In this experiment, inductively coupled plasma tandem mass spectrometry (ICP-MS/MS) was used to determine the content of 30 elements in rice from six places of production and to explore the relationship between the multielement content in rice and the producing area. The contents of Ca, P, S, Zn, Cu, Fe, Mn, K, Mg, Na, Ge, Sb, Se, As, Sr, Mo, Ni, Co, Cr, Al, Li, Cs, Pb, Cd, B, In, and Sn in rice were determined by ICP-MS/MS in the SQ and MS/MS mode. By passing H₂, O₂, He, and NH₃/He reaction gas into the ICP-MS/MS, respectively, the interference was eliminated by means of in situ mass spectrometry and mass transfer. The detection limit of each element was 0.0000662–0.144 mg/kg, and the limit of quantification was in the range of 0.000221–0.479 mg/kg, the linear correlation coefficient was greater or equal to 0.9987 ($R^2 \geq 0.9987$), and the detection results had low detection limit and great linear regression. Recovery of the method was in the range of 80.6% to 110.5% with spike levels of 0.10–100.00 mg/kg, and relative standard deviations were lower than 10%. For the multielement content of rice from different producing areas, the principal component factor analysis can get six principal component factors, 87.878% cumulative contribution rate, and the distribution of the principal components scores of each element and different producing areas. Based on the multielement content and cluster analysis, the samples were accurately divided into two major categories and six subcategories according to the places of production, which proved that there was a significant correlation between the multielement content in rice and the place of production, so that the place of rice origin can be traced.

1. Introduction

Rice is the main staple food of our country, which contains sugar, protein, fat and dietary fiber, and other main nutrition elements and also contains a lot of necessary trace elements, such as Ca, Fe, Zn, Se, and other mineral elements [1]. Heavy and toxic metals, especially As and Cd, present due to environmental pollution are taken up by the rice plant [2–5]. In China, rice varieties are rich and diverse, with large planting area span and large quality difference. China is a vast country with diverse climatic and geographical conditions, and the crops have different biological characteristics and physical and chemical indexes. Therefore, it is valuable to analyze and compare the differences of multielement contents in rice from south to north China and to provide theoretical basis and technical support for distinguishing rice from different places of origin.

At present, the origin traceability indexes in food mainly include stable isotope [6–11], multielement composition [12, 13], characteristic content of organic component [14, 15], DNA fingerprint [16], and near-infrared spectrum [17–21]. There are some common problems in multielement analysis, such as few element types, high detection limit of low content elements, and unquantifiable trace elements. The determination methods of poly element contents in rice include an electrochemical method, atomic absorption spectroscopy (AAS) [22], atomic fluorescence spectrometry (AFS) [23], inductively coupled plasma optical emission spectrometer (ICP-OES) [24], and inductively coupled plasma mass spectrometry (ICP-MS) [25, 26]. However, there are some common problems in these methods, which hamper the rapid determination of trace elements in rice, thus causing the reduction of the accuracy of traceability of multielement composition in rice. The advantage of the ICP-
MS/MS method is to reduce elemental interference [27]. Alexander Simpson et al. [28], found that by using ICP-MS/MS and NH₃ reagent gas, isotope interference can be reduced and the sensitivity of ¹⁷⁶Lu and ¹⁷⁶Yb can be improved. In terms of multielement determination, ICP-MS/MS has higher accuracy and greater diversity of elements proved. In terms of multielement determination, ICP-MS/MS/MS method is to reduce elemental interference [27].

In this paper, ICP-MS/MS was first used to determine the 30 elements’ contents in rice from six rice-production areas in Anhui, Guangxi, Guangdong, Jilin, Heilongjiang, and Inner Mongolia. Under SQ and MS/MS models [33], He, NH₃/He [34], O₂ [35], and H₂ [36] were selected as reactive gases for different elements to eliminate mass spectrum interference and reduce detection limit, and the relationship between the element content and the origin was studied by principal component analysis and cluster analysis, which provides technical support for quality control and origin traceability of rice.

2. Materials and Methods

2.1. Reagents and Solutions. Li, Na, Mg, Al, B, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Sr, Mo, Cd, In, Sn, Sb, Cs, Ba, Pb, Sc, Bi, Rh, and Y element standard solution (1000 μg/mL, Guobiao Testing & Certification Co., Ltd., Beijing, China), GBW0043, GBW10044, and GBW10045 Rice reference materials (Institute of Geophysical and Geochemical Exploration IGGE, Langfang, China), 65% BV-III grade of HNO₃ (Beijing Institute of Chemical Reagents, Beijing, China), 30% H₂O₂ (Sinopharm Chemical Reagent Co., Ltd., Beijing, China), and deionized water (18.2 MΩ/cm), prepared by using the Milli-Q system (Millipore, Bedford, MA), were used.

2.2. Sample Collection and Preparation. The samples were collected from six rice-producing areas in Anhui Province, Guangxi Province, Guangdong Province, Jilin Province, Heilongjiang Province, and Inner Mongolia. We purchased common local rice samples with large planting areas in each rice market, a total of 18 batches. Three independent packages were purchased for each batch, and mixed samples were taken to ensure uniformity. The rice samples of each batch were hulled, ground, crushed, and stored in a sealed, low-temperature, and dark place.

In a PTFE digestion tank, each rice sample which weighs 0.3–0.5 g (accurate to 0.001 g) was added to 4 mL HNO₃ and 1 mL H₂O₂ and soaked for 3–4 h or overnight, the upper cap was screwed, and it was digested with the microwave digestion instrument (CEM MARSH, CEM, Matthews, USA). The conditions of the microwave digestion instrument are shown in Table 1. Then, they were placed on the temperature-controlled electric heating plate (BH-09C, Shanghai Botong Chemical Technology Co., Ltd., Shanghai, China) and heated at 100°C for 20–30 min for degassing. After cooling, the samples were diluted to 50 mL with deionized water and shook well for later use. For each group of samples, blanks (deionized water and reagents) and reference materials were included throughout the entire sample preparation and analytical process.

2.3. Inductively Coupled Plasma Tandem Mass Spectrometry Analysis. This experiment was carried out by tandem mass spectrometry. The concentration of 30 isotopes (³Li, ²³Na, ²⁷Al, ³¹P, ³²S, ³⁹K, ⁴⁴Ca, ⁴⁷Ti, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶³Cu, ⁶⁶Zn, ⁷²Ge, ⁷⁵As, ⁷⁸Se, ⁸⁸Sr, ⁹⁵Mo, ¹¹¹Cd, ¹¹⁵In, ¹¹⁸Sn, ¹²¹Sb, ¹³³Cs, ¹³⁵Ba, and ²⁰⁸Pb) in rice was determined by inductively coupled plasma tandem mass spectrometry (Agilent 8900 Series, Agilent, USA). 1 μg/mL mixed solution of Li, Co, Ti, Ce, and Mg was used as the tuning solution, and 0.10 rps speed of the peristaltic pump was used to continuously feed the solution. Through the tuning program, the conditions of no gas, H₂, O₂, He, and NH₃/He multimode analysis methods were optimized. In the no-gas mode, the monitored ions were 7, 89, and 205. In the He mode, the monitored ions were 59, 89, and 205. In the H₂ mode, the monitored ions were Q₁ = Q₂ = 59, 89, and 205. In the O₂ mode, the monitored ions were Q₁ = Q₂ = 59, Q₁ = 89, Q₂ = 105, and Q₁ = Q₂ = 205. In the NH₃/He mode, the monitored ions were Q₁ = Q₂ = 59, Q₁ = 89, Q₂ = 191, and Q₁ = Q₂ = 205. Under different modes, RF power was 1550 W, auxiliary gas was 0.90 L/min, plasma gas was 15.0 L/min, sampling depth was 8.0 mm, and extraction lens was −7.6 V. The instrument’s other conditions of ICP-MS/MS are shown in Table 2.

For the selection of element determination mode and reagent gas, this method involves two modes: the SQ (single quadrupole) standard mode and MS/MS tandem mode. There are He and no-gas reagent gas modes in the SQ mode and He, NH₃/He, H₂, O₂, and no-gas reagent gas modes in the MS/MS mode. The elements are measured in all modes, and the mode with the lowest detection limit of each element is determined as the best measurement mode.

Through the measured experimental conditions and methods, the elements Sc, Y, Rh, and Bi were used as the internal standard elements. Analyzing the experimental data can get a linear fitting standard curve with the X-axis as the concentration point and the Y-axis as the response value. Through this standard curve, the detection limit and background equivalent concentration of the analysis element can be obtained by calculating the element standard deviation. The linear correlation coefficient and range, internal standard elements, limit of detection (LOD), and limit of quantification (LOQ) are shown in Table 3.

At the same time, the content of each element in rice reference materials (GBW10043, GBW10044, and GBW10045) was determined, the standard value was compared, and the recovery rate was calculated to prove the accuracy and reliability of the method, and the recovery experiment was conducted.
2.4. Statistical Analysis. All analyses were conducted in triplicate. The results reported were the average of these three replicates. Each sample was considered as an assembly of 30 variables represented by the data of chemical information. The analysis data and the fitted linear regression curve were analyzed by Agilent Mass Hunter software (Agilent Inc., USA). A normal distribution test of multielements, principal component analysis, and clustering analysis were performed with SPSS 25.0 software (SPSS, IBM Corp., USA).

3. Results and Discussion

3.1. Mass Spectrometry Mode Selection and Interference Elimination. In this experiment, the SQ (single quadrupole) standard mode and MS/MS tandem mode were used to simultaneously determine the concentration of multielements. The elements were measured in different modes and different reaction gas modes, and the element detection limit was used as the criterion to determine the best measurement mode for each element. The results are shown in Table 4.

### Table 1: The condition of microwave digestion.

| Step | Climbing time (min) | Hold time (min) | Temperature (°C) | Power (W) |
|------|---------------------|-----------------|------------------|-----------|
| 1    | 06:00               | 03:00           | 120              | 1500      |
| 2    | 08:00               | 06:00           | 155              | 1500      |
| 3    | 08:00               | 15:00           | 180              | 1500      |

### Table 2: Instrument parameters of ICP-MS/MS.

| Instrument conditions | No-gas mode | H₂ mode | He mode | O₂ mode | NH₃/He mode |
|-----------------------|-------------|---------|---------|---------|-------------|
| Q₁ deflection voltage (V) | −3.0        | 1.0     | −3.0    | 1.0     | 1.0         |
| Q₂ deflection voltage (V) | −3.0        | −18.0   | −15.0   | −10.0   | −12.0       |
| Collision pool gas     | —           | H₂      | He      | O₂      | NH₃/He      |
| Gas flow rate of collision pool (L·min⁻¹) | —           | 7.0     | 5.0     | 4.5     | 4.5/1.0     |
| Deflection voltage of eight-stage pole (V) | −8.0        | −18.0   | −18.0   | −3.0    | −5.0        |

### Table 3: Linear range and detection limit of isotopes.

| Calibration (µg/L) | R² | Internal standard | LOD (mg/kg) | LOQ (mg/kg) |
|-------------------|----|------------------|-------------|-------------|
| Li²⁷              | 0–100 | 0.9998 | Sc | 0.000659 | 0.0220 |
| Na²⁴             | 0–1000 | 0.9999 | Sc | 0.144 | 0.479 |
| Mg²⁴             | 0–1000 | 0.9999 | Sc | 0.00372 | 0.0124 |
| Al¹³               | 0–100 | 0.9987 | Sc | 0.0907 | 0.302 |
| B¹¹               | 0–100 | 0.9995 | Sc | 0.0375 | 0.125 |
| P³¹               | 0–1000 | 0.9994 | Sc | 0.0204 | 0.0679 |
| S³²               | 0–1000 | 0.9997 | ScO | 0.0614 | 0.205 |
| K³⁹               | 0–1000 | 1.0000 | Sc | 0.0291 | 0.0970 |
| Ca⁴⁴               | 0–1000 | 1.0000 | Sc | 0.105 | 0.351 |
| Ti⁴⁵               | 0–100 | 0.9999 | ScO | 0.00219 | 0.00731 |
| V³³               | 0–1000 | 0.9999 | ScO | 0.000946 | 0.00315 |
| Cr⁵²               | 0–100 | 0.9997 | ScO | 0.00521 | 0.0174 |
| Mn⁵⁵               | 0–1000 | 1.0000 | Sc | 0.00148 | 0.00495 |
| Fe⁵⁶               | 0–1000 | 1.0000 | Sc(NH₃)₂ | 0.0170 | 0.0567 |
| Co⁵⁷               | 0–100 | 1.0000 | Sc(NH₃)₂ | 0.000510 | 0.00170 |
| Ni⁶⁰               | 0–100 | 1.0000 | Sc(NH₃)₂ | 0.00133 | 0.00444 |
| Cu⁶¹               | 0–1000 | 1.0000 | Sc | 0.00474 | 0.0158 |
| Zn⁶⁰               | 0–1000 | 1.0000 | Sc | 0.0115 | 0.0383 |
| Ge⁷⁴               | 0–100 | 1.0000 | Y | 0.000206 | 0.000686 |
| As⁷⁵               | 0–100 | 1.0000 | YO | 0.00250 | 0.00832 |
| Se⁷⁸               | 0–100 | 1.0000 | Y | 0.00152 | 0.00507 |
| Sr⁸⁸               | 0–100 | 1.0000 | Y | 0.000929 | 0.00310 |
| Mo⁹⁵               | 0–100 | 0.9999 | YNH₃ | 0.000605 | 0.00202 |
| Cd¹¹¹             | 0–100 | 1.0000 | Rh | 0.000662 | 0.000221 |
| In¹¹⁵             | 0–100 | 0.9998 | Rh | 0.00123 | 0.00410 |
| Sn¹¹⁸             | 0–100 | 1.0000 | Rh | 0.00176 | 0.000588 |
| Sb¹²¹             | 0–100 | 1.0000 | Rh | 0.000196 | 0.000653 |
| Cs¹³³             | 0–100 | 1.0000 | Rh | 0.000227 | 0.000756 |
| Ba¹³⁷               | 0–100 | 1.0000 | Rh | 0.00158 | 0.00525 |
| Pb²⁰⁸              | 0–100 | 1.0000 | Bi | 0.000949 | 0.00317 |
The interference was eliminated by making full use of the collision mode between the element and the reaction gas. In the SQ mode, the mass ions of $^{63}$Cu, $^{111}$Cd, $^{118}$Sn, $^{121}$Sb, and $^{208}$Pb had the characteristics of high abundance value and less interference. The corresponding $Q_2$ mass number was the only one that needed to be set during the determination.

In the MS/MS mode, the NH$_3$/He mixture gas collided with $^{7}$Li, $^{24}$Mg, $^{44}$Ca, $^{66}$Ni, $^{99}$Mo, and $^{137}$Ba ions in the reaction cell, H$_2$ collided with $^{23}$Na, $^{27}$Al, $^{50}$Mn, $^{66}$Zn, $^{72}$Ge, $^{78}$Se, $^{88}$Sr, and $^{115}$In ions, and O$_2$ collided with $^{39}$K and $^{133}$Cs ions, respectively. The interference was eliminated by in situ mass spectrometry, which means the elements only collide with the reaction gas and do not combine with each other. Therefore, the mass number of the front and after tetrodes to be set remains unchanged ($Q_1 = Q_2$). However, the system will still have the same amount of heterotopic number signal superposition interference and double charge ion interference; for example, ions Ni$^{2+}$, SiH, CO, and NO may interfere with $^{35}$P; ions Zn$^{2+}$, NO, and OO may interfere with $^{32}$S; ions CaR and ArO interfere with $^{52}$Cr; ions ArCl, CaCl, and CoO interfere with $^{75}$As; ions ArO and MnH interfere with $^{56}$Fe; and ions Sn$^{2+}$, NiH, and MgCl interfere with $^{59}$Co.

### Table 4: Isotope mass spectrometry.

| Element | Mode   | Reaction gas | Mass number | Eliminate interference       |
|---------|--------|--------------|-------------|------------------------------|
| $^{7}$Li | MS/MS  | NH$_3$/He    | $Q_1 = Q_2 = 7$ | In situ mass spectrometry    |
| $^{23}$Na | MS/MS  | H$_2$        | $Q_1 = Q_2 = 23$ | In situ mass spectrometry    |
| $^{24}$Mg | MS/MS  | NH$_3$/He    | $Q_1 = Q_2 = 24$ | In situ mass spectrometry    |
| $^{27}$Al | MS/MS  | H$_2$        | $Q_1 = Q_2 = 27$ | In situ mass spectrometry    |
| $^{11}$B | MS/MS  | NH$_3$/He    | $Q_1 = 11, Q_2 = 60$ | Mass transfer               |
| $^{31}$P | MS/MS  | O$_2$        | $Q_1 = 31, Q_2 = 47$ | Mass transfer               |
| $^{32}$S | MS/MS  | O$_2$        | $Q_1 = 32, Q_2 = 48$ | Mass transfer               |
| $^{39}$K | MS/MS  | O$_2$        | $Q_1 = Q_2 = 39$ | In situ mass spectrometry    |
| $^{44}$Ca | MS/MS  | NH$_3$/He    | $Q_1 = Q_2 = 44$ | In situ mass spectrometry    |
| $^{47}$Ti | MS/MS  | O$_2$        | $Q_1 = 47, Q_2 = 63$ | Mass transfer               |
| $^{51}$V | MS/MS  | O$_2$        | $Q_1 = 51, Q_2 = 67$ | Mass transfer               |
| $^{52}$Cr | MS/MS  | O$_2$        | $Q_1 = 52, Q_2 = 68$ | Mass transfer               |
| $^{55}$Mn | MS/MS  | H$_2$        | $Q_1 = Q_2 = 55$ | In situ mass spectrometry    |
| $^{58}$Fe | MS/MS  | NH$_3$/He    | $Q_1 = 56, Q_2 = 90$ | Mass transfer               |
| $^{59}$Co | MS/MS  | NH$_3$/He    | $Q_1 = 59, Q_2 = 93$ | Mass transfer               |
| $^{63}$Ni | MS/MS  | NH$_3$/He    | $Q_1 = Q_2 = 60$ | In situ mass spectrometry    |
| $^{66}$Zn | MS/MS  | H$_2$        | $Q_1 = Q_2 = 66$ | In situ mass spectrometry    |
| $^{72}$Ge | MS/MS  | H$_2$        | $Q_1 = Q_2 = 72$ | In situ mass spectrometry    |
| $^{73}$As | MS/MS  | O$_2$        | $Q_1 = 75, Q_2 = 91$ | Mass transfer               |
| $^{78}$Se | MS/MS  | H$_2$        | $Q_1 = Q_2 = 78$ | In situ mass spectrometry    |
| $^{88}$Sr | MS/MS  | H$_2$        | $Q_1 = Q_2 = 88$ | In situ mass spectrometry    |
| $^{95}$Mo | MS/MS  | NH$_3$/He    | $Q_1 = Q_2 = 95$ | In situ mass spectrometry    |
| $^{111}$Cd | SQ    | He           | $Q_2 = 63$ | —                            |
| $^{115}$In | MS/MS | H$_2$        | $Q_1 = Q_2 = 115$ | In situ mass spectrometry    |
| $^{118}$Sn | SQ    | He           | $Q_2 = 118$ | —                            |
| $^{121}$Sb | SQ    | No gas       | $Q_2 = 121$ | —                            |
| $^{133}$Cs | MS/MS | O$_2$        | $Q_1 = Q_2 = 133$ | In situ mass spectrometry    |
| $^{137}$Ba | MS/MS | NH$_3$/He    | $Q_1 = Q_2 = 137$ | In situ mass spectrometry    |
| $^{208}$Pb | SQ    | No gas       | $Q_2 = 208$ | —                            |

**Figure 1:** Interference cancellation model of the MS/MS mode. The ions collided with gas in the ORC.
**Table 5:** Recovery rate of reference materials.

| Recovery (%) | As | B  | Ba | Ca | Cd | Co | Cr | Cs | Cu | Fe | Ge | K  | Li | Mg | Mn | Mo | Na | Ni | P  | Pb | S  | Sb | Se | Sr | Sn | Ti | V  | Al | Zn | In |
|--------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| GBW10043     | 92.6 | 91.6 | 92.6 | 95.2 | 109 | 89.4 | 91.7 | 103 | 92.2 | 104 | 106 | 96.5 | 92.8 | 105 | 96.5 | 88.6 | 95.3 | 90.6 | 102 | 89.5 | 95.3 | 106 | 105 | 95.6 | ND | 94.8 | 105 | 92.6 | 95.6 | ND |
| GBW10044     | 95.1 | 93.8 | 104 | 105 | 108 | 90.2 | 93.5 | 107 | 85.6 | 108 | 109 | 94.8 | 107 | 103 | 91.5 | 85.7 | 92.1 | 105 | 106 | 115 | 90.7 | 108 | 109 | 96.1 | ND | 93.8 | 109 | 90.2 | 94.1 | ND |
| GBW10045     | 96.3 | 103 | 105 | 93.8 | 102 | 96.5 | 107 | 87.5 | 93.8 | 95.6 | 112 | 95.9 | 111 | 96.5 | 90.3 | 82.9 | 94.8 | 92.8 | 103 | 106 | 93.1 | 110 | 103 | 92.8 | ND | 91.1 | 113 | 93.5 | 103 | ND |

*ND means not detected.*
Therefore, in the determination of some specific elements, if the reactant gas and the element collide with each other to generate ions with a new mass number, the abovementioned interferences can be better avoided. In addition, when the gas collided with the analysis element, new mass ions were formed in the reaction, that is, mass transfer (Figure 1). In the experiment, NH₃/He mixture gas can react with ¹¹B⁺ and ⁵⁶Fe⁺ to form ¹¹B₄⁺⁺ NH(NH₃)₂⁺ and ⁵⁶Fe(NH₃)₂⁺⁺ cluster ions. Also, the O₂ mode was more widely used, which can undergo mass transfer with ³¹P⁺, ³₂S⁺, ⁴⁷Ti⁺, ⁵¹V⁺, ⁵²Cr⁺, ⁷₅As⁺, and generated ³¹P₁⁶O⁺⁺, ³₂S₁⁶O⁺⁺, ⁴⁷Ti₁⁶O⁺⁺, ⁵¹V₁⁶O⁺⁺, ⁵²Cr₁⁶O⁺⁺, and ⁷₅As₁⁶O⁺⁺ cluster ions, respectively.

3.2. Standard Material Determination and Precision. Multielement determination was performed on the standard materials GBW10043, GBW10044, and GBW10045, and the

| Element | Background (mg/kg) | Added (mg/kg) | Recovery (%) | RSD (%) |
|---------|--------------------|---------------|--------------|---------|
| As      | 0.127              | 10            | 105.3        | 3.5     |
|         |                    | 1             | 108.1        | 3.2     |
|         |                    | 0.1           | 104.6        | 1.1     |
| B       | 0.506              | 10            | 98.6         | 0.6     |
|         |                    | 1             | 86.1         | 2.8     |
|         |                    | 0.1           | 105.8        | 1.6     |
| Ba      | 0.351              | 10            | 94.3         | 2.8     |
|         |                    | 1             | 95.2         | 2.6     |
|         |                    | 0.1           | 82.8         | 8.9     |
| Ca      | 41.6               | 100           | 93.6         | 0.9     |
|         |                    | 50            | 95.4         | 2.2     |
|         |                    | 10            | 102.6        | 1.0     |
| Cd      | 0.0272             | 10            | 107.6        | 5.8     |
|         |                    | 1             | 92.5         | 0.9     |
|         |                    | 0.1           | 108.6        | 3.5     |
| Co      | 0.00675            | 10            | 91.6         | 4.5     |
|         |                    | 1             | 95.3         | 4.1     |
|         |                    | 0.1           | 106.8        | 0.9     |
| Cr      | 0.0138             | 10            | 84.3         | 5.0     |
|         |                    | 1             | 93.5         | 1.5     |
|         |                    | 0.1           | 89.6         | 1.1     |
| Cs      | 0.00152            | 10            | 110.5        | 0.6     |
|         |                    | 1             | 92.3         | 2.8     |
|         |                    | 0.1           | 94.2         | 2.3     |
| Cu      | 2.06               | 10            | 95.1         | 0.5     |
|         |                    | 1             | 96.7         | 4.1     |
|         |                    | 0.1           | 97.6         | 4.8     |
| Fe      | 2.45               | 10            | 105.6        | 2.3     |
|         |                    | 1             | 103.9        | 6.8     |
|         |                    | 0.1           | 107.5        | 0.5     |
| Ge      | 0.00261            | 10            | 85.3         | 2.4     |
|         |                    | 1             | 96.4         | 2.9     |
|         |                    | 0.1           | 95.8         | 6.3     |
| K       | 510                | 100           | 84.3         | 2.5     |
|         |                    | 50            | 82.2         | 2.7     |
|         |                    | 10            | 93.6         | 4.1     |
| Li      | 0.00365            | 10            | 109.5        | 0.9     |
|         |                    | 1             | 106.4        | 2.2     |
|         |                    | 0.1           | 93.6         | 5.4     |
| Mg      | 105                | 100           | 104.3        | 3.6     |
|         |                    | 50            | 106.4        | 1.1     |
|         |                    | 10            | 83.2         | 1.8     |
| Mn      | 7.46               | 10            | 92.6         | 2.0     |
|         |                    | 1             | 91.1         | 1.5     |
|         |                    | 0.1           | 93.7         | 2.9     |
| Mo      | 0.496              | 10            | 94.5         | 0.4     |
|         |                    | 1             | 105.6        | 7.1     |
|         |                    | 0.1           | 93.2         | 3.8     |
| Na      | 1.97               | 10            | 108.9        | 4.5     |
|         |                    | 1             | 103.7        | 4.8     |
|         |                    | 0.1           | 82.6         | 1.5     |
| Ni      | 0.168              | 10            | 91.6         | 0.5     |
|         |                    | 1             | 106.3        | 0.8     |
|         |                    | 0.1           | 87.5         | 1.6     |
Table 7: Element content of rice.

| No. | Li  | B  | Na  | Al  | Ca  | Si | Cr  | Mn  | Mo  | Sn  | Fe  | Cu  | Sb  | Pb  | Ge  | Sr  | K  | Sn  | Cd  | Ce  | Ba  | Zn  |
|-----|-----|----|-----|-----|-----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|-----|-----|-----|-----|-----|
| A-1 | 1.39| 0.049| 2.01| 0.041| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| A-2 | 0.18| 0.078| 1.56| 0.049| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| A-3 | 0.14| 0.056| 1.23| 0.039| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| X-1 | 0.33| 0.048| 2.01| 0.041| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| X-2 | 0.28| 0.049| 1.56| 0.049| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| X-3 | 0.24| 0.056| 1.23| 0.039| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| D-1 | 0.46| 0.049| 2.01| 0.041| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| D-2 | 0.33| 0.049| 1.56| 0.049| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| D-3 | 0.28| 0.056| 1.23| 0.039| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| J-1 | 0.17| 0.049| 2.01| 0.041| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| J-2 | 0.24| 0.049| 1.56| 0.049| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| J-3 | 0.28| 0.056| 1.23| 0.039| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| H-1 | 0.31| 0.049| 2.01| 0.041| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| H-2 | 0.28| 0.049| 1.56| 0.049| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|
| H-3 | 0.24| 0.056| 1.23| 0.039| 0.011| 0.078| 0.012| 0.017| 0.016| 0.014| 0.013| 0.012| 0.011| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010| 0.010|

The data unit is mg/kg, among which the element data unit of Li, Ti, V, Cr, Mn, Ni, Cu, Fe, Sn, Cd, Cs, Co, Pb, and Hg is μg/kg. A- Anhui Province, X- Guangxi Province, D- Guangdong Province, J- Jilin Province, H- Heilongjiang Province, N- Inner Mongolia.
Figure 2: The degree of dispersion.

Table 8: Results of principal component analysis.

| Component | Initial eigenvalue | Rotate the sum of squares loading |
|-----------|-------------------|----------------------------------|
|           | Total | Variance (%) | Accumulate (%) | Total | Variance (%) | Accumulate (%) |
| 1         | 10.41 | 38.56        | 38.56           | 7.547 | 27.95        | 27.95           |
| 2         | 4.800 | 17.78        | 56.34           | 4.870 | 18.04        | 45.99           |
| 3         | 3.142 | 11.64        | 67.97           | 3.225 | 11.94        | 57.94           |
| 4         | 2.243 | 8.306        | 76.28           | 3.223 | 11.94        | 69.87           |
| 5         | 1.850 | 6.852        | 83.13           | 2.809 | 10.41        | 80.28           |
| 6         | 1.282 | 4.749        | 87.88           | 2.052 | 7.599        | 87.88           |

Table 9: Contribution value of the element’s principal component.

| Element | 1     | 2     | 3     | 4     | 5     | 6     |
|---------|-------|-------|-------|-------|-------|-------|
| Li      | −0.697| 0.551 | −0.164| 0.167 | 0.154 | −0.115|
| B       | −0.367| 0.753 | 0.162 | 0.324 | 0.003 | −0.068|
| Na      | −0.927| −0.009| −0.038| 0.184 | −0.016| −0.114|
| Mg      | −0.318| 0.846 | −0.124| −0.167| −0.185| 0.045 |
| K       | 0.324 | 0.644 | −0.263| 0.291 | 0.289 | 0.282 |
| Ca      | −0.684| 0.515 | 0.360 | 0.011 | −0.278| −0.083|
| P       | 0.236 | 0.617 | −0.559| −0.079| 0.253 | 0.182 |
| S       | 0.855 | 0.381 | −0.277| 0.102 | 0.108 | 0.094 |
| Ti      | 0.772 | 0.070 | 0.141 | 0.016 | −0.375| −0.333|
| V       | −0.512| 0.660 | 0.405 | 0.087 | −0.092| 0.132 |
| Cr      | −0.693| −0.380| −0.096| −0.508| 0.140 | 0.175 |
| Mn      | −0.091| −0.002| 0.794 | 0.261 | −0.281| 0.353 |
| Ni      | 0.847 | 0.248 | 0.297 | −0.177| −0.010| 0.113 |
| Cu      | 0.809 | 0.346 | −0.112| 0.180 | −0.213| 0.212 |
| Fe      | −0.476| 0.361 | −0.587| −0.277| −0.133| −0.014|
| Co      | 0.984 | 0.033 | −0.093| −0.020| −0.007| 0.000 |
| Zn      | 0.472 | 0.092 | 0.364 | −0.633| −0.052| 0.401 |
| Ge      | 0.818 | 0.301 | −0.192| −0.039| −0.363| −0.216|
| Se      | 0.432 | −0.003| 0.368 | 0.081 | 0.778 | −0.154|
| Sr      | −0.221| −0.212| −0.822| 0.384 | −0.008| 0.107 |
| As      | 0.244 | 0.383 | 0.273 | −0.316| 0.480 | −0.448|
| Mo      | 0.822 | 0.277 | −0.040| −0.395| 0.056 | −0.117|
| Cd      | 0.715 | −0.172| 0.034 | 0.380 | −0.209| 0.165 |
| Sb      | −0.368| 0.308 | 0.329 | 0.438 | 0.062 | −0.237|
| Cs      | 0.547 | −0.332| 0.152 | 0.521 | 0.399 | 0.247 |
| Ba      | 0.860 | 0.097 | −0.044| 0.198 | −0.203| −0.350|
| Pb      | −0.087| 0.706 | 0.132 | −0.114| 0.148 | 0.236 |
results are shown in Table 5. The average recoveries of element content of reference materials were in the range between 82.9% and 115%.

The recoveries of analytes were evaluated by adding the standard solutions with three different concentration levels to the known amounts of samples. The data of recovery and precision are given in Table 6, and the average recoveries of element content in rice were in the range between 80.6% and 110.5%. The RSDs were in the range of 0.4%–8.9%. The measurement results show that this method has high accuracy and meets the requirements of analysis and measurement.

3.3. Multielement Analysis of Samples. There are obvious differences in the content of Ba, Ge, Co, Cu, Cr, Ti, S, Ca, Mg, Na, Li, and other elements in rice from different producing areas in north and south China. In southern China, there are differences in the content of Na, Mg, K, Ca, V, Ge, Cs, Ba, and other elements in rice produced in Anhui Province, Guangxi Province, and Guangdong Province. However, in northern China, there are obvious differences in the content of B, Na, Ca, P, Cr, Mn, Ni, Co, Zn, Sr, Mo, Cs, and other elements in batches of rice in Jilin Province, Heilongjiang Province, and Inner Mongolia (Table 7). The contents of Al, In, and Sn were not detected.

We conducted further statistical analysis on the abovementioned experimental data, by calculating the standard deviation of each element and judging the difference of each element in different regions according to the degree of dispersion of the value of each element. As shown in Figure 2, the standard deviations of S, P, K, Cd, Mg, and other elements were large, and the degree of dispersion was relatively higher than that of other elements, which can be initially used as indicative elements for traceability.

3.4. Multielement Normal Distribution Test. The Kolmogorov–Smirnov test was conducted on the content of 30 elements in rice from different origins. The asymptotic significance (bilateral) value was calculated. The content data of 24 elements obeyed normal distribution.
3.5. Principal Component Analysis. Principal component analysis (PCA) is a multivariate statistical analysis method that analyses a few variables which can reveal the internal structure sufficiently by studying the relationship between multiple original variables.

According to the rule that the characteristic value is greater than 1 and the cumulative variance contribution rate is greater than 80%, six principal component factors were obtained through rotation and extraction factors, and the total contribution rate was 87.878%, indicating that the experimental data can fully reflect the original information (Table 8).

The first principal component is mainly composed of S, Ti, Ni, Cu, Co, Ge, Mo, Cd, Cs, Ba, Zn, and Se elements. The second principal component is mainly composed of Li, B, Mg, K, Ca, P, V, Pb, Fe, and As elements. The third principal component is mainly composed of Mn and Sb elements (Table 9). The first principal component, the second principal component, and the third principal component were used to analyze the contribution of the principal components of samples from different origins (Figure 3). The contribution scores of the principal components of samples from the same origin were concentrated, while the distribution of different origins is scattered. On the whole, rice samples from the north and south of China have a large difference in the contribution scores of the principal components which can be clearly distinguished. This result has certain guiding significance for the distinction of rice from different production places.

3.6. Cluster Analysis. The contents of multielements in rice from different areas were analyzed by cluster analysis. The samples were successfully divided into two categories (the north and south of China) and six subcategories (six rice-producing areas) by the method of intergroup connection (Figure 4). The results show that there were obvious differences in the contents of multielements in rice from different producing areas, and they had certain regional characteristics. Therefore, by measuring the multielement content of rice, it is possible to accurately classify the samples according to the place of origin and finally realize the traceability of the production place of the rice.

4. Conclusions

In this experiment, the ICP-MS/MS method was developed to determine the content of 30 elements in rice from different production areas. The determination mode and reaction gas conditions were optimized, and the optimal determination conditions were selected for each element in five determination modes of no gas, H2, O2, He, and NH3/He. In addition, in situ mass spectrometry and mass transfer technology were used to eliminate the interference and reduce the detection limit. To achieve the determination of ultratrace elements, we established a complete detection method, which provided a method basis for rice origin traceability. Through the principal component analysis of the multielement content of 18 batches of samples from different origins, the distribution of the six principal components of the samples and the characteristic elements of each principal component were determined. Through cluster analysis, the samples were accurately classified according to the place of production based on the multielement content, which proved that there was a significant correlation between the content of multielement in rice and the place of production, providing technical support and research direction for the traceability of the origin of rice.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this article.

Authors’ Contributions

YZ, QL, and YW conceived and designed the study. YW and XXY wrote the paper. YZ, QL, JMM, and SFF reviewed and edited the manuscript. All authors read and approved the manuscript.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (Project no. 2018YFC1603400), State Administration for Market Regulation Special Technical Support Program (Project no. 2019YJ009), and Scientific Research Projects of Hebei Market Supervision and Administration Bureau (Project no. 2021ZC07).

References

[1] V. Taleon, S. Gallego, J. C. Orozco, and C. Grenier, "Retention of Zn, Fe and phytic acid in parboiled bio fortified and non-biofortified rice," Food Chemistry X, vol. 8, Article ID 100105, 2020.
[2] M. Jaafar, A. Shrivastava, S. Rai Bose, M. Felipe-Sotelo, and N. I. Ward, "Transfer of arsenic, manganese and iron from water to soil and rice plants: an evaluation of changes in dietary intake caused by washing and cooking rice with groundwater from the Bengal Delta, India," Journal of Food Composition and Analysis, vol. 96, Article ID 103748, 2021.
[3] M. Tatahmentan, S. Nyachoti, L. Scott et al., "Toxic and essential elements in rice and other grains from the United States and other countries," International Journal of Environmental Research and Public Health, vol. 17, no. 21, p. 8128, 2020.
[4] Z. Y. Min, L. S. Si, L. B. Yu et al., "Enrichment of cadmium in rice (Oryza sativa L.) grown under different exogenous pollution sources," Environmental Science and Pollution Research International, vol. 27, pp. 44249–44256, 2020.
[5] F. Zhang, F. Gu, H. Yan et al., "Effects of soaking process on arsenic and other mineral elements in brown rice," Food Science and Human Wellness, vol. 9, no. 2, pp. 168–175, 2020.
[6] L. Wang and Y. Jin, “Possible application of stable isotope compositions for the identification of metal sources in soil,” Journal of Hazardous Materials, vol. 407, p. 5, 2021.

[7] W. Jie, Z. Tengteng, and G. Yangbin, “C/N/H/O stable isotope analysis for determining the geographical origin of American ginseng (Panax quinquefolius),” Journal of Food Composition and Analysis, vol. 96, Article ID 103756, 2021.

[8] S. Yaeko, M. Shotaro, T. Tomoki et al., “Preliminary study for tracing the geographical origin of wheat flour in breads using stable isotope analysis of wheat proteins,” Food Analytical Methods, vol. 14, p. 1, 2020.

[9] J. Wang, T. Chen, W. Zhang, Y. Zhao, S. Yang, and A. Chen, “Tracing the geographical origin of rice by stable isotopic analyses combined with chemometrics,” Food Chemistry, vol. 313, Article ID 126093, 2020.

[10] P. Vera, G. Raquel, C. B. Dias, and M. Cabrita, “Combination of stable isotope analysis and chemo metrics to discriminate geoclimatically and temporally the virgin olive oils from three mediterranean countries,” Foods, vol. 9, p. 12, 2020.

[11] Y.-Y. SU, J. Gao, Y. F. Zhao et al., “Geographical origin classification of Chinese wines based on carbon and oxygen stable isotopes and elemental profiles,” Journal of Food Protection, vol. 83, p. 8, 2020.

[12] N. W. Ling, B. L. Jie, G. Gary et al., “Multivariate statistical analysis of stable isotope signatures and element concentrations to differentiate the geographical origin of retail milk sold in Singapore,” Food Control, vol. 123, Article ID 107736, 2020.

[13] L. Qian, F. Zuo, H. Liu, C. Zhang, X. Chi, and D. Zhang, “Determination of geographical origin of wuchang rice with the geographical indicator by multielement analysis,” Journal of Food Quality, vol. 2, pp. 1–7, 2019.

[14] J. Zhang, Z. Tian, Y. Ma et al., “Origin identification of the sauce-flavor Chinese baijiu by organic acids, trace elements, and the stable carbon isotope ratio,” Journal of Food Quality, vol. 2019, Article ID 7525201, 7 pages, 2019.

[15] M. Du, Y. Fang, F. Shen et al., “Multiangle discrimination of geographical origin of rice based on analysis of mineral elements and characteristic volatile components,” International Journal of Food Science & Technology, vol. 53, p. 9, 2018.

[16] P. Cheajesadagul, C. Arnaudguilhem, J. Shiowatana, A. Siripinyanond, and J. Szpunar, “Discrimination of geographical origin by multi-element analysis,” Journal of Food Quality, vol. 2019, Article ID 7525201, 7 pages, 2019.

[17] S. O. Yeon, I. M. Atikul, S. J. Hyeon et al., “Elemental composition of pork meat from conventional and animal welfare farms by inductively coupled plasma-optical emission spectrometry (ICP-OES) and ICP-mass spectrometry (ICP-MS) and their authentication via multivariate chemo metric analysis,” Meat Science, vol. 172, Article ID 108344, 2021.

[18] B. M. Freire, V. D. S. Santos, P. D. C. F. Neves et al., “Elemental chemical composition and as speciation in rice varieties selected for bio fortification,” Analytical Methods, vol. 12, p. 16, 2020.

[19] L. Emily, F. Juraj, G. Sarah, J. Hutson, and L. Mosley, “A simple and rapid ICP-MS/MS determination of sulfur isotope ratios (34S/32S) in complex natural waters: a new tool for tracing seawater intrusion in coastal systems,” Talanta, vol. 235, Article ID 122708, 2021.

[20] S. Alexander, G. Sarah, T. Renee et al., “In-situ Lusingle bondHF geochronology of garnet, apatite and xenotime by LA ICP MS/MS,” Chemical Geology, vol. 577, Article ID 120299, 2021.

[21] S. Yoshinari, M. Kirara, and Y. Yukiya, “Assignment of PM2.5 sources in western Japan by non-negative matrix factorization of concentration-weighted trajectories of GED-ICP-MS/MS element concentrations,” Environmental Pollution, vol. 207, Article ID 116054, 2021.

[22] L. Xiaojing, D. Shuofei, Y. Yahu et al., “36Sr/34Sr isotope ratios in rocks determined using inductively coupled plasma tandem mass spectrometry in O2 mode without prior Sr purification,” Rapid Communications in Mass Spectrometry, vol. 34, Article ID e8690, 2020.

[23] A. Akif, E. A. Pelin, and O. G. Eftade, “Chemical characterization of size-segregated particulate matter (PM) by inductively coupled plasma – tandem mass spectrometry (ICP-MS/MS),” Talanta, vol. 208, Article ID 120350, 2020.

[24] J. Hirata, D. Itabashi, and M. Aimoto, “Determination of ultra-trace tellurium in steel by ID-ICP-MS/MS with liquid-liquid extraction,” Analytical Sciences, 2021.

[25] T. M. A. M. Tamer, I. H. E. Dalia, and S. S. Abdelsalam, “Determination of some common heavy metals and radionuclides in some medicinal herbs using ICP-MS,” Journal of AOAC International, vol. 102, p. 5, 2020.

[26] L. Fu and S. Shi, “A novel strategy to determine the compositions of inorganic elements in fruit wines using ICP-MS/MS,” Food Chemistry, vol. 299, Article ID 125172, 2019.

[27] O. Pérez-Arvizu and J.-P. Bernal, “Measurement of sulfur in environmental samples using the Interference Standard Method with a O2-pressurized reaction cell and a single quadrupole inductively coupled plasma mass spectrometer,” Rapid Communications in Mass Spectrometry: Rapid Communications in Mass Spectrometry, vol. 35, p. 9034, 2020.
[36] F. Liang, X. Hualin, H. Jianhua, and L. Chen, ”Determination of the non-metallic elements in herbal tea by inductively coupled plasma tandem mass spectrometry,” *Biological Trace Element Research*, vol. 199, pp. 769–778, 2021.