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Discrimination of geographical origin of Korean and Chinese red pepper paste via inductively coupled plasma atomic emission spectroscopy and mass spectrometry

Suel Hye Hur[1†], Hwang-Ju Jeon[2†], Ji Hye Lee[1], Eun Joo Baek[1], Hyoyoung Kim[1] and Ho Jin Kim[1*]

Abstract

Background Red pepper paste is a common ingredient used in food in Korea. The discrimination of the geographical origin of agricultural products is important to protect the agricultural industry and customers from the misinformation regarding the product origin. Several studies have attempted to identify the geographical origin of red pepper based on its characteristic features using diverse methods, such as inorganic elemental analysis. However, similar studies on red pepper pastes have not been conducted thus far.

Results In, this study, we established methods based on inductively coupled plasma optical emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) for determining inorganic elements in red pepper pastes. The limit of detection (LOD) of ICP-AES was in the range of 0.006–0.531 $mg{\cdot}kg^{-1}$ and the limit of quantification (LOQ) was 0.017–1.593 $mg{\cdot}kg^{-1}$. In addition, LOD and LOQ ranges for ICP-MS were 0.001–1.553, and 0.002–5.176 $\mu g{\cdot}kg^{-1}$, respectively. The concentrations of Ca, K, Mg, Na, P, S, Cr, Mn, Co, Ni, Cu, Ga, As, Sr, Zr, Mo, Pd, Cd, Sn, Sb, Ce, Pt, Pb, and U were high in the Korean red pepper paste. All the employed discrimination models could clearly distinguish between Korean and Chinese red pepper pastes. In particular, among the four different models, CDA showed the most accurate ability to discriminate the geological origin of Korean and Chinese red pepper paste compared to that achieved using the other models with 100% accuracy.

Conclusions Based on, the findings of this study, the use of ICP-AES and ICP-MS analyses for discriminating the inorganic elements in food products in combination with the aforementioned statistical analysis models could help the mitigation of issues associated with the misinformation of the geographical origin of agricultural products, aiding customer protection.

Keywords ICP-AES, ICP-MS, Red pepper paste, Geographical origin, Discrimination

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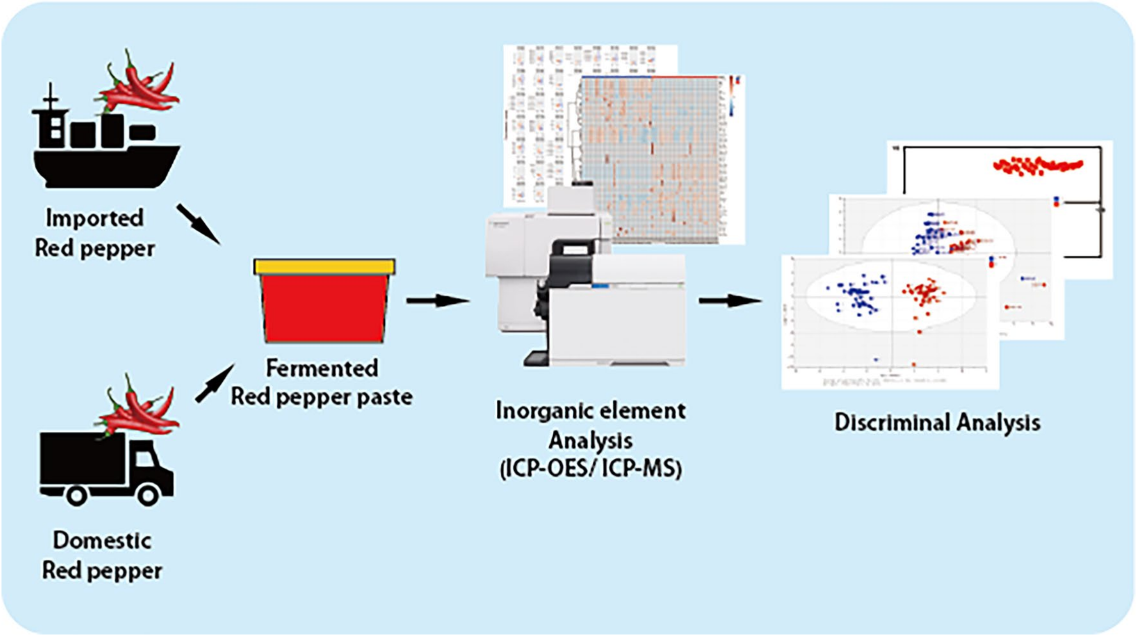
[†] Suel Hye Hur and Hwang-Ju Jeon have contributed equally to this work as first authors.

*Correspondence:
Ho Jin Kim
Rex7878@korea.kr
Full list of author information is available at the end of the article

Graphical Abstract



Introduction

Red pepper (*Capsicum annuum* L.) is a plant bearing fruits that are used as a spice worldwide for imparting a spicy taste to food. This Bolivia-originated plant has been widely grown around the world since its introduction to Asia by the Portuguese [1, 2]. Additionally, the fruits of this plant are used in traditional medicines for cough, toothache, sore throat, parasitic infections, rheumatism, and wound healing; furthermore, they are utilized as antiseptic, counterirritant, appetite stimulator, antioxidant, and immunomodulator [3–5]. Capsaicin (trans-8-methyl-N-vanillyl-6-nonenamide), which is an active compound isolated from the *Capsicum* family, has received significant research attention owing to its diverse biological activities [6]. Moreover, it possesses notable antiobesity and anticancer properties [6]. Owing to the aforementioned unique properties, various red pepper products, such as red pepper powder and fermented red pepper paste (Gochujang, RP), which can be consumed as food, are gaining increasing attention [7, 8].

RP is a red-colored Korean traditional grain-based sauce, prepared by mixing ingredients including red pepper powder, Meju (fermented soybean) powder, grain starch, and salt. The manufacturer ferments this mixture using their unique method to acquire high-quality RP. RP is generally used to impart a spicy taste in several Korean foods. Notably, the global retail market size of red pepper paste is expanding because of the increasing interest in Korean foods. In 2018, the export of red pepper paste from South Korea to various countries, including the United States, China, and Japan, amounted to 38.8 million USD, which gradually increased to 52.8 million USD in 2021 [9]. Although RP is primarily produced in South Korea, the geographical origin of red pepper used to make Gochujang can vary. Accordingly, the product costs may differ depending on the quality and customer preferences. Generally, the quality of final processed food products is considerably affected by the quality of agricultural products, such as red pepper, used as ingredients. Imported agricultural products require considerable time to reach the market from the place of their harvest, and they may possibly undergo additional quarantine processes before their export and import to various countries. During the quarantine processes, the agricultural products may be exposed to various chemicals, several of which may remain in these products as residues. Moreover, the price of imported and domestic products differs, and producers frequently mix these two varieties to reduce production costs. Based on these factors, an identification method for discriminating the origin of red pepper in Gochujang is necessary to protect customers from misinformation.

Previous studies have demonstrated that plants and crops are significantly affected by various environmental factors, such as climate, soil conditions, and precipitation. Plants uptake nutrients and water required for their growth from the surrounding environment, mainly from soil. They absorb carbon, hydrogen, oxygen, nitrogen, and sulfur, which are essential elements for growth, from the soil in the form of various organic and inorganic compounds through the roots. The absorbed materials are then translocated to the stems and leaves for creating primary and secondary metabolites. During this process, organic nutrients and inorganic elements are co-translocated into the plant through the roots, accumulating in the plant body. Therefore, the organic compounds and inorganic elements contents in plants and corresponding agricultural products provide information regarding the environment at their place of origin. Based on this concept, numerous studies have attempted to distinguish the geographical origin of agricultural products by analyzing their related information, including metabolites, and inorganic elements.

Researchers have attempted to determine the geographical origin of plants and their crops by applying different analytical techniques, including liquid chromatography–high-resolution mass spectrometry [10], gas chromatography–high-resolution mass spectrometry [11], nuclear magnetic resonance spectroscopy [12], inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) [13], and Fourier-transform infrared spectroscopy [14]. Several studies have been conducted utilizing various techniques to determine the different properties or compositions of the samples, such as metabolites [15] and inorganic elements [16]. However, all these trials were performed based on the general assumption that differences exist between the samples that are grown in different geographical areas. Recently, statistical methods combined with high-throughput data analysis, such as canonical discriminant analysis (CDA), cluster analysis (CA), linear discriminant analysis, principal component analysis (PCA), partial least squares-discriminant analysis (PLS-DA), and orthogonal PLS-DA (OPLS-DA), have been demonstrated to efficiently discriminate the origin of agricultural products [16–18]. The use of these statistical models renders the determination of the geographical origin of agricultural products easy. The discrimination of the origin of the agricultural products and well-known processed foods, such as soy sauces and soybean pastes, is challenging and has recently received significant attention [14, 19]. Researchers have attempted to identify the origin of the main ingredient of processed foods to prevent various issues caused by mislabeling or misinformation. For example, deceiving imported agricultural products as domestics due to the price and preference of consumers. Establishing methods for determining the origin of agricultural products and processed products using these products has been demanded to address such problems and protect consumers.

Herein, we present a method for discriminating the origin of the main ingredient of processed foods to restore consumer's trust. RPs produced using red peppers of two different origins, i.e., RPs made using Korean and Chinese red peppers, were used in this study. In the proposed method, a combination of the ICP-AES and ICP-MS analyses of the inorganic contents in the RPs and statistical modeling methods, such as CDA, PCA, PLS-DA, and OPLS-DA, was employed.

Materials and methods

Chemicals

The multielement standard (100 $mg \cdot kg^{-1}$ in 2–5% nitric acid, AccuStandard Inc., New Haven, CT, USA), custom ICP standard (100 $mg \cdot kg^{-1}$ in 2–5% nitric acid, AccuStandard Inc.), and zinc standard for ICP (1000 $mg \cdot kg^{-1}$ in nitric acid, Sigma-Aldrich, St. Louis, MO, USA) were employed for ICP-AES analysis. For ICP-MS analysis, the multielement complete standard (10 $mg \cdot kg^{-1}$ in nitric acid, Inorganic ventures Co., Christiansburg, VA, USA) was used. The purity of all the other reagents used in this study was higher than the analytical grade.

Sample collection and preparation

All the RP samples used in this study were purchased from a local market. Specifically, 46 Korean and 44 Chinese RP samples were used in the experiment conducted for discriminating the geological origin of RPs. In the modeling experiments, 60 and 30 samples were used for the training set and test set for validation, respectively. For the analysis of the inorganic elements in fermented red pepper paste, samples were prepared according to a previously reported method with slight modifications [20]. The samples were stored in a refrigerator at − 40 ℃ for 24 h, followed by lyophilization for 72 h at − 72 ℃ in a lyophilizer. The freeze-dried samples were homogenized using a ceramic homogenizer to obtain corresponding powders (Pulverisette 14, FRITSCH, Idar-Oberstein, Germany). Thereafter, 0.3 g of the homogenized sample was transferred to a Pyrex tube. Subsequently, ultrapure water (1 mL) and nitric acid (4 mL) were added to the tube, which was then placed in a single reaction chamber for microwave digestion using a microwave digestion system (ultraWAVE 3, Milestone, Sorisole, Italy) at 220 ℃ and 1500 W for 20 min.

Determination of sample contents

To calculate the concentrations of the different elements in the original RP samples, the concentrations found in the freeze-dried samples were corrected for moisture, and that moisture was calculated using the method of the Association of Official Analytical Chemists method (AOAC 1999).

Instrumental analysis

The qualitative and quantitative analyses of the inorganic elements in the samples were performed using a previously reported method [20]. Briefly, inorganic element contents were determined using two different techniques, namely, ICP-AES (Agilent 5100, Agilent Technologies, Santa Clara, CA, USA) and ICP-MS (Agilent 7900, Agilent Technologies). ICP-AES was used to determine the content of nine inorganic elements––Al, Ca, Fe, K, Mg, Na, P, S, and Zn––at wavelengths of 396.152, 317.933, 238.204, 766.491, 285.213, 589.592, 213.618, 181.972, and 206.200 nm, respectively. ICP-MS was used to determine the contents of 51 inorganic elements in the samples, including ^{9}Be, ^{48}Ti, ^{51}V, ^{55}Mn, ^{59}Co, ^{61}Ni, ^{63}Cu, ^{71}Ga, ^{72}Ge, ^{75}As, ^{78}Se, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{101}Ru, ^{103}Rh, ^{105}Pd, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Sm, ^{153}Eu, ^{157}Gd, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{182}W, ^{185}Re, ^{189}Os, ^{193}Ir, ^{195}Pt, ^{197}Au, ^{205}Tl, ^{208}Pb, ^{232}Th, and ^{238}U. The background equivalent concentration was determined, and the concentration ranges of the standard were 0.1–100 mg·kg^{-1} and 0.1–100 μg·kg^{-1} for the calibration curves of ICP-AES and ICP-MS analyses, respectively. The analytical method was validated with the limit of detection (LOD), the limit of quantification (LOQ), and the linearity (R^2) of calibration curves of each element. To confirm the LOD value, triplicate measurement, and standard deviation were calculated by 10 times repetitions of blank samples. LOQ value was also acquired by a standard deviation of 10 times repetition. Acquired LOD and LOQ values are shown in Additional file 1: Tables S2, S3.

Statistical analysis

Statistical analyses, such as PCA, PLS-DA, OPLS-DA, and receiver operating characteristic (ROC) analysis, were performed using SIMCA version 16 (Sartorius AG, Goettingen, Germany). For PCA, PLS-DA, and OPLS-DA, samples were divided into two categories––Korean and Chinese red pepper pastes. Variable importance in projections (VIPs) which score is higher than 1 for OPLS-DA were selected for the validation of the results by plotting the ROC curve. CDA was performed using the UNISTAT statistics software (Unistat Ltd., London, UK). In CDA, the Korean and Chinese red pepper pastes were referred as “1” and “2”, respectively. The entire data set for CDA was divided into two groups––calibration ($n = 90$) and validation ($n = 30$) sets.

Results and discussion

Determination of the content of target elements using ICP-AES

The method validation data for analysis using ICP-AES are shown in Additional file 1: Table S2. The limit of detection (LOD) of ICP-AES values were ranging 0.006–0.531 mg·kg^{-1}, and the limit of quantification (LOQ) values were ranging 0.017–1.593 mg·kg^{-1}. In addition, the recovery rates of the elements were above 98.4%. The contents of the nine targeted elements determined using ICP-AES are listed in Table 1. In both the Korean and Chinese RPs, the most abundant element was Na (45,748.69 and 43,676.96 mg·kg^{-1}, respectively), followed by K (9344.09 and 8202.15 mg·kg^{-1}, respectively) (Table 1). Considering the use of excess salt during the production process of red pepper paste, a high salt content is expected in the analyzed samples. Furthermore, a similar trend has been observed for kimchi, which is a fermented Korean traditional food [20]. The order of the nine analyzed elements based on their content in the Korean and Chinese RPs determined using ICP-AES was Na > K > P > S > Mg > Ca > Al > Fe > Zn (Table 1). Although the order of the abundance of elements was same for both the Korean and Chinese RPs, the Korean RP possessed higher concentrations of several fundamental elements (Ca, K, Mg, Na, P, and S), whereas the Al, Fe, and Zn contents in it were slightly lower. In particular, the Mg content in the Korean RP (1703.31 mg·kg^{-1}) was approximately two times higher than that in the Chinese RP (843.47 mg·kg^{-1}) (Table 1, Additional file 1: Figure S1). For kimchi, which also contains red pepper as a major ingredient, the Al, Fe, and Zn contents were higher in the Korean samples than those in the Chinese group [20]. Although red pepper powder is a main ingredient

Table 1 Comparison of the contents of the inorganic elements determined using ICP-OES (unit: mg·kg^{-1})

Element	Korean		Chinese	
	Max	Average	Max	Average
Al*	114.92	74.11	111.38	87.67
Ca*	1209.28	690.18	782.58	442.06
Fe	57.79	33.50	51.97	35.72
K*	15700.70	9344.09	11470.11	8202.15
Mg*	4086.21	1703.31	1463.69	843.47
Na	82468.52	45748.69	48857.81	43676.96
P*	3282.13	2014.13	2186.92	1671.18
S*	4156.75	1931.62	1520.28	1172.34
Zn	27.74	9.44	55.11	10.54

* The comparison of relative levels of elements in different groups revealed a significant difference between the Korean and Chinese red pepper pastes ($p < 0.05$)

of kimchi, considering the mass of cabbage used for preparing kimchi, the observed difference in the trend of the elemental content appears to have not been caused by the use of red pepper. Additionally, the samples of Chinese red pepper powder, which is the major ingredient of kimchi and RP, comprise higher Al and Fe contents than the domestic samples [21]. The proportion of red pepper in RP is substantially higher than that in kimchi. Considering these factors, although many ingredients, such as rice, fermented soybean powder, and soy sauce, are used to produce RP, the proportion of the red pepper is substantially higher than those of any other ingredients, and it may affect the inorganic element concentration.

Determination of the 51 target elements using ICP-MS

The validation data for analysis method for 51 elements using ICP-MS are shown in Additional file 1: Table S3. The range of LOD and LOQ were 0.001–1.553, and 0.002–5.176 μg·kg-1, respectively. The contents of the 51 targeted elements determined using ICP-MS are listed in Table 2. In both the Korean and Chinese RP samples, the most abundant inorganic element was ^{55}Mn (15.03 and 11.80 mg·kg^{-1} in Korean and Chinese RPs, respectively), followed by ^{88}Sr (10.65 and 51.21 mg·kg^{-1} in Korean and Chinese RPs, respectively). In the ICP-MS analysis, among the 51 targeted inorganic elements, ^{101}Ru, ^{103}Rh, ^{165}Ho, ^{169}Tm, ^{175}Lu, ^{185}Re, and ^{193}Ir were not detected in both the Korean and Chinese RPs (Table 2, Additional file 1: Figure S2). Although ^{107}Ag, ^{166}Er, ^{172}Yb, and ^{181}Ta were detected, their contents were below 3 μg·kg^{-1} in both the Korean and Chinese RPs (Table 2, Additional file 1: Figure S2). The concentrations of ^{9}Be, ^{48}Ti, ^{51} V, ^{72}Ge, ^{78}Se, ^{93}Nb, ^{125}Te, ^{133}Cs, ^{137}Ba, ^{139}La, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{163}Dy, ^{178}Hf, ^{182}W, ^{189}Os, ^{197}Au, ^{205}Tl, and ^{232}Th in the Chinese RP were higher than those in the Korean RP. Particularly, compared with those in the Korean RP, the determined contents of ^{9}Be, ^{147}Sm, and ^{163}Dy in the Chinese RP were higher by 62.68, 11.85, and 17.41 times, respectively. Conversely, the Korean RP comprised a higher content of ^{52}Cr, ^{55}Mn, ^{59}Co, ^{61}Ni, ^{63}Cu, ^{71} Ga, ^{75}As, ^{88}Sr, ^{90}Zr, ^{95}Mo, ^{105}Pd, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{140}Ce, ^{195}Pt, ^{208}Pb, and ^{238}U than the Chinese RP.

Using hierarchical CA, the differences in the inorganic element content between the Korean and Chinese RP samples were expressed in the form of a heatmap (Additional file 1: Figure S3). The heatmap is generated using MetaboAnalyst 5.0 utilizing the determined element content as the raw dataset [22]. In the CA heatmap, the same row represents the inorganic element content obtained from the same ICP analysis and the same column represents that of the same RP samples. ^{107}Ag, ^{182}W, ^{52}Cr, ^{60}Ni, ^{93}Nb, ^{197}Au, ^{181}Ta, ^{189}Os, ^{125}Te, ^{195}Pt, ^{75}As, ^{166}Er, and ^{172}Yb are marked predominantly in gray on the heatmap

Table 2 Contents of the inorganic elements determined using ICP-MS (unit: μg·kg^{-1})

Element	Korea		Chinese	
	Max	Average	Max	Average
^{9}Be*	0.89	0.02	5.44	1.24
^{48}Ti	4896.59	2075.45	3555.80	2265.45
^{51} V*	90.80	18.79	446.28	63.89
^{52}Cr	27583.17	962.70	2556.86	525.70
^{55}Mn*	15713.13	15037.42	18331.09	11749.11
^{59}Co*	132.11	55.86	76.56	43.30
^{60}Ni	73695.93	2909.93	1485.27	657.76
^{63}Cu*	8780.86	3444.14	4117.29	2721.67
^{71} Ga*	76.15	57.12	63.38	52.70
^{72}Ge*	3.73	1.18	3.44	1.62
^{75}As*	188.90	83.78	81.34	47.17
^{78}Se	164.56	27.09	63.62	27.16
^{88}Sr*	30477.02	10650.45	9656.69	5099.18
^{90}Zr*	222.92	175.73	211.98	161.71
^{93}Nb	0.77	0.02	3.07	0.18
^{95}Mo*	4160.37	852.08	643.71	317.34
^{101}Ru	0.00	0.00	0.00	0.00
^{103}Rh	0.00	0.00	0.00	0.00
^{105}Pd	17.68	5.58	18.68	4.75
^{107}Ag	1.59	0.03	0.00	0.00
^{111}Cd*	45.98	27.75	30.88	17.57
^{118}Sn*	2196.72	1679.27	1945.29	1580.31
^{121}Sb	6.25	0.46	3.04	0.16
^{125}Te*	0.91	0.05	2.63	0.25
^{133}Cs*	24.23	13.08	26.92	18.30
^{137}Ba*	2543.35	1566.87	3232.03	1854.54
^{139}La*	26.63	7.25	34.60	16.93
^{140}Ce	2651.33	1911.69	2423.30	1875.03
^{141}Pr*	5.98	0.50	5.22	2.19
^{146}Nd*	31.30	5.78	29.93	15.05
^{147}Sm*	3.57	0.09	4.13	1.12
^{153}Eu*	0.46	0.05	1.04	0.15
^{157}Gd	81.00	59.50	73.23	60.08
^{163}Dy*	1.61	0.04	2.65	0.61
^{165}Ho	0.00	0.00	0.00	0.00
^{166}Er	0.14	0.00	0.38	0.02
^{169}Tm	0.00	0.00	0.00	0.00
^{172}Yb	0.15	0.00	0.21	0.01
^{175}Lu	0.00	0.00	0.00	0.00
^{178}Hf*	3.31	1.73	3.81	2.60
^{181}Ta	0.00	0.00	2.62	0.10
^{182}W*	200.67	7.81	110.23	25.51
^{185}Re	0.00	0.00	0.00	0.00
^{189}Os	5.60	0.13	46.45	2.07
^{193}Ir	0.00	0.00	0.00	0.00
^{195}Pt	11.18	0.60	5.59	0.29
^{197}Au*	50.34	2.84	251.10	18.33

Table 2 (continued)

Element	Korea		Chinese	
	Max	**Average**	**Max**	**Average**
^{205}Tl	9.63	2.25	10.81	2.67
^{208}Pb*	114.19	49.04	53.13	42.00
^{232}Th*	6.47	0.20	5.77	2.40
^{238}U	17.97	2.63	7.17	1.49

* The comparison of relative levels of elements in different groups revealed a significant difference between the Korean and Chinese red pepper pastes ($p < 0.05$)

for both the groups. In the Korean samples, ^{147}Sm, ^{163}Dy, ^{141}Pr, ^{146}Nd, ^{139}La, ^{232}Th, ^{9}Be, Al, ^{178}Hr, ^{137}Ba, ^{51} V, Fe, ^{48}Ti, and ^{133}Cs contents were lower, and on the heatmap, ^{147}Sm, ^{163}Dy, ^{141}Pr, ^{146}Nd, ^{139}La, and ^{232}Th appeared to be the same.

PCA and PLS-DA for the geographical discrimination of red pepper pastes

The dataset of 46 Korean samples and 44 Chinese samples was used to discriminate the origin of the red peppers used to produce RPs. Using this dataset, PCA and PLS-DA were conducted to distinguish between two classified RP samples. PLS-DA and PCA are commonly used multivariate analysis methods for data analysis [23]. Compared with PCA, class labeling can lead to dimensionality reduction in PLS-DA [23]. Generally, PLS-DA is recommended for datasets with large volumes, numerous features, noise, and missing data, such as chemometric and chemomic data [24, 25], and can be applied for feature selection or classification, owing to the awareness of the class labels [23]. Therefore, these statistical analysis methods were applied to the inorganic element data to distinguish the origin of the RPs. Although certain deviations were observed, two groups could be slightly distinguished using both PCA and PLS-DA models. The PLS-DA plot revealed a clear separation of samples based on their origin (Fig. 1). The Q2 and R2X values of the PLS-DA model (Q2 = 0.674 and R2X = 0.208) were larger than those of the PCA model (Q2 = 0.136 and R2 = 0.211), which implies that the two groups can be distinctly distinguished using the PLS-DA model (Fig. 1a, b). The VIP score method is a frequently employed variable ranking approach [25]. Generally, elements with VIP scores higher than 1 are considered as significantly influencing variates in the model. In our results, 22 elements (^{178}Hf, ^{232}Th, ^{139}La, ^{146}Nd, ^{141}Pr, ^{111}Cd, ^{147}Sm, ^{163}Dy, S, ^{133}Cs, Mg, Ca, ^{9}Be, Al, ^{172}Yb, ^{71} Ga, ^{95}Mo, ^{166}Er, ^{88}Sr,

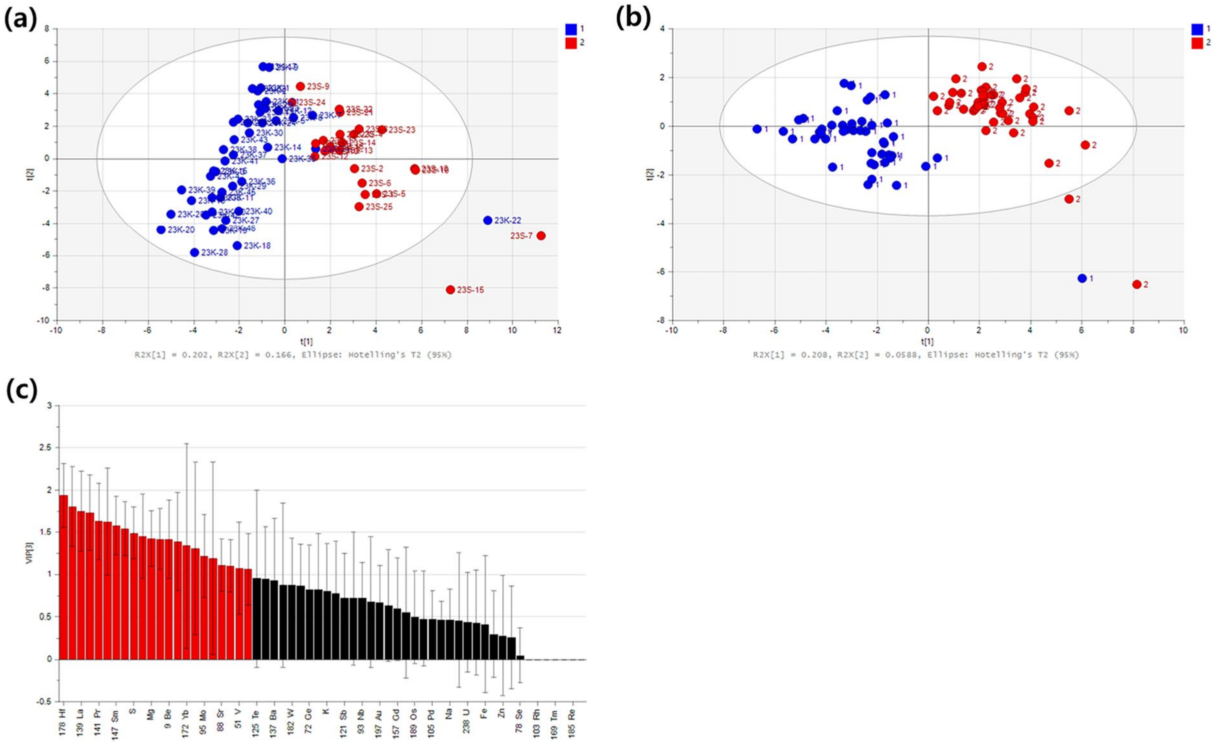


Fig. 1 Discriminant analysis of red pepper paste using partial least squares-discriminant analysis (PLS-DA) model. **a** Principal component analysis plot, **b** PLS-DA plot for imported and domestic fermented red pepper pastes. Red and blue color indicating imported and domestic fermented red pepper paste, respectively. **c** Variable importance in projections (VIP), the elements with larger than 1 VIP values represented as red color

^{55}Mn, ^{51} V, and P) possessed VIP scores of ≥ 1 (Fig. 1c). These elements significantly influence the discrimination of the two groups, i.e., Korean-origin and Chinese-origin RPs [23, 26].

OPLS-DA and ROC analysis

Furthermore, OPLS-DA modeling is conducted to confirm the applicability of our discrimination model (Fig. 2). Comparing the PCA and PLS-DA results, the OPLS-DA model yielded more clearly separated clusters of the Korean and Chinese RPs, implying that OPLS-DA is an optimized model for discriminating the origin of the ingredients used for producing RPs (Fig. 2a). The R2X (0.436) and Q2 (0.826) values support this conjecture. The VIP scores of OPLS-DA are illustrated in Fig. 2b. Based on the VIP analysis, 20 elements possessed scores higher than 1 (^{178}Hf, ^{232}Th, ^{139}La, ^{146}Nd, ^{141}Pr, ^{111}Cd, ^{147}Sm, ^{163}Dy, S, ^{133}Cs, Mg, Ca, ^{9}Be, Al, ^{71} Ga, ^{95}Mo, ^{88}Sr, ^{55}Mn, ^{51} V, and P; Fig. 2b). The OPLS-DA model was validated using the ROC curve (Fig. 2c). To confirm the accuracy of OPLS-DA modeling, ROC and permutation tests were performed, and the ROC curve was obtained by plotting sensitivity and specificity on the y and x axes, respectively [27]. The area under the ROC curve (AUC) indicates the ability of the test to determine the presence or absence of a specific condition [27].

The AUC value determined from the ROC curve of our OPLS-DA model was 1. The obtained AUC values indicate that the classification using our model is highly predictable [28]. Based on the AUC values obtained from the ROC curve, the discrimination accuracy for the RP using the OPLS-DA model was 100% for both the Korean-origin and Chinese-origin RPs. Sensitivity and Specificity were 100% and 95% for PLS-DA and 100% and 96% for OPLS-DA, respectively. The permutation test was performed for the further validation of our model (Fig. 2d). R2 and Q2 values obtained via the permutation test were 0.289 and − 0.417, respectively. These results indicate that our model is not overfitted [28]. The superior discrimination ability of the OPLS-DA model to that of PCA and PLS-DA has been previously reported [20, 29]. PLS-DA is a frequently used method for classification [30]; however, in contrast to PLS-DA, OPLS-DA can remove the first components orthogonal to the dependent variable from the data [30, 31]. Owing to this forced reduction of classification information, OPLS-DA improves interpretation,

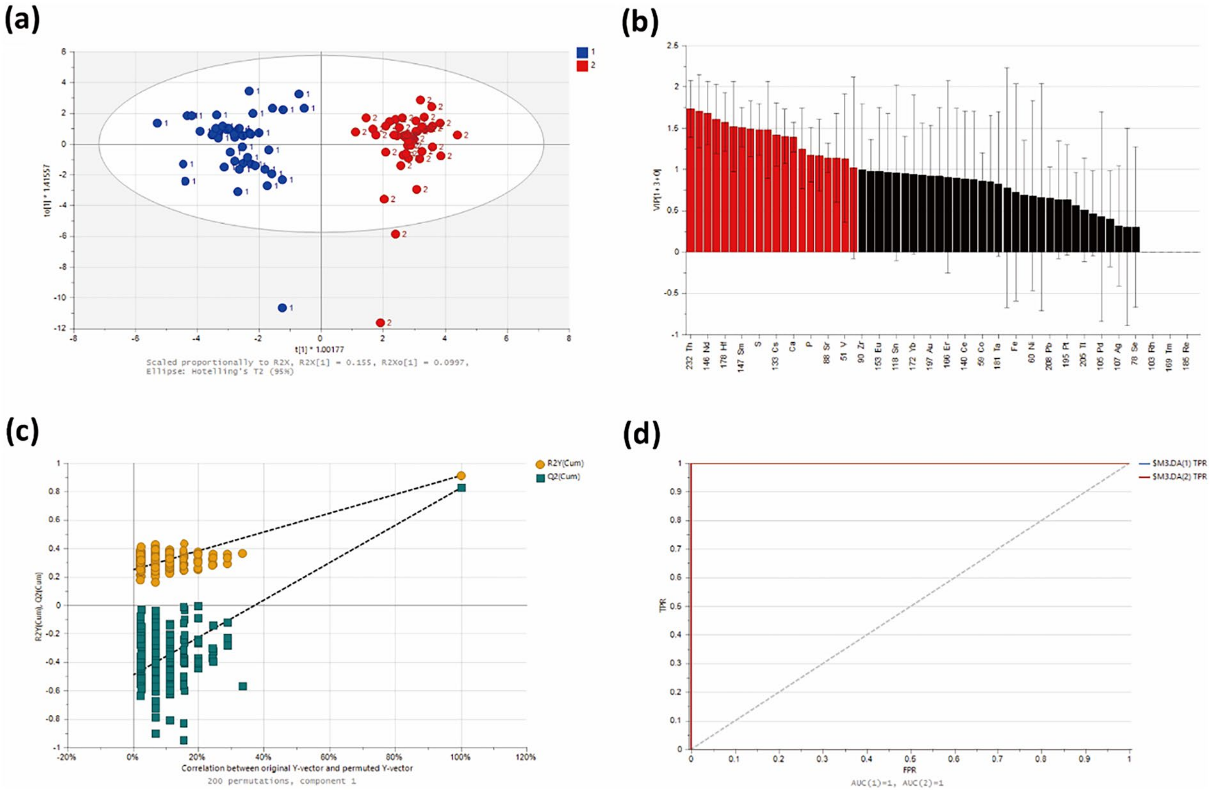


Fig. 2 Discriminant analysis of different origin of fermented red pepper pastes using orthogonal partial least squares-discriminant analysis (OPLS-DA) model. **a** OPLS-DA plot of domestic and imported fermented red pepper pastes. Red and blue color indicating imported and domestic fermented red pepper paste, respectively. **b** Variable importance in projections (VIP), the elements with larger than 1 VIP values represented as red color. **c** The results of the permutation test for validation. **d** ROC of OPLS-DA using 20 VIP

which leads to the enhancement of the discrimination ability of the prediction model [30, 31]. Therefore, among the three analyzed models, namely, PCA, PLS-DA, and OPLS-DA, the OPLS-DA model yielded the most promising results.

CDA for discriminating the origin of red pepper pastes

CDA was performed to discriminate the geographical origin of RPs using the concentration data of 60 inorganic elements in 46 Korean and 44 Chinese RP samples as independent variables (Fig. 3). The difference in the central value of the two clustered groups can be expressed as the distance between centroids, and the calculated distance indicates the discrimination ability of the CDA model. Generally, when the distance between the groups is longer than 2, the groups can be distinguished [32]. The calculated canonical discriminant functions (center values) of the Korean and Chinese RPs were −9.4729 and 9.99035, respectively. Based on these values, the distance between the two RP groups was 19.3765, indicating that the Korean and Chinese RPs are well distinguished. Moreover, the discrimination ability of CDA was confirmed via the eigenvalues, percentage, cumulative, and correlation value, which were 95.9478, 100%, 100%, and 0.9948, respectively. In the validation test, the validation set included 30 samples, and the classification accuracy was 100%. Based on these results, CDA model showed the best ability to discriminate Korean and Chinese RPs among the 4 different models built in this study.

Conclusions

Due to the increasing interest in Korean food, the demand for RPs has also increased globally. But the price of Chinese red pepper, one of the main ingredients of RPs, is much lower than that of Korean, and the quality is also lagging behind. In addition, many studies have tried to determine the geological origin of agricultural products, but research on determining the origin of processed food has not been extensively tried. Therefore, establishing methods for determining the geographical origin of red pepper for making RPs is necessary. The discrimination of the geological origin of the ingredient of processed food, red pepper in RPs was conducted by determining the inorganic element contents in 46 Korean and 44 Chinese RPs using two different techniques, ICP-AES and ICP-MS. By projecting the inorganic element data of the RPs under supervised or unsupervised conditions, the two different geographical origins of Korean and Chinese RPs could be clearly distinguished using all models. Especially, CDA showed the best discrimination ability with 100% accuracy among the four different statistical analyses, including PCA, PLS-DA, and OPLS-DA. Our results verified that the geological origin of ingredients for making processed food could also be discriminated by determining inorganic elements in processed food using various discrimination models and the use of inorganic element analysis in conjunction with discrimination models could help address the issues caused by the misinformation of the origin of ingredients for processed foods.

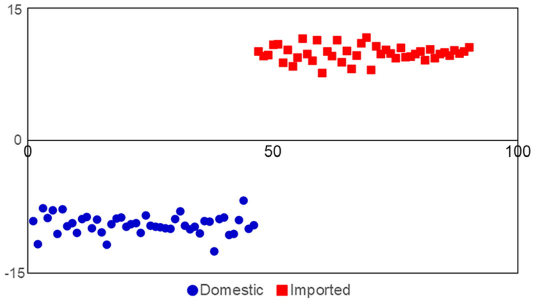


Fig. 3 Discriminant analysis of fermented red pepper paste using determined inorganic element data. Canonical discriminant analysis plot. Red and blue colors represent imported and domestic fermented red pepper paste, respectively

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40538-024-00559-z.

Additional file 1: Figure S1. Determined level of inorganic elements in the Korean and Chinese red pepper paste using ICP-AES. The determined concentration of nine elements using inductively coupled plasma optical emission spectrometry. The concentrations of each element were expressed as mg·kg^{-1}. **Figure S2.** Discriminant level of inorganic elements in the Korean and Chinese red pepper paste using ICP-MS. The determined level of fifty-one inorganic elements using inductively coupled plasma mass spectrometry. The concentrations of each element were expressed as mg·kg^{-1}. **Figure S3.** Heatmap of inorganic element contents using inductively coupled plasma optical emission spectrometry and inductively coupled plasma mass spectrometry. The contents of inorganic elements are indicated by various colors, with the darkest red color indicating a high content and the darkest blue indicating a low content. **Table S1.** Information for Korean and Chinese red pepper paste used for ICP analysis. **Table S2.** Method validation for the analysis of inorganic element using ICP-AES (unit: mg·kg^{-1}). **Table S3.** Method validation for the analysis of inorganic element using ICP-MS (unit: µg·kg^{-1}).

Declaration of Generative AI and AI-assisted technologies in the writing process

The authors declare that no Generative AI and AI-assisted technologies were used during the preparation of this study.

Author contributions

SHH: investigation, writing—review and editing, conceptualization, data curation, formal analysis. HJJ: investigation, writing—original draft, data curation. JHL: investigation, data curation, formal analysis. EJB: investigation, methodology, formal analysis. HK: investigation, formal analysis, writing—review and editing. HK: supervision, funding acquisition, writing—review and editing.

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Availability of data and materials

The data that support the findings of this study are available from the corresponding author H. Kim, upon reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this study.

Author details

[1]National Agricultural Products Quality Management Service, Gimcheon 39660, Republic of Korea. [2]Red Riveer Research Station, Louisiana State University AgCenter, 262 Research Station Dr., Bossier City, LA 71112, USA.

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