups and minimises the variance within the group by creating new variables (discriminant functions), which are linear combinations of the original variables (supervised analysis) (Le Bot, Oulhote, Deguen, & Glorennec, 2011).

3. Results and discussion

3.1. Elemental concentration in rice

The limits of detection (LOD) for all elements were estimated from three times the standard deviation of the blank measurements. The LOD values of the HR-ICP-MS (in the μg L⁻¹ level) were determined as follows: B (0.130), Co (0.002), Sr (0.027), Mo (0.009), Cd (0.002), Cs (0.0004), Ba (0.16), Pb (0.013), Ti (0.039), V (0.001), As (0.001), Se (0.020), Mn (0.012), Cu (0.17), Rb (0.003), Mg (13.1), Al (1.60), Cr (0.025), Fe (0.37), Ni (0.042) and Zn (0.47), which are adequate for the determination of trace elements concentrations in rice.

Accuracy validation of the HR-ICP-MS procedure was made by analysing a certified reference material – NIST-SRM 1568a reference material (rice flour). The results are shown in Table S1, the elemental concentrations obtained from the experiment agreed well with the certified values (recoveries ranging from 78% to 112%). Precision, expressed as the relative standard deviation (RSD) of the 3 repeated measurements was within 5%.

Thirty-six rice samples were analysed and quantified for elemental concentrations by HR-ICP-MS after acid digestion. Results observed for the mean values and standard deviation of elemental concentrations in rice samples according to their regions of origin are summarised in Table S2. The concentrations of most elements are possible to be used for discriminating source of origin of rice samples.

![Fig. 1](image1.png)

![Fig. 2](image2.png)
On the basis of this information, Thai jasmine rice has elemental concentration ranges similar to those of foreign rice. Thai rice has rather high concentration of some trace elements such as Co, Cs, Ba and Rb. However, the concentration of Mg and Cd in Thai rice is lower than the others. Besides, some elements such as B, Fe, Se, Sr and Mo were found distinctly high in rice samples from India and Pakistan. The concentration of Mn, Cu, Zn and As was found to be similar level in all rice whereas Al, Cr, Ni, Ti, V and Pb could be merely found in some rice.

3.2. Discrimination of the geographical origin of rice samples

The concentrations of each element were evaluated with 36 rice samples and used as a chemical descriptor in the statistical analysis for the discrimination of rice grains according to their geographical origins. As can be observed, some of the measured concentration values in some samples were below the limits of detection of the adopted method. Thus, elements with concentrations less than the detection limits were replaced with zero to complete statistical process. In this study, three methods were investigated to classify the geographical origins of rice samples.

3.2.1. Radar plot analysis

A radar plot based on the elemental composition has been used for distinguishing geographical origin of rice samples because the method allows simple, rapid and routine discrimination. In this study, radar plots were applied in rice samples to classify their countries of origin by using relative elemental concentrations. For ease of comparison, radar plots analysis was performed on the basis of six elements (B, Co, Sr, Mo, Rb and Se). These elements were chosen because their concentrations showed high variation in each rice sample (<48% RSD). Moreover, some of them have been identified as the most influencing indicators of the geographical origin of agricultural samples due to their different concentrations in soil and their effective uptake by plants (Kelly et al., 2002).

Distributions of elemental patterns of each rice sample from various countries in Fig. 1 show clearly different characteristic patterns. This pattern is the same for all the rice of a same country. Indeed, radar plots analysis was applied into 30 Thai jasmine rice samples collected from different regions of Thailand (see location in Fig. S1). Fig. 2 illustrates that the distribution of elemental patterns show the same characteristic, although rice samples were collected from different regions of Thailand. Whether similarity in pattern was due to similarity in rice cultivar or in the soil being cultivated will need more investigation.

3.2.2. Principal component analysis (PCA)

Principal component analysis was performed on the concentrations of elements to enable a discrimination of the rice. Initially, PCA was performed on elemental concentrations based on 21 vari-
Fig. 4. (A) Discriminant analysis on elemental concentrations based on 12 variables in 36 rice samples from different geographical origins. Grouping according to geographical location is shown by discriminant functions 1 and 2, which explained 96.83% and 3.17% of the variance, respectively. (B) Discriminant analysis on elemental concentrations based on 7 variables in 31 Thai jasmine rice samples from different regions in Thailand. Grouping according to geographical location is shown by discriminant functions 1 and 2, explained 95.22% and 4.78% of the variance, respectively.

Table 2
The observations of the cross-validation results together with the classification of rice samples using discriminant analysis model.

<table>
<thead>
<tr>
<th>Origin</th>
<th>Assigned origin for all rice samples with 12 variables</th>
<th>Assigned origin for Thai jasmine rice samples with 7 variables</th>
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<tbody>
<tr>
<td></td>
<td>Asia</td>
<td>Europe</td>
</tr>
<tr>
<td>Asia</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Europe</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Thailand</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>
ables for classifying all rice samples from different geographical origins (Asia, Europe and Thailand). As shown in Fig. 3A, the PCA score plot illustrates a clear separation pattern between Thai and foreign rice samples (from France, India, Italy, Japan and Pakistan) while the corresponding loading plot (Fig. 3B) describes the variables (specific elements) related to the separation. Elements such as B, Sr, Mo, Se, Cd, Cu and Mg control the discrimination of foreign rice from Thai rice. The plots were defined by the principle components 1 and 2 and explained 28.85% and 11.86% of the variance, respectively. However, only a partial separation of Thai jasmine rice from three regions of Thailand was possible.

In order to improve their discrimination, PCA was applied on the concentration values of 21 elements. As shown in Fig. 3C and D, the score plot and the loading plot show primarily it is possible to distinguish central region Thai jasmine rice samples from the other regions whereas rice from northern and northeastern regions were still difficult to separate. Elements such as B, Cd, Rb and Mo influence on the separation of rice from central region. Only 17.83% and 14.77% of the dataset were explained by the principle components 1 and 2, respectively. Obviously, the use of PCA in combination with the multi-element fingerprinting did not enable a good discrimination of the geographical origin of rice.

3.2.3. Discriminant analysis (DA)

Discriminant analysis of elemental concentrations measured by HR-ICP-MS in rice samples from different geographical origins was applied to classify groups and to assign rice samples to the groups. After applying DA, discriminant functions (F1 and F2) correlated with the variables were obtained. The coefficients of the different variables in the discriminant functions for rice classification were shown in Table S3. In this study, the calculation was performed using 12 variables (B, Mg, Co, Cu, Zn, As, Rb, Sr, Mo, Cd, Cs and Ba) for classifying all rice samples (Asia, Europe and Thailand) and 7 variables (B, Mn, Fe, Zn, Rb, Sr, and Cd) for classifying 31 Thai jasmine rice samples (northern, northeastern and central regions).

Fig. 4A shows the distribution patterns of all rice samples according to their origins in the plot defined by the discriminant functions. The variations between groups were explained by the discriminant functions 1 (96.83%) and 2 (3.17%), respectively. Thai rice, European rice (Italy and France) and Asian rice (Japan, India and Pakistan) were completely separated. This confirms that Thai jasmine rice shows unique elemental fingerprint characteristics that can be differentiated from other types of rice and all techniques (radar plots, PCA and DA) are able to create for clear separation of Thai jasmine rice.

DA was further performed on the results of elemental concentrations based on 7 variables in Thai jasmine rice samples with different regions of country as presented in Fig. 4B. The distribution pattern of Thai jasmine rice defined by the discriminant functions 1 and 2 was plotted and explained 95.22% and 4.78% of the variance, respectively. The plot shows clear classification of Thai jasmine rice origins from three regions of Thailand (northern, northeastern and central regions). Therefore, DA method could provide better discrimination of Thai jasmine rice over the PCA method.

To check the reliability of the developed classification model, cross-validation method was operated to compute the classification and probability of rice samples. Table 2 summarises the observation of the cross-validation results together with the classification of rice samples using discriminant analysis model. The results enable a 100% of correct classification of all rice samples (Asia, Europe and Thailand) and 90.32% of correct classification of 31 Thai jasmine rice samples (northern, northeastern and central regions), respectively.

4. Conclusions

High resolution ICP-MS multi-element fingerprinting combined with multivariate statistical analysis is a promising analytical tool for geographical origin classification of rice grains. Thai jasmine white rice can be differentiated from foreign rice samples (from France, India, Italy, Japan and Pakistan) by simple and rapid method (radar plots based on elemental composition) and multivariate data analysis. Discriminant analysis (DA) was much more effective than principal component analysis (PCA) for classification of rice, especially Thai jasmine rice which can be further identified the region (northern, northeastern and central regions) where it comes from.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2013.06.060.

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