Current Research in Food Science 6 (2023) 100532

Contents lists available at ScienceDirect

Current Research in Food Science

journal homepage: www.sciencedirect.com/journal/current-research-in-food-science

Geographical discrimination of dried chili peppers using femtosecond laser ablation-inductively coupled plasma-mass spectrometry (fsLA-ICP-MS)

Suel Hye Hur [a,1], Seyeon Kim [a,1], Hyoyoung Kim [a], Seongsoo Jeong [b], Hoeil Chung [b], Yong-Kyoung Kim [a,**], Ho Jin Kim [a,*]

[a] National Agricultural Products Quality Management Service, Gimcheon, 39660, Republic of Korea
[b] Department of Chemistry and Research Institute for Convergence of Basic Science, Hanyang University, Seoul, 04763, Republic of Korea

ARTICLE INFO

Keywords:
Femtosecond laser ablation-inductively coupled plasma-mass spectrometry
Dried chili pepper
OPLS-DA
Canonical discriminant analysis
Heatmap
Geographical discrimination

ABSTRACT

This study presents a method for discriminating the geographical origin of dried chili peppers using femtosecond laser ablation-inductively coupled plasma-mass spectrometry (fsLA-ICP-MS) and multivariate analysis, such as orthogonal partial least squares discriminant analysis (OPLS-DA), heatmap analysis, and canonical discriminant analysis (CDA). Herein, 102 samples were analyzed for the content of 33 elements using optimized conditions of 200 Hz (repetition rate), 50 μm (spot size), and 90% (energy). Significant differences in count per second (cps) values of the elements were observed between domestic and imported peppers, with variations of up to 5.66 times (^{133}Cs). The OPLS-DA model accuracy achieved an R^2 of 0.811 and a Q^2 of 0.733 for distinguishing dried chili peppers of different geographical origins. The variable importance in projection (VIP) and s-plot identified elements 10 and 3 as key to the OPLS-DA model, and in the heatmap, six elements were estimated to be significant in discriminating between domestic and imported samples. Furthermore, CDA showed a high accuracy of 99.02%. This method can ensure food safety for consumers, and accurately determine the geographic origin of agricultural products.

1. Introduction

Chili pepper (*Capsicum* sp.) is a crop native to Central and South America, which is used and cultivated worldwide (Barchenger and Bosland, 2019). Chili pepper is rich in amino acids, such as aspartic and glutamic acids, and nutrients, such as vitamin C, lutein, β-carotene, calcium, and magnesium (Olatunji and Afolayan, 2018). In particular, its active component capsaicin shows anti-inflammatory and anti-obesity properties and prevents cardiovascular diseases when taken regularly and in appropriate amounts (Zhang et al., 2021).

The consumption of chili peppers is prevalent in South Korea, predominantly in the form of dried chili peppers. Hereby, Korean consumers prefer domestically grown chili papers to imported ones (Hong and Kim, 2013). Owning to different geographical environments, the same agricultural products show different compositions of elements and active components (Chung et al., 2016; Choi et al., 2020). Therefore, consumers' preferences differ depending on the country or region where these products are cultivated (Thøgersen et al., 2019). The authenticity of food products based on their geographical origin is an important factor in controlling food quality and ensuring high food safety, which has been attracting more attention from consumers and promoting active research on geographical origin analysis (Promchan et al., 2016).

In addition to organic components, an analysis method of the geographical origin of food products based on inorganic components is actively progressing worldwide (Choi et al., 2016; Lee et al., 2020a) because they are chemically stable and representative of the elements in the soil and environmental impact on the area where the crop grows (Bong et al., 2012). Microwave-assisted acid digestion is commonly used to prepare samples for inorganic analyses (Altundag and Tuzen, 2011). However, the preparation procedure for solid samples is time-consuming and may lead to sample contamination and loss during processing (Schneider et al., 2018). In addition, the analysis is performed with diluted liquid samples, which can result in poor limits of detection (LOD). Strongly acidic solutions are often used, potentially

* Corresponding author.
** Corresponding author.
E-mail addresses: ykkim79@korea.kr (Y.-K. Kim), rex7878@korea.kr (H.J. Kim).
[1] Suel Hye Hur and Seyeon Kim contributed equally to this work.

https://doi.org/10.1016/j.crfs.2023.100532
Received 31 March 2023; Received in revised form 9 May 2023; Accepted 7 June 2023
Available online 8 June 2023

posing a risk to the safety of the experimenter (Reyes and Campos, 2006; Bolea-Fernandez et al., 2015). For the analyses of inorganic components, instruments, including energy-dispersive X-ray fluorescence spectrometry (ED-XRF), isotope ratio mass spectrometry, inductively coupled plasma-optical emission spectroscopy (ICP-OES), and inductively coupled plasma-mass spectrometry (ICP-MS), are used. ICP-MS and ICP-OES can perform quantitative and qualitative elemental analyses of different food samples with high sensitivity and precision. However, microwave-assisted acid pretreatment is still required. While ED-XRF analysis does not require sample pretreatment for powder-type samples, it may not be suitable for accurately identifying trace elements due to its low sensitivity or high standard deviation. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a powerful analytical technique that combines LA with the high-sensitivity multi-element analysis function of ICP-MS for solid sampling (Nunes et al., 2016). LA-ICP-MS enables direct analysis of solid samples with minimal reagent consumption, short pretreatment time, and minimal risk of sample contamination or loss. In addition, a small amount of sample can be analyzed non-destructively, providing rapid and isotopic information on specific elements (de Francesco et al., 2018; von Wuthenau et al., 2021). This technology has successfully demonstrated its applicability for determining the origin of metals, glass, porcelain, and relics (Devos et al., 2000; Trejos et al., 2003; Bartle and Watling, 2007; Pornwilard et al., 2011; Grainger et al., 2012), as well as of various foods, such as milk powder, vanilla, almond, and rice (Hondrogiannis et al., 2013; Promchan et al., 2016; Hoffman et al., 2018; von Wuthenau et al., 2022). However, despite its potential, there have been limited studies on the use of LA-ICP-MS for the geographical discrimination of agricultural products.

Furthermore, statistical analysis is essential to effectively evaluate experimental results and draw accurate conclusions from the data. Multivariate statistical analysis methods, such as Principal Component Analysis (PCA), Partial Least Squares Discriminant Analysis (PLS-DA), Orthogonal Partial Least Squares Discriminant Analysis (OPLS-DA), and Canonical Discriminant Analysis (CDA), have been widely used to increase the efficiency and accuracy of geographical discriminant analyses. These methods have been employed to build geographical discrimination models based on experimental data, demonstrating high accuracy and efficiency (Lee et al., 2020b; Fiamegos et al., 2021; Ghidotti et al., 2021).

In this study, we hypothesize that the geographical origin of dried chili peppers can be accurately determined using fsLA-ICP-MS and statistical data processing and that this method can overcome the shortcomings of the commonly used chemical methods of geographical discriminant analysis.

2. Materials and methods

2.1. Sample collection and pellet preparation

In 2021, the National Agricultural Product Quality Management Service (NAQS) in Korea collected 102 samples of dried chili peppers, including 51 domestic and 51 imported (Table S1). Domestic products were purchased from food stores in Gyeonggi, Gangwon, Chungnam, Gyeongbuk, Gyeongnam, Jeonbuk, Jeonnam, and Jeju. Imported dried chili pepper samples from China and Vietnam were purchased from a store that directly imports and sells agricultural products. First, 200 g of dried chili pepper was evenly mixed in a homogenizer (UBC-DV, Universal Biological & Chemical, Goyang, Korea) and dried for 5 h at 40 °C in a hot air dryer. The powder was passed through a 0.5 mm filter using an experimental grinder, dried again in a hot air dryer for 3 h, and used as a sample for further analysis. Multi-element analysis using laser ablation examines only a small area of a sample; therefore, it is important to ensure that each sample is homogeneous and representative of the entire sample (Papaslioti et al., 2019). Using a PP35 pellet press (Retsch, Haan, Germany), approximately 2 g of ground dried chili pepper was pressed at 10 ton cm^{-1} to form pellets approximately 2–4 mm thick and 13 mm in diameter. The workflow of this study is illustrated in Fig. 1.

2.2. Optimization of the fsLA-ICP-MS method

Femtosecond (fs) LA-ICP-MS is an analytical instrument composed of a J200 fsLA (Applied Spectrum, USA) and an Agilent 7900 ICP-MS (Agilent, USA) instrument. The analytical efficiency of fsLA-ICP-MS depends on various parameters, such as the ablation mode, scanning rate, spot size, laser fluence, repetition rate, laser energy, carrier flow, pulse length, and wavelength (Zaeem et al., 2021). These parameters affect the ablation process, plasma, and signal stability during analysis and can lead to inaccurate results (Voss et al., 2017). The RF power, RF match, and He flow of the ICP-MS were set to 1600 W, 1.40 V, and 2.0 mL min^{-1}, respectively. The optimized parameters of the fsLA-ICP-MS are summarized in Table S2. All experiments were performed inside the ablation chamber (100 mm × 100 mm) of the fsLA device.

2.3. Sample measurements using fsLA-ICP-MS

Using the optimized experimental conditions, multi-element analysis of 61 elements (^{9}Be, ^{23}Na, ^{24}Mg, ^{27}Al, ^{31}P, ^{34}S, ^{39}K, ^{43}Ca, ^{44}Ca, ^{48}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{61}Ni, ^{63}Cu, ^{66}Zn, ^{71}Ga, ^{72}Ge, ^{75}As, ^{78}Se, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{101}R, ^{103}Rh, ^{105}Pd, ^{107}Ag, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}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) was performed based on 102 dried chili pepper samples. Four single-line scanning laser ablation modes were used in three different areas of the dried chili pepper pellet.

2.4. Data pre-processing and multivariate analysis

The data obtained with fsLA-ICP-MS were pre-processed to improve quality. The relative standard deviation (RSD) for each element was calculated from the line scan data and elements were excluded from all chili samples if the RSD was >30% and low signal intensity.

R^2, Q^2, receiver operating characteristic (ROC) curve, and permutation test were used to evaluate the OPLS-DA model. R^2 and Q^2 are generally used as indicators to explain the model and how accurately it predicts the class, respectively. Moreover, the ROC curve is the ability of a model to express the balance between its sensitivity and specificity. The OPLS-DA model was fitted using an autofit function (SIMCA) and then optimized by removing the furthest outliers from the score plot and the residual normal probability plot until the fitted model showed the highest R^2 and Q^2 values. S-plot and variable importance in projection (VIP) scores were used to identify elements that had a significant effect on the data set. The elements with a VIP score >1 were selected to confirm their significance for the determination of the geographical origin of dried chili pepper samples. A permutation test ($n = 200$) was performed to check whether the model data was overfitted as cross-validation, and the plots showed the correlation between the original y-variable and the permuted y-variable, displayed on the x-axis, and the cumulative R^2 and Q^2, displayed on the y-axis, then a regression line was drawn, where the intercept was a measure of the overfitting. OPLS-DA was conducted using the SIMCA multivariate data analysis software.

Inorganic element results were analyzed using Metaboanalyst 5.0 (http://www.metaboanalyst.ca), a web-based metabolite analysis platform, and they were displayed in color as a visual distribution on a heat map (Hur et al., 2023).

CDA was performed using the UNISTAT statistical software (Unistat, London, UK) by setting the counts per second (cps) values of dried chili pepper samples as independent variables. Hereby, domestic samples were classified as “1” and imported samples as “2.”

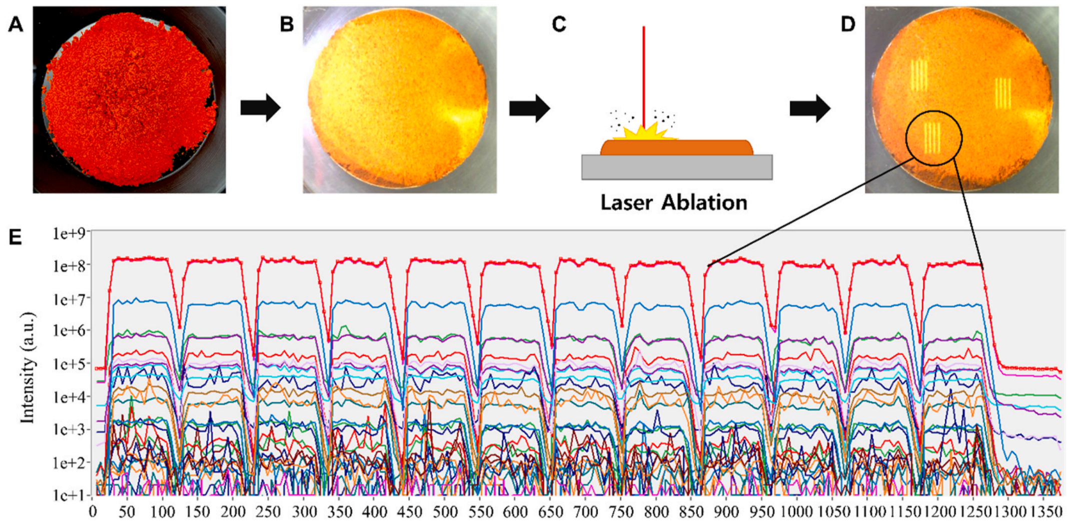

Fig. 1. Illustration of the study workflow. (A) Dried chili pepper powder, (B) pressed dried chili pepper powder, (C) laser ablation of the pressed dried chili pepper powder, (D) traces of lines after laser ablation, and (E) time-resolved analysis (TRA) graph of 33 different elements.

3. Results and discussion

3.1. Optimization of fsLA conditions

As known, an internal standard (IS) enables the normalization of unstable signal data. In this study, the naturally stable isotope ^{13}C was used as the IS in fsLA-ICP-MS (Nunes et al., 2016; Makino and Nakazato, 2021). The experimental parameters were rigorously optimized across various repetition rates (10, 50, 100, 200, 500, 700, and 1000 Hz), spot sizes (20, 30, 40, 50, and 60 μm), energies (60, 70, 80, 90 and 100%), and gas flow rates (from 0.1 to 1.4 L min^{-1}). The resulting data revealed that the optimal conditions for consistent stable cps values and reproducible analysis with low relative standard deviations (RSD) were achieved at a repetition rate of 200 Hz, a spot size of 50 μm, an energy level of 90%, as well as helium and argon gas flow rates of 1.2 and 1.0 L min^{-1}, respectively (Figs. S1A–C). In the subsequent experiments, this robust method was applied to measure the chemical compositions of 102 dried chili pepper samples, yielding comprehensive and reliable results. The fsLA-ICP-MS method used in this study has been previously validated (Kim et al., 2023)

3.2. Sample analysis using fsLA-ICP-MS

Thirty-three elements were selected through a data pre-processing step. To confirm the differences in elemental content based on geographical origin, the minimum, maximum, and average cps values of 51 domestic and 51 imported dried chili peppers were compared for 33 different elements, as shown in Table S3. Both the domestic and imported dried chili pepper exhibited the highest average cps values of 9.42×10^8 and 9.41×10^8 for ^{39}K, respectively. The average cps values

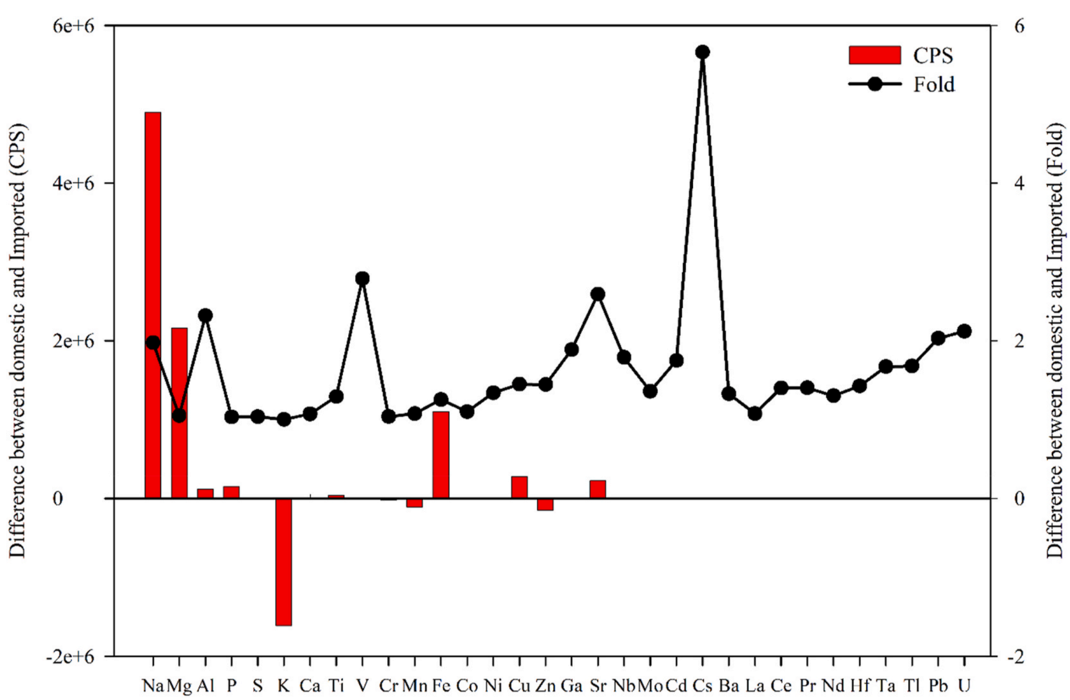

Fig. 2. Comparison of the average cps values for domestic and imported dried chili pepper samples. Red bars: difference in cps values based on the imported samples, black line: cps fold difference calculation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

of ^{24}Mg and ^{23}Na were also high in both groups. Domestic samples had the highest average cps values for ^{31}P, ^{56}Fe, ^{55}Mn, and ^{44}Ca: 4.69×10^6, 4.33×10^6, 1.53×10^6, and 7.59×10^5, respectively, while imported samples had the highest average cps values for ^{56}Fe, ^{31}P, ^{55}Mn, and ^{63}Cu: 5.43×10^6, 4.84×10^6, 1.42×10^6, and 8.98×10^5, respectively. The lowest cps values in domestic and imported samples were found in ^{178}Hf (57.61 and 82.16 cps) and ^{131}Ta (82.70 and 138.27 cps). Subsequently, low cps values were detected for ^{238}U, ^{71}Ga, and ^{146}Nd in domestic and imported products. In addition, 15 elements with a difference of more than 1.43 times in average cps values were identified depending on the geographical origin (Fig. 2). For 14 elements except for ^{66}Zn, average cps values were higher in imported than in domestic products. The element showing the greatest difference (5.66 times) between the two groups was ^{133}Cs. In addition, imported samples showed approximately 2.79 and 2.59 times higher amounts of ^{51}V and ^{88}Sr, respectively. It was also confirmed that the amounts of ^{27}Al, ^{238}U, ^{208}Pb, and ^{23}Na were at least twice as high in imported samples, and a difference of at least 1.43 times was found for the remaining elements (^{71}Ga, ^{93}Nb, ^{111}Cd, ^{205}Tl, ^{181}Ta, ^{63}Cu, and ^{178}Hf) except ^{66}Zn, which showed approximately 1.44 times higher concentration of ^{66}Zn in domestic products. In contrast, ^{39}K, ^{31}P, ^{34}S, and ^{52}Cr exhibited the smallest differences. The descriptive statistics of the 15 elements with the highest cps difference in domestic and imported chili peppers are shown in Fig. 3. Because of the difficulty of quantification in the LA-ICP-MS analysis, the elements' cps values of domestic and imported chili pepper samples were compared in this study. The results of this comparison were consistent with previous studies (Hwang et al., 2019; Mi et al., 2020).

3.3. Geographical origin discrimination using multivariate analysis

3.3.1. OPLS-DA

OPLS-DA is a suitable method for discriminating two groups by assigning a dependent variable, called a set, by classifying and highlighting the influence of variables that contribute to discrimination (Jiang and Leem, 2016; Zhang et al., 2022). OPLS-DA was performed using the SIMCA software to differentiate between domestic and imported products. In the OPLS-DA, the elements used as variables in the geographical origin discrimination analysis are shown in Fig. 4A. The R^2 of 0.811 and Q^2 of 0.733 confirm that it is a reliable model that distinguishes between domestic and imported products. OPLS-DA is a regression analysis that rotates the data matrix to easily identify observations and variations between different groups (Bylesjö et al., 2006). The VIP of OPLS-DA confirmed the factors that influenced the classification of domestic and imported products into the two groups. The criterion for discrimination between domestic and imported samples were elements (^{133}Cs, ^{88}Sr, ^{51}V, ^{27}Al, ^{71}Ga, ^{63}Cu, ^{111}Cd, ^{66}Zn, ^{23}Na, or ^{93}Nb) with a VIP value greater than 1 (Fig. 4B), which was confirmed to have high discriminative power in OPLS-DA (Fig. 4A). The S-plot is a visualization method that combines covariance on the x-axis and correlation on the y-axis. In this study, ten elements selected from the VIP

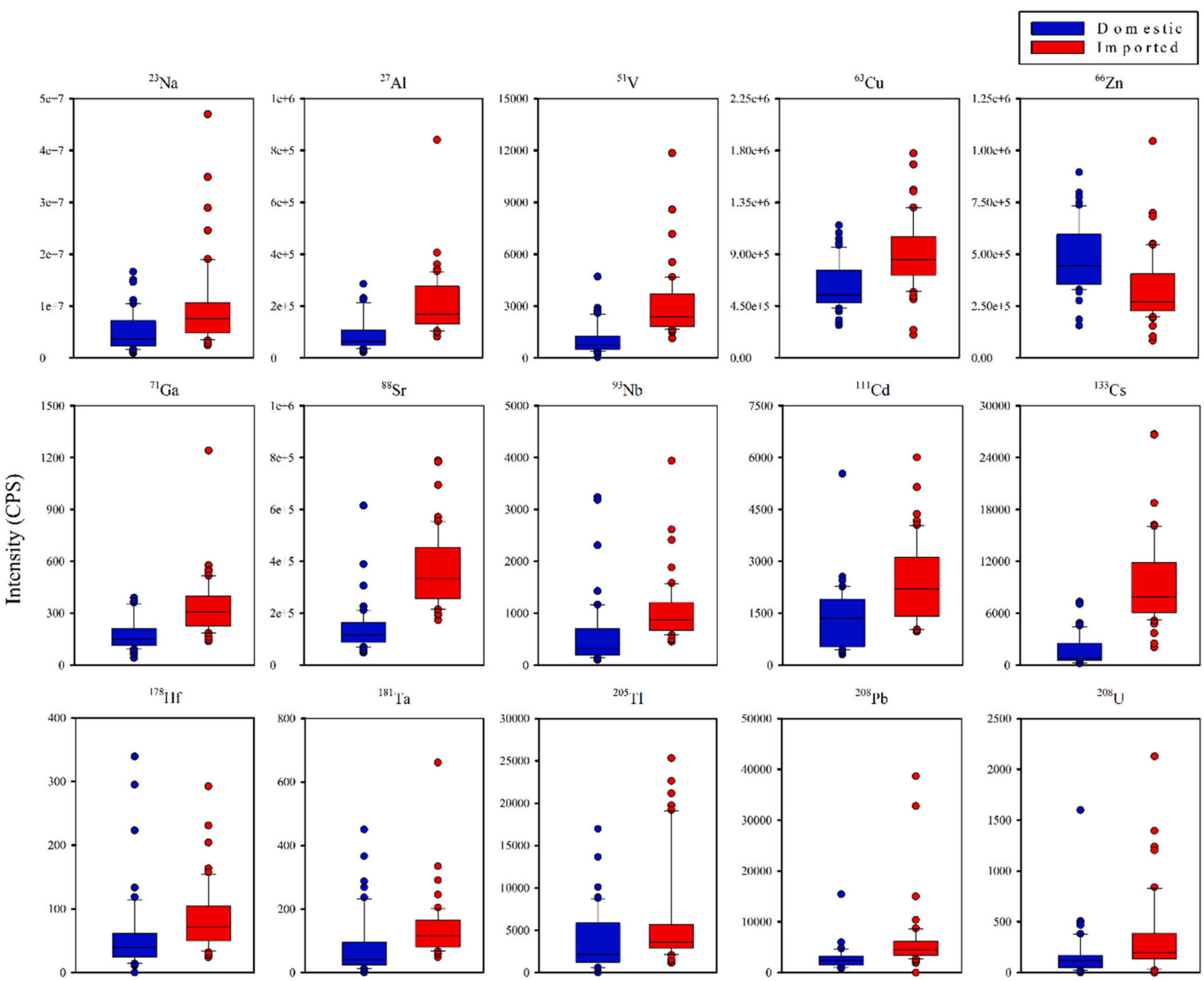

Fig. 3. Boxplot of minimum, maximum, and average count per second (cps) values for 15 elements measured in domestic and imported dried chili pepper samples.

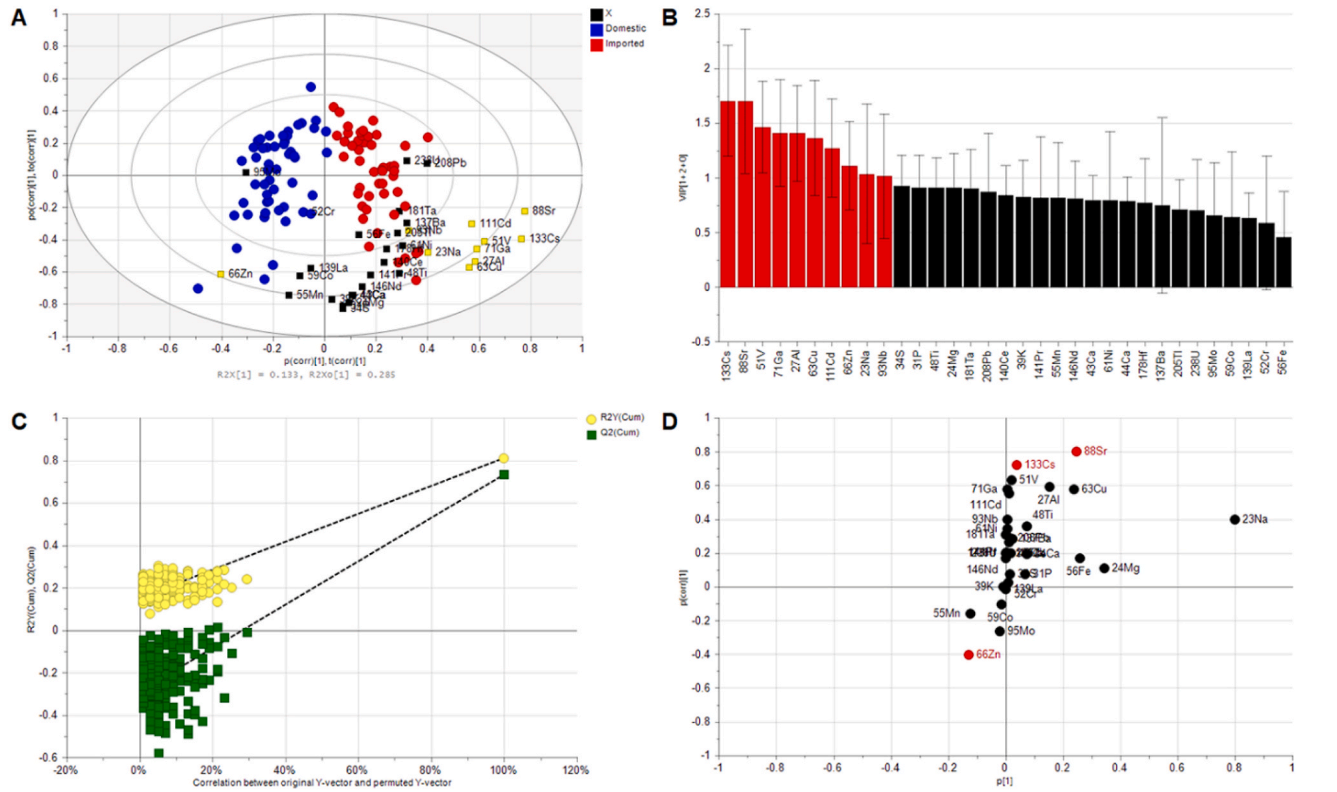

Fig. 4. Geographical origin discriminant analysis using 33 different elements in dried chili pepper samples. (A) Biplot used to differentiate between domestic (blue) and imported (red) samples in OPLS-DA. (B) Inorganic elements responsible for the significant differences between the two groups are represented by VIP score greater than 1. (C) Permutation test performed on the OPLS-DA (A); the quality parameters shown in the y-axis intercepts were $R^2 = (0.0, 0.153)$, and $Q^2 = (0.0, -0.289)$. (D) Corresponding loading S-plot with statistically meaningful elements. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

score were located at $|p(corr)| \geq 0.4$ of the S-plot. Nine elements were located at $p(corr) \geq 0.4$ of the S-plot and were elements with high cps values in the imported samples. Conversely, the other element was located at $p(corr) \leq -0.4$ of the S-plot and showed higher cps in the domestic samples. In particular, the three elements (^{88}Sr, ^{133}Cs, and ^{66}Zn) located at both ends of the S-plot were inferred to have a significant effect on distinguishing the geographical origin of dried chili peppers (Fig. 4D). For these elements, the difference in average cps values was significant according to the geographical origin. The ^{88}Sr and ^{133}Cs cps values were more than twice as high in imported products as in domestic products, and the ^{66}Zn cps value in domestic products was approximately 1.4 times higher than that in imported products.

The permutation test was used to verify the statistical significance of OPLS-DA. As known, the regression intercept values of the R^2 and Q^2 regression lines represent the fit to the data and the predictive ability of the model, respectively. If all points to the left of R^2 and Q^2 are lower than the two points to the right (100% in the x-axis), and the slopes of the regressions of R^2 and Q^2 are positive, the model fits. Furthermore, the R^2 and Q^2 should not exceed 0.3 and 0.05, respectively (Liu et al., 2018; Lee et al., 2022). Based on the permutation test results, R^2 of 0.153 and Q^2 of -0.289 are within the acceptable range, indicating good repeatability and predictability of the model (Fig. 4C).

Generally, ROC is used as one of the important evaluation indicators to describe the performance of a model (Hajian-Tilaki, 2013; Obuchowski and Bullen, 2018; Vitale et al., 2018). Here, an OPLS-DA model was created using 33 elements to determine the geographic origin of domestic dried peppers and imported dried peppers, and ROC analysis was shown with 98.7% accuracy (Fig. 5).

3.3.2. Heatmap

A heatmap was generated using measured cps values of domestic and imported dried chili peppers, where "1" denotes domestic and "2" represents imported samples (Fig. 6). A value of 5 or more indicates the highest content and it is shown in dark red; whereas −5 indicates the lowest content and it is shown in dark blue. In the heatmap, domestic products were generally depicted as light blue, and imported products as red; thus, the difference between domestic and imported products was evident based on the heatmap. In addition, 10 significant elements previously identified in OPLS-DA were shown in the heatmap. Among those elements, ^{133}Cs and ^{88}Sr, which showed the largest cps differences between domestic and imported samples, as well as ^{23}Na, ^{63}Cu, and ^{111}Cd, were also located in one group. And ^{66}Zn, which showed a higher cps value in domestic than in imported samples, belonged to another group. Thus, 6 out of 10 elements selected in OPLS-DA were significant in distinguishing between domestic and imported products. However, further verifications are necessary to confirm whether 6 elements are sufficient to discriminate the geographical origin of agricultural products.

3.3.3. CDA

To further differentiate between domestic and imported dried chili peppers, CDA was performed using 33 elements as independent variables (Table S4). The CDA shows the discriminant score, which is the center value of each group in which the two groups can be well distinguished and is calculated from the function value for determining the two groups. The geographical origin discrimination results showed an eigenvalue of 4.7902, a percentage of 100%, a cumulative of 100%, and a correlation coefficient of 0.9096, confirming a significant difference between the domestic and imported dried chili pepper groups. The distance between the domestic and imported groups in the plot was 4.3342, indicating a significant difference between the two groups (Fig. S2). The group classification accuracy rates for the 51 domestic and

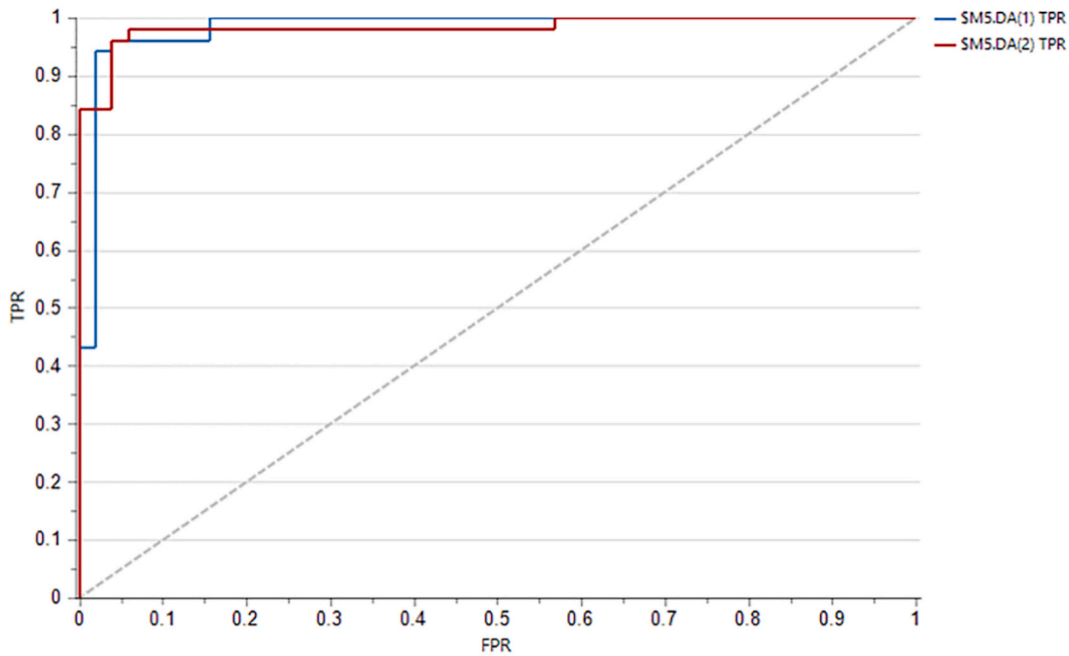

Fig. 5. Receiver operating characteristic (ROC) curve for 33 elements in OPLS-DA.

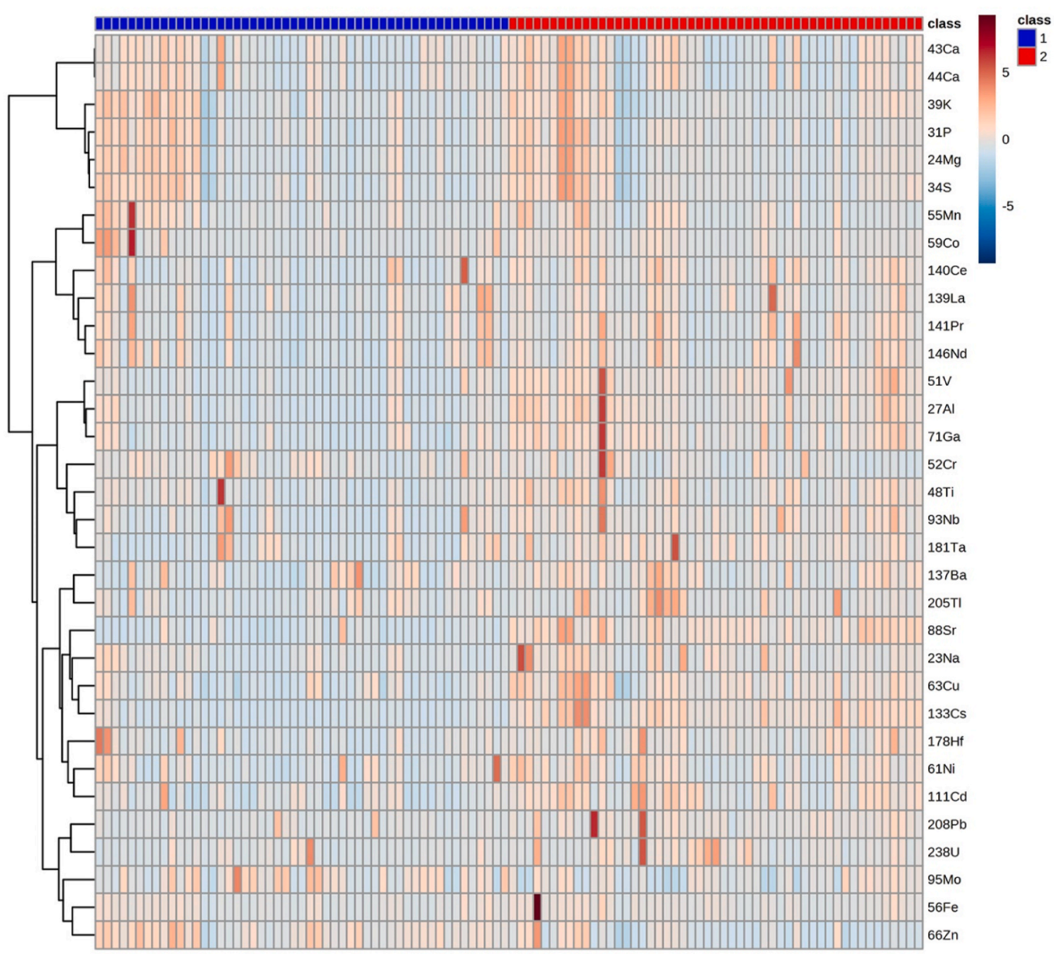

Fig. 6. Heatmap of 33 elements in 51 domestic (class 1) and 51 imported (class 2) dried chili peppers.

51 imported products were high at 99.02%.

All multivariate analysis (OPLS-DA, Heatmap, CDA) used in this study achieved satisfactory accuracy in classifying domestic and imported chili peppers, with CDA providing the best classification results among these methods.

Furthermore, fsLA-ICP-MS demonstrated an excellent performance without pretreatment, in contrast to previous studies that used various analytical tools for geographical discrimination. In summary, the geographical origin of dried chili peppers was accurately determined using fsLA-ICP-MS and statistical data processing by analyzing 33 different inorganic elements and overcoming the shortcomings of commonly used chemical methods of geographical discriminant analysis.

4. Conclusions

Domestic and imported dried chili pepper samples were analyzed using fsLA-ICP-MS under optimized conditions and multivariate analysis. Our findings based on a multivariable analysis of the data obtained using fsLA-ICP-MS confirmed that domestic and imported dried chili peppers could be distinguished with high accuracy. This study aimed to develop an analytical technique that can rapidly and conveniently identify the geographical origins of agricultural products, without the sample pretreatment with acids used in the conventional microwave-assisted ICP analysis. This technique has the potential to be a safe and environmentally friendly alternative for the inorganic analysis of agricultural products. Therefore, additional research should explore the potential of the LA-ICP-MS technique for analyzing other agricultural products and its applications in the field of safety management.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

CRediT authorship contribution statement

Suel Hye Hur: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources. **Seyeon Kim:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources. **Hyoyoung Kim:** Methodology, Validation, Formal analysis, Investigation, Resources. **Seongsoo Jeong:** Investigation, Formal analysis, Data curation. **Hoeil Chung:** Interpretation, review, Writing – review & editing. **Yong-Kyoung Kim:** Conceptualization, Methodology, Investigation, Resources, Supervision, Project administration. **Ho Jin Kim:** Conceptualization, Methodology, Investigation, Resources, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This study was supported by the research grant receive from the National Agricultural Products Quality Management Service.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.crfs.2023.100532.

References

Altundag, H., Tuzen, M., 2011. Comparison of dry, wet and microwave digestion methods for the multi element determination in some dried fruit samples by ICP-OES. Food Chem. Toxicol. 49, 2800–2807. https://doi.org/10.1016/j.fct.2011.07.064.

Barchenger, D.W., Bosland, P.W., 2019. Wild Chile pepper (*capsicum* L.) of north America. North American crop wild relatives. Import. Spec. 2, 225–242. https://doi.org/10.1007/978-3-319-97121-6_7.

Bartle, E.K., Watling, R.J., 2007. Provenance determination of oriental porcelain using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). J. Forensic Sci. 52 (2), 341–348. https://doi.org/10.1111/j.1556-4029.2006.00364.x.

Bolea-Fernandez, E., Balcaen, L., Resano, M., Vanhaecke, F., 2015. Interference-free determination of ultra-trace concentrations of arsenic and selenium using methyl fluoride as a reaction gas in ICP-MS/MS. Anal. Bioanal. Chem. 407 (3), 919–929. https://doi.org/10.1007/s00216-014-8195-8.

Bong, Y.S., Shin, W.J., Gautam, M.K., Jeong, Y.J., Lee, A.R., Jang, C.S., Lim, Y.P., Chung, G.S., Lee, K.S., 2012. Determining the geographical origin of Chinese cabbages using multielement composition and strontium isotope ratio analyses. Food Chem. 135 (4), 2666–2674. https://doi.org/10.1016/j.foodchem.2012.07.045.

Bylesjö, M., Rantalainen, M., Cloarec, O., Nicholson, J.K., Holmes, E., Trygg, J., 2006. OPLS discriminant analysis: combining the strengths of PLS-DA and SIMCA classification. J. Chemom. 20 (8–10), 341–351. https://doi.org/10.1002/cem.1006.

Choi, S.H., Bong, Y.S., Park, J.H., Lee, K.S., 2020. Geographical origin identification of garlic cultivated in Korea using isotopic and multi-elemental analyses. Food Control 111. https://doi.org/10.1016/j.foodcont.2019.107064.

Choi, Y.H., Hong, C.K., Park, G.Y., Kim, C.K., Kim, J.H., Jung, K., Kwon, J.H., 2016. A nondestructive approach for discrimination of the origin of sesame seeds using ED-XRF and NIR spectrometry with chemometrics. Food Sci. Biotechnol. 25 (2), 433–438. https://doi.org/10.1007/s10068-016-0059-x.

Chung, I.M., Kim, J.K., Jin, Y.I., Oh, Y.T., Prabakaran, M., Youn, K.J., Kim, S.H., 2016. Discriminative study of a potato (*Solanum tuberosum* L.) cultivation region by measuring the stable isotope ratios of bio-elements. Food Chem. 212, 48–57. https://doi.org/10.1016/j.foodchem.2016.05.161.

de Francesco, A.M., Barca, D., Bocci, M., Cortegoso, V., Barberena, R., Yebra, L., Durán, V., 2018. Provenance of obsidian artifacts from the Natural Protected Area Laguna del Diamante (Mendoza, Province Argentina) and upper Maipo valley (Chile) by LA-ICP-MS method. Quat. Int. 468, 134–140. https://doi.org/10.1016/j.quaint.2017.10.004.

Devos, W., Senn-Luder, M., Moor, C., Salter, C., 2000. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for spatially resolved trace analysis of early-medieval archaeological iron finds. Fresenius' J. Anal. Chem. 873–880. https://doi.org/10.1007/s002160051588.

Fiamegos, Y., Papoci, S., Dumitrascu, C., Ghidotti, M., Zdiniakova, T., Ulberth, F., de la Calle Guntiñas, M.B., 2021. Are the elemental fingerprints of organic and conventional food different? ED-XRF as screening technique. J. Food Compos. Anal. 99 https://doi.org/10.1016/j.jfca.2021.103854.

Ghidotti, M., Fiamegos, Y., Dumitrascu, C., de la Calle, M.B., 2021. Use of elemental profiles to verify geographical origin and botanical variety of Spanish honeys with a protected denomination of origin. Food Chem. 342 https://doi.org/10.1016/j.foodchem.2020.128350.

Grainger, M.N.C., Manley-Harris, M., Coulson, S., 2012. Classification and discrimination of automotive glass using LA-ICP-MS. J. Anal. At. Spectrom. 27 (9), 1413–1422. https://doi.org/10.1039/c2ja30093a.

Hajian-Tilaki, K., 2013. Receiver operating characteristic (ROC) curve analysis for medical diagnostic test evaluation. Caspian J Intern Med. 4 (2), 627–635.

Hoffman, T., Jaćimović, R., Bay, L.J., Griboff, J., Jagodic, M., Monferrán, M., Ogrinc, N., Podkolzin, I., Wunderlin, D., Almirall, J., 2018. Development of a method for the elemental analysis of milk powders using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and its potential use in geographic sourcing. Talanta 186, 670–677. https://doi.org/10.1016/j.talanta.2018.04.040.

Hondrogiannis, E.M., Ehrlinger, E., Poplaski, A., Lisle, M., 2013. Use of laser ablation-inductively coupled plasma-time of flight-mass spectrometry to identify the elemental composition of vanilla and determine the geographic origin by discriminant function analysis. J. Agric. Food Chem. 61 (47), 11332–11337. https://doi.org/10.1021/jf4025536.

Hong, S., Kim, S., 2013. The analysis on the production and consumption of red-pepper in Korea. Korean J. Agric. Sci. 40 (4), 405–410. https://doi.org/10.7744/cnujas.2013.40.4.405.

Hur, S.H., Kim, H., Kim, Y.K., An, J.M., Lee, J.H., Kim, S., Kim, H.J., 2023. Discrimination of the geographical origin of dry red pepper using inorganic elements: a multielement fingerprinting analysis. J. Food Compos. Anal. 116, 105076 https://doi.org/10.1016/j.jfca.2022.105076.

Hwang, I.M., Moon, E.W., Lee, H.W., Jamila, N., Su Kim, K., Ha, J.H., Kim, S.H., 2019. Discrimination of chili powder origin using inductively coupled plasma–mass spectrometry (ICP-MS), inductively coupled plasma–optical emission spectroscopy (ICP-OES), and near infrared (NIR) spectroscopy. Anal. Lett. 52 (6), 932–947. https://doi.org/10.1080/00032719.2018.1508293.

Jiang, G., Yoon Leem, J., 2016. Comparative analysis of cultivation region of Angelica gigas using a GC-MS-based metabolomics approach. Korean J. Medicinal Crop. Sci. 24 (2), 93–100. https://doi.org/10.7783/KJMCS.2016.24.2.93.

Kim, S., Shin, H.C., Kim, H., Hur, S.H., Kim, N., Park, S.U., Kim, Y.K., 2023. Femtosecond laser ablation–inductively coupled plasma mass spectrometry (fsLA-ICP-MS) for direct elemental analysis of rice. Anal. Lett. 1–8 https://doi.org/10.1080/00032719.2023.2197236.

Lee, J.E., Hwang, J., Choi, E., Shin, M.J., Chun, H.S., Ahn, S., Kim, B.H., 2020a. Rubidium analysis as a possible approach for discriminating between Korean and Chinese perilla seeds distributed in Korea. Food Chem. 312 https://doi.org/10.1016/j.foodchem.2019.126067.

Lee, J.H., An, J.M., Kang, D.J., Kim, H.J., Lee, S.H., 2022. Use of LC-Orbitrap MS and FT-NIRS with multivariate analysis to determine geographic origin of Boston butt pork. Int. J. Food Prop. 25 (1), 128–143. https://doi.org/10.1080/10942912.2022.2027962.

Lee, J.-H., Kang, D.-J., Jang, E.-H., Hur, S.-H., Shin, B.-K., Han, G.-T., Lee, S.-H., 2020b. Discrimination of geographical origin for soybeans using ED-XRF. Korean J. Food Sci. Technol. 52 (2), 125–129. https://doi.org/10.9721/KJFST.2020.52.2.125.

Liu, J., Chen, N., Yang, J., Yang, B., Ouyang, Z., Wu, C., Yuan, Y., Wang, W., Chen, M., 2018. An integrated approach combining HPLC, GC/MS, NIRS, and chemometrics for the geographical discrimination and commercial categorization of saffron. Food Chem. 253, 284–292. https://doi.org/10.1016/j.foodchem.2018.01.140.

Makino, Y., Nakazato, T., 2021. Determination of trace elements in polymers using fsLA-ICP-MS with internal standardization by carbon. J. Anal. At. S. 36 (9), 1895–1899. https://doi.org/10.1039/D1JA00198A.

Mi, S., Yu, W., Li, J., Liu, M., Sang, Y., Wang, X., 2020. Characterization and discrimination of chilli peppers based on multi-element and non-targeted metabolomics analysis. Lebensm. Wiss. Technol. 131, 109742 https://doi.org/10.1016/j.lwt.2020.109742.

Nunes, M.A.G., Voss, M., Corazza, G., Flores, E.M.M., Dressler, V.L., 2016. External calibration strategy for trace element quantification in botanical samples by LA-ICP-MS using filter paper. Anal. Chim. Acta 905, 51–57. https://doi.org/10.1016/j.aca.2015.11.049.

Obuchowski, N.A., Bullen, J.A., 2018. Receiver operating characteristic (ROC) curves: review of method with applications in diagnostic medicine. Phys. Med. Biol. 63 (7) https://doi.org/10.1088/1361-6560/aab4b1.

Olatunji, T.L., Afolayan, A.J., 2018. The suitability of chili pepper (*Capsicum annuum* L.) for alleviating human micronutrient dietary deficiencies: a review. Food Sci. Nutr. 6 (8), 2239–2251. https://doi.org/10.1002/fsn3.790.

Papaslioti, E.M., Parviainen, A., Román Alpiste, M.J., Marchesi, C., Garrido, C.J., 2019. Quantification of potentially toxic elements in food material by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) via pressed pellets. Food Chem. 274, 726–732. https://doi.org/10.1016/j.foodchem.2018.08.118.

Pornwilard, M.M., Hansawek, R., Shiowatana, J., Siripinyanond, A., 2011. Geographical origin classification of gem corundum using elemental fingerprint analysis by laser ablation inductively coupled plasma mass spectrometry. Int. J. Mass Spectrom. 306 (1), 57–62. https://doi.org/10.1016/j.ijms.2011.06.010.

Promchan, J., Günther, D., Siripinyanond, A., Shiowatana, J., 2016. Elemental imaging and classifying rice grains by using laser ablation inductively coupled plasma mass spectrometry and linear discriminant analysis. J. Cereal. Sci. 71, 198–203. https://doi.org/10.1016/j.jcs.2016.08.017.

Reyes, M.N.M., Campos, R.C., 2006. Determination of copper and nickel in vegetable oils by direct sampling graphite furnace atomic absorption spectrometry. Talanta 70 (5), 929–932. https://doi.org/10.1016/j.talanta.2006.05.055.

Schneider, M., Cadorim, H.R., Welz, B., Carasek, E., Feldmann, J., 2018. Determination of arsenic in agricultural soil samples using High-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sample analysis. Talanta 188, 722–728. https://doi.org/10.1016/j.talanta.2018.06.052.

Thøgersen, J., Pedersen, S., Aschemann-Witzel, J., 2019. The impact of organic certification and country of origin on consumer food choice in developed and emerging economies. Food Qual. Prefer. 72, 10–30. https://doi.org/10.1016/j.foodqual.2018.09.003.

Trejos, T., Montero, S., Almirall, J.R., 2003. Analysis and comparison of glass fragments by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and ICP-MS. Anal. Bioanal. Chem. 376 (8), 1255–1264. https://doi.org/10.1007/s00216-003-1968-0.

Vitale, R., Marini, F., Ruckebusch, C., 2018. SIMCA modeling for overlapping class: fixed or Optimized decision threshold? Anal. Chem. 90 (18), 10738–10747. https://doi.org/10.1021/acs.analchem.8b01270.

von Wuthenau, K., Müller, M.S., Cvancar, L., Oest, M., Fischer, M., 2022. Food authentication of almonds (*Prunus dulcis* mill.). Fast origin analysis with laser ablation inductively coupled plasma mass spectrometry and chemometrics. J. Agric. Food Chem. 70 (16), 5237–5244. https://doi.org/10.1021/acs.jafc.2c01088.

von Wuthenau, K., Segelke, T., Kuschnereit, A., Fischer, M., 2021. Glass authentication: laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) for origin discrimination of glass bottles. Talanta 235. https://doi.org/10.1016/j.talanta.2021.122686.

Voss, M., Nunes, M.A.G., Corazza, G., Flores, E.M.M., Müller, E.I., Dressler, V.L., 2017. A new approach to calibration and determination of selected trace elements in food contact polymers by LA-ICP-MS. Talanta 170, 488–495. https://doi.org/10.1016/j.talanta.2017.04.048.

Zaeem, M., Nadeem, M., Huong Pham, T., Ashiq, W., Ali, W., Shah Mohioudin Gillani, S., Moise, E.R.D., Leier, H., Kavanagh, V., Galagedara, L., Cheema, M., Thomas, R., 2021. Development of a hyperspectral imaging technique using LA-ICP-MS to show the spatial distribution of elements in soil cores. Geoderma 385. https://doi.org/10.1016/j.geoderma.2020.114831.

Zhang, D., Sun, X., Battino, M., Wei, X., Shi, J., Zhao, L., Liu, S., Xiao, J., Shi, B., Zou, X., 2021. A comparative overview on chili pepper (*capsicum* genus) and Sichuan pepper (*zanthoxylum* genus): from pungent spices to pharma-foods. Trends Food Sci. Technol. 117, 148–162. https://doi.org/10.1016/j.tifs.2021.03.004.

Zhang, X., Chen, Z.Y., Qiu, Z.D., Liu, M., Xu, J., Frankevich, V., Chingin, K., 2022. Molecular differentiation of *Panax notoginseng* grown under different conditions by internal extractive electrospray ionization mass spectrometry and multivariate analysis. Phytochemistry 194, 113030. https://doi.org/10.1016/j.phytochem.2021.113030.