

METHOD AND SYSTEM FOR QUANTITATIVELY DETECTING COPPER IN RICE LEAVES

TECHNICAL FIELD

5 The present invention relates to the field of heavy metal detection, in particular to a method and system for quantitatively detecting copper (Cu) in rice leaves.

BACKGROUND

10 Rice is an important food crop in the world. With the largest rice production in the world, China has about 65% of population feeding on rice. The functional leaves of rice are important organs for grain formation, whose photosynthetic products contribute more than 80% of the grain yield of rice. Human activities such as industry, agriculture and urban pollution have caused the accumulation of heavy metals in the environment. Copper (Cu) is an essential micronutrient for plants, which acts as a coenzyme in the respiration and photosynthesis of rice leaves. However, 15 Cu is toxic to rice growth at high concentrations. Therefore, the rapid detection of Cu in rice leaves is conducive to determining heavy metals in rice plants and their surrounding environment. It provides technical means for studying the accumulation and absorption laws of heavy metals in plants, and is of great significance for rice safety supervision.

20 Traditional laboratory chemical testing method is mostly used to detect heavy metal in rice, which requires a high-temperature and high-acid environment for sample pretreatment, and has random errors, high costs and low efficiency. As an effective metal element detection technique, laser-induced breakdown spectroscopy (LIBS) uses high-energy laser pulses to ablate the test sample to instantly generate plasma with extremely high temperature and brightness on the surface of the sample. LIBS spectra reflects elements information of test sample, showing a 25 certain quantitative relationship. The LIBS technique has the advantages of convenient, fast, micro-trace, simultaneous multi-element detection, and has been applied in aerospace, environment, food and other fields.

30 Comparatively, the application of LIBS in the field of plants is more challenging. The LIBS plasma spectra contain thousands of variable information, including emission lines of the target element, continuous background information and the complex matrix information. The plant samples have complex and diverse composition, which eventually cause a complex matrix effect. The matrix effect affects the signals of LIBS and interferes with the applicability of conventional element emission lines for quantitative detection of plant elements. The Cu emission lines may be disturbed by matrix effect and cannot express Cu content of rice leaves accurately. In order to

remove interference of the matrix effect and improve the rapid detection accuracy of LIBS on the Cu content of rice leaves, it is necessary to fully consider the linear and nonlinear relationships contained in LIBS spectra.

5 **SUMMARY**

An objective of the present invention is to provide a method and system for quantitatively detecting copper (Cu) in rice leaves, so as to realize the accurate and fast detection of Cu content.

To achieve the above purpose, the present invention provides the following technical solutions.

- 10 A method for quantitatively detecting copper (Cu) in rice leaves includes:
 - obtaining rice leaf samples;
 - acquiring laser-induced breakdown spectroscopy (LIBS) data of the rice leaf samples;
 - measuring a true Cu content y in the rice leaf samples by using inductively coupled plasma mass spectrometry (ICP-MS);
- 15 obtaining a characteristic band with a highest correlation with the true Cu content from the spectral data by using a characteristic variable screening method;
 - quickly locating n Cu emission lines in the characteristic band, which are recorded as $\lambda_1, \lambda_2, \dots, \lambda_n$;
 - using a simple linear regression (SLR) method to establish n SLR models of Cu emission
- 20 line intensity and Cu content of the test samples, and obtaining correlations $R_1, R_2, \dots, R_n$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$;
 - obtaining a maximum correlation R_i among $R_1, R_2, \dots, R_n$;
 - calculating a predicted Cu content y_i based on an SLR model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_i ;
- 25 using an exponential regression (ER) equation to establish n ER models of Cu emission line intensity and Cu content of the test samples, and obtaining correlations $R_{e1}, R_{e2}, \dots, R_{en}$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$;
 - obtaining a maximum correlation R_{ej} among $R_{e1}, R_{e2}, \dots, R_{en}$;
 - calculating a predicted Cu content y_j based on an ER model of Cu emission line intensity
- 30 and Cu content corresponding to the maximum correlation R_{ej} ;
 - using a multiple linear regression (MLR) method to establish n MLR models of Cu emission line intensity and Cu content of the test samples, and obtaining a correlation R_d between the true Cu content y and a predicted content y_d ;
 - calculating the predicted Cu content y_d based on an MLR model of Cu emission line

intensity and Cu content corresponding to the correlation R_d ;

establishing a linear regression model of multi-equation combination predicted content and true Cu content by using a linear regression method by taking Cu contents y_i , y_j and y_d as an input vector and the true content y as an output vector; and

5 determining Cu content in the rice leaf samples on the linear regression model of multi-equation combination predicted content and true Cu content.

Optionally, the obtaining rice leaf samples specifically includes:

selecting plants with similar growth vigor for stress treatment in a CuCl_2 solution at different concentrations; collecting samples after 20 d of stress treatment, and washing, rapidly drying,
10 grinding, sieving and tableting as samples to be tested.

Optionally, the SLR model of Cu emission line intensity and Cu content of n test samples is specifically expressed as:

$y_1 = a_1 I\lambda_1 + b_1, y_2 = a_2 I\lambda_2 + b_2, \dots, y_n = a_n I\lambda_n + b_n$, $n = 1, 2, 3, \dots$, where $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ are intensities of the n Cu emission lines; $a_1, a_2, \dots, a_n$ are slopes of a fitting formula to fit the Cu
15 emission line intensities and the true Cu content by using the SLR method; $b_1, b_2, \dots, b_n$ are intercepts of the fitting formula to fit the Cu emission line intensities and the true Cu content by using the SLR method.

Optionally, the ER model of Cu emission line intensity and Cu content of n test samples is specifically expressed as:

20 $y_1 = a_1 I\lambda_1^{b_1}, y_2 = a_2 I\lambda_2^{b_2}, \dots, y_n = a_n I\lambda_n^{b_n}$, $n = 1, 2, 3, \dots$, where $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ are intensities of the n Cu emission lines; $a_1, a_2, \dots, a_n$ are slopes of a fitting formula to fit the Cu emission line intensities and the true Cu content by using the ER method; $b_1, b_2, \dots, b_n$ are exponents of the fitting formula to fit the Cu emission line intensities and the true Cu content by using the ER method.

25 Optionally, the MLR model of Cu emission line intensity and Cu content of n test samples is specifically expressed as:

$y_d = f + f_1 I\lambda_1 + f_2 I\lambda_2 + \dots + f_n I\lambda_n$, $n = 1, 2, 3, \dots$, where $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ are intensities of the n Cu emission lines, and $f_1, f_2, \dots, f_n$ are coefficients corresponding to each intensity.

30 Optionally, the linear regression model of multi-equation combination predicted content and true Cu content is specifically expressed as:

$y = k + k_1 y_i + k_2 y_j + k_3 y_d$
 $= k + k_1 a_i I\lambda_i + k_1 b_i + k_2 a_n I\lambda_n^{b_n} + k_3 f + k_3 f_1 I\lambda_1 + k_3 f_2 I\lambda_2 + \dots + k_3 f_n I\lambda_n$, where
 $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ are intensities of the n Cu emission lines, k_1, k_2, k_3 are coefficients

corresponding to y_i, y_j, y_d in the linear regression model, and $f, f_1, f_2, \dots, f_n$ are coefficients corresponding to each intensity.

Optionally, the concentrations of CuCl_2 solution are 0 μM , 5 μM , 25 μM , 50 μM and 100 μM CuCl_2 .

Optionally, the characteristic variable screening method includes one of interval partial least squares (iPLS), synergy interval partial least squares (Si-PLS), backward interval partial least squares (BiPLS), genetic algorithm (GA), successive projections algorithm (SPA), decision tree (DT), random forest (RF), regularized model, mean decrease in accuracy (MDA) and recursive feature elimination (RFE).

The present invention further provides a system for quantitatively detecting Cu in rice leaves, where the detection system includes:

a sample obtaining module, configured to obtain rice leaf samples;

an LIBS data acquisition module, configured to acquire LIBS data of the rice leaf samples;

a true Cu content determination module, configured to measure a true Cu content y in the rice leaf samples by using ICP-MS;

a characteristic band determination module, configured to obtain a characteristic band with a highest correlation with the true Cu content from the spectral data by using a characteristic variable screening method;

an emission line determination module, configured to quickly locate n Cu emission lines in the characteristic band, which are recorded as $\lambda_1, \lambda_2, \dots, \lambda_n$;

a Cu emission line intensity-copper content SLR model establishment module, configured to use an SLR method to establish n SLR models of Cu emission line intensity and Cu content of the test samples, and obtain correlations $R_1, R_2, \dots, R_n$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$;

a first maximum correlation obtaining module, configured to obtain a maximum correlation R_i among $R_1, R_2, \dots, R_n$;

a first Cu content calculation module, configured to calculate a predicted Cu content y_i based on an SLR model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_i ;

a Cu emission line intensity-copper content ER model establishment module, configured to use an ER equation to establish n ER models of Cu emission line intensity and Cu content of the test samples, and obtain correlations $R_{e1}, R_{e2}, \dots, R_{en}$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$;

a second maximum correlation obtaining module, configured to obtain a maximum

correlation R_{ej} among $R_{e1}, R_{e2}, \dots, R_{en}$;

a second Cu content calculation module, configured to calculate a predicted Cu content y_j based on an ER model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_{ej} ;

5 a Cu emission line intensity-copper content MLR model establishment module, configured to use an MLR method to establish n MLR models of Cu emission line intensity and Cu content of the test samples, and obtain a correlation R_d between the true Cu content y and a predicted content y_d ;

10 a third Cu content calculation module, configured to calculate the predicted Cu content y_d based on an MLR model of Cu emission line intensity and Cu content corresponding to the correlation R_d ;

a multi-equation combination predicted content-true Cu content linear regression model establishment module, configured to establish a linear regression model of multi-equation combination predicted content and true Cu content by using a linear regression method by taking
15 Cu contents y_i , y_j and y_d as an input vector and the true content y as an output vector; and

a fourth Cu content calculation module, configured to determine Cu content in the rice leaf samples on the linear regression model of multi-equation combination predicted content and true Cu content.

20 According to specific examples provided by the present invention, the present invention discloses the following technical effects.

The method of the present invention quickly locates the positions of element emission lines related to the content of the target element, and has the characteristics of no contact with strong acid/alkaline reagents, simple and fast operation and low cost. The present invention fully analyzes the mathematical relationships between the laser-induced breakdown spectroscopy
25 (LIBS) spectra and the true Cu content of rice leaves, improving the quantitative detection accuracy and sensitivity, and realizing rapid and large-scale detection of Cu in rice leaves.

BRIEF DESCRIPTION OF DRAWINGS

To describe the technical solutions in the examples of the present invention or in the prior art
30 more clearly, the accompanying drawings required for the examples are briefly described below. Apparently, the accompanying drawings in the following description show merely some examples of the present invention, and a person of ordinary skill in the art may still derive other accompanying drawings from these accompanying drawings without creative efforts.

FIG. 1 is a flowchart of a method for quantitatively detecting copper (Cu) in rice leaves

according to an example of the present invention.

FIG. 2 is a structural diagram of a system for quantitatively detecting Cu in rice leaves according to an example of the present invention.

5 **DETAILED DESCRIPTION**

The technical solutions in the examples of the present invention are clearly and completely described below with reference to the accompanying drawings in the examples of the present invention. Apparently, the described examples are merely a part rather than all of the examples of the present invention. All other examples obtained by a person of ordinary skill in the art based
10 on the examples of the present invention without creative efforts should fall within the protection scope of the present invention.

An objective of the present invention is to provide a method and system for quantitatively detecting copper (Cu) in rice leaves, so as to realize the accurate and fast detection of Cu content.

In order to make the above objectives, features and advantages of the present invention more
15 understandable, the present invention is described in further detail below with reference to the accompanying drawings and specific implementations.

FIG. 1 is a flowchart of a method for quantitatively detecting Cu in rice leaves according to an example of the present invention. As shown in FIG. 1, the method includes the following steps:

Step 101: obtain rice leaf samples.

20 Specifically:

Rice seeds were sterilized, germinated and cultivated in a nutrient solution until a root length of about 6 cm. 50 rice plants with similar growth vigor were selected for stress treatment in a CuCl_2 solution at 5 concentrations, such as 0 μM , 5 μM , 30 μM , 70 μM and 100 μM . After 40 days of stress, the functional leaves of each plant in second leaf positions were collected, and
25 soaked in 20 mM of Na_2EDTA solution for 15 min. Then the functional leaves were washed with distilled water, rapidly dried, ground, sieved and tableted as samples to be tested. The samples had a mass of 0.10 g and a size of $10 \times 10 \times 1$ mm (length, width and height, equal within an error range). Specifically, the samples were dried in an oven at 80°C , quickly ground by an automatic grinder at 60 Hz for 80 s, and tableted as samples having a mass of 0.20 g and a size of
30 $10 \times 10 \times 2$ mm (length, width and height).

Step 102: acquire laser-induced breakdown spectroscopy (LIBS) data of the rice leaf samples.

An experimental device was debugged based on a three-factor orthogonal experiment scheme to obtain the optimal acquisition parameters such as energy 70 mJ, delay time 2 μs , and

integral time 10 μ s. A LIBS spectrum X of the test samples was obtained by using the parameters of laser wavelength 532 nm, gain 1,500 and focal depth 2 mm. The tableted samples were fixed on an x-y-z three-dimensional (3D) moving platform. The platform was adjusted to move in sequence so that a laser ablates 16 spots on the samples. Each spot was stricken 5 times in total, and a 4×4 array was formed. The LIBS spectra of a sample was the average of the sample's 80 times of laser ablation.

Step 103: measure a true Cu content y in the rice leaf samples by using inductively coupled plasma mass spectrometry (ICP-MS).

ICP-MS uses an inductively coupled plasma as the ion source and a mass spectrometer as the detector to obtain an ion mass spectrum. It provides information on each atomic mass unit in the range of 3-250 amu, and can simultaneously detect and analyze multiple heavy metal elements (except mercury). Its sensitivity is high, and most of its detection limits reach ppt level.

The statistical values of each Cu stress group are shown in Table 1:

Table 1 Cu content in different groups of rice leaves (mg/kg)

Groups	CK	1	2	3	4
Number	10	10	10	10	10
Min	0.976	22.550	159.104	215.091	301.264
Max	14.210	155.594	213.823	300.281	404.777
Mean	6.406	85.943	185.618	262.564	348.061
S.D.	3.921	45.680	18.976	32.331	35.965

Step 104: obtain a characteristic band with a highest correlation with the true Cu content from the spectral data by using a characteristic variable screening method.

This step used a suitable characteristic variable screening method, including interval partial least squares (iPLS), synergy interval partial least squares (Si-PLS), backward interval partial least squares (BiPLS), genetic algorithm (GA), successive projections algorithm (SPA), decision tree (DT), random forest (RF), regularized model, mean decrease in accuracy (MDA) and recursive feature elimination (RFE), etc.

In an example of the present invention, the BiPLS method was used to screen a characteristic band highly correlated with the true Cu content y , which was recorded as x . The full spectrum was divided into 19 intervals by the BiPLS method, and the optimal bands were selected as 324.6-325.1 nm and 327.3-327.8 nm.

Step 105: quickly locate n Cu emission lines in the characteristic band, which are recorded as

$$\lambda_1, \lambda_2, \dots, \lambda_n.$$

Specifically, according to a database of the National Institute of Standards and Technology (NIST), two Cu emission lines were quickly located in the characteristic band x as $\lambda_1 = 324.87$ nm and $\lambda_2 = 327.46$ nm, respectively.

5 Step 106: use a simple linear regression (SLR) method to establish n SLR models of Cu emission line intensity and Cu content of the test samples, and obtain correlations $R_1, R_2, \dots, R_n$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$.

Specifically, the n SLR models of Cu emission line intensity and Cu content of the test samples were established by the SLR method by taking the Cu emission line intensities $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ as an input vector and the true content y as an output vector, as follows:

10 $y_1 = a_1 I\lambda_1 + b_1, y_2 = a_2 I\lambda_2 + b_2, \dots, y_n = a_n I\lambda_n + b_n, n = 1, 2, 3, \dots$, where $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ were intensities of the n Cu emission lines; $a_1, a_2, \dots, a_n$ were slopes of a fitting formula to fit the Cu emission line intensities and the true Cu content by using the SLR method; $b_1, b_2, \dots, b_n$ were intercepts of the fitting formula to fit the Cu emission line intensities and the true Cu content by using the SLR method.

In an example of the present invention, the SLR models of Cu emission line intensity and Cu content of the test samples were established by taking intensity of each Cu emission line in Step 105 as an input vector and the true content y as an output vector. R_1 and R_2 of regression models established by each Cu emission line are shown The and in Table 2. Table 2 shows that the SLR model of the Cu I 324.87 nm had the better result, $y_i = 0.0633I_{324} - 90.91$.

Table 2 Regression models and R of emission lines

Cu lines	Equations	R
x = 324.87 nm	y = 0.0633x - 90.91	0.919
x = 327.46 nm	y = 0.0964x - 119.23	0.918

Step 107: obtain a maximum correlation R_i among $R_1, R_2, \dots, R_n$.

Step 108: calculate a predicted Cu content y_i based on an SLR model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_i .

25 The predicted Cu content y_i of the model is calculated by $y_i = a_i I\lambda_i + b_i$.

Step 109: use an exponential regression (ER) equation to establish n ER models of Cu emission line intensity and Cu content of the test samples, and obtain correlations $R_{e1}, R_{e2}, \dots, R_{en}$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$.

Specifically, the n ER models of Cu emission line intensity and Cu content of the test samples were established by the ER equation by taking one of the Cu emission line intensities

$I\lambda_1, I\lambda_2, \dots, I\lambda_n$ as an input vector and the true content y as an output vector, and the correlations $R_{e1}, R_{e2}, \dots, R_{en}$ between the true Cu content y and the predicted contents $y_1, y_2, \dots, y_n$ were obtained, as follows:

$$y_1 = a_1 I\lambda_1^{b_1}, y_2 = a_2 I\lambda_2^{b_2}, \dots, y_n = a_n I\lambda_n^{b_n}, \quad n=1, 2, 3, \dots, \quad \text{where } I\lambda_1, I\lambda_2, \dots, I\lambda_n \text{ were}$$

intensities of the n Cu emission lines; $a_1, a_2, \dots, a_n$ were slopes of a fitting formula to fit the Cu emission line intensities and the true Cu content by using the ER method; $b_1, b_2, \dots, b_n$ were exponents of the fitting formula to fit the Cu emission line intensities and the true Cu content by using the ER method.

In an example of the present invention, the ER models of copper emission line intensity and Cu content of two test samples were established by taking the intensities of the copper emission lines in Step 105 as an input vector and the true content y as an output vector. The regression models and the corresponding R of the Cu emission lines are shown in Table 3. Table 3 shows that the ER model of the Cu I 324.87 nm line had the best effect, $y_j = 1E - 08I_{324}^{2.784}$.

Table 3 Regression models and R of emission lines

Cu lines	Equations	R
$x = 324.87 \text{ nm}$	$y = 1E - 08x^{2.784}$	0.932
$x = 327.46 \text{ nm}$	$y = 9E - 10x^{3.1975}$	0.915

Step 110: obtain a maximum correlation R_{ej} among $R_{e1}, R_{e2}, \dots, R_{en}$.

Step 111: calculate a predicted Cu content y_j based on an ER model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_{ej} .

Step 112: use a multiple linear regression (MLR) method to establish n MLR models of Cu emission line intensity and Cu content of the test samples, and obtain a correlation R_d between the true Cu content y and a predicted content y_d .

Specifically, the MLR models of Cu emission line intensity and Cu content of the test samples were established by the MLR method by taking Cu emission line intensities $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ as an input vector and the true content y as an output vector, and the correlation R_d between the true Cu content y and the predicted content y_d was obtained, as follows:

$$y_d = f + f_1 I\lambda_1 + f_2 I\lambda_2 + \dots + f_n I\lambda_n, \quad n=1, 2, 3, \dots, \quad \text{where } I\lambda_1, I\lambda_2, \dots, I\lambda_n \text{ were intensities of}$$

the n Cu emission lines, and $f_1, f_2, \dots, f_n$ were coefficients corresponding to each intensity. The Cu emission line (λ_i) corresponding to the maximum correlation R expressed the information of Cu in rice leaves to the greatest extent. Due to the interference of the complex matrix effect of rice leaves, the copper emission line corresponding to the lower R did not fully express the Cu information, but contained a lot of matrix effect information.

In an example of the present invention, the MLR model of LIBS Cu emission line intensity and Cu content of the test samples was established as $y_d = -105.6952 + 0.0319I_{324} + 0.0481I_{327}$ by taking the intensities of the two Cu emission lines in Step 105 as an input vector and the true content y as an output vector. The correlation between y and I_λ was 0.920, and the Cu content predicted by the linear regression model was y_d .

Step 113: calculate the predicted Cu content y_d based on an MLR model of Cu emission line intensity and Cu content corresponding to the correlation R_d .

Step 114: establish a linear regression model of multi-equation combination predicted content and true Cu content by using a linear regression method by taking Cu contents y_i , y_j and y_d as an input vector and the true content y as an output vector, as follows:

$$y = k + k_1y_i + k_2y_j + k_3y_d$$

$$= k + k_1a_iI\lambda_i + k_1b_i + k_2a_nI\lambda_n^{b_n} + k_3f + k_3f_1I\lambda_1 + k_3f_2I\lambda_2 + \dots + k_3f_nI\lambda_n$$
, where $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ were intensities of the n Cu emission lines, k_1, k_2, k_3 were coefficients corresponding to y_i, y_j, y_d in the linear regression model, and $f, f_1, f_2, \dots, f_n$ were coefficients corresponding to each intensity.

Step 115: determine Cu content in the rice leaf samples on the linear regression model of multi-equation combination predicted content and true Cu content.

The linear regression model of multi-equation combination predicted content and true Cu content maintained the information from y_i , y_j and y_d . The linear regression model of multi-equation combination contained the mathematical relationships such as linear, exponential and non-linear relationships between the LIBS spectra and the Cu content of the rice leaves to the maximum extent. This model removed the matrix interference information to a certain extent and thus achieved accurate quantification of the Cu content.

$y = -0.2927 + 0.0005y_i - 0.0073y_j + 1.0084y_d$, that is

$$y = -0.2927 + 0.0005(0.0633I_{324} - 90.91) - 0.0073(1E-08I_{324}^{2.784}) + 1.0084(-105.6952 + 0.0319I_{324} + 0.0481I_{327})$$

Such that:

$$y = 0.0322I_{324} - 7.3 \times 10^{-11}I_{324}^{2.784} + 0.0485I_{327} - 106.9210$$

The correlation between y and x was 0.940, indicating that the model had the best effect, and the correlation was higher than that obtained in the above steps, thereby achieving accurate quantitative detection.

FIG. 2 is a structural diagram of a system for quantitatively detecting Cu in rice leaves according to an example of the present invention. This detection system includes: a sample obtaining module, an LIBS data acquisition module, a true Cu content determination module, a

characteristic band determination module, an emission line determination module, a Cu emission line intensity-copper content SLR model establishment module, a first maximum correlation obtaining module, a first Cu content calculation module, a Cu emission line intensity-copper content ER model establishment module, a second maximum correlation obtaining module, a second Cu content calculation module, an Cu emission line intensity-copper content MLR model establishment module, a third Cu content calculation module, a multi-equation combination predicted content-true Cu content linear regression model establishment module and a fourth Cu content calculation module.

The sample obtaining module 201 is configured to obtain rice leaf samples.

The LIBS data acquisition module 202 is configured to acquire LIBS data of the rice leaf samples.

The true Cu content determination module 203 is configured to measure a true Cu content y in the rice leaf samples by using ICP-MS.

The characteristic band determination module 204 is configured to obtain a characteristic band with a highest correlation with the true Cu content from the spectral data by using a characteristic variable screening method.

The emission line determination module 205 is configured to quickly locate n Cu emission lines in the characteristic band, which are recorded as $\lambda_1, \lambda_2, \dots, \lambda_n$.

The Cu emission line intensity-copper content SLR model establishment module 206 is configured to use an SLR method to establish n SLR models of Cu emission line intensity and Cu content of the test samples, and obtain correlations $R_1, R_2, \dots, R_n$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$.

The first maximum correlation obtaining module 207 is configured to obtain a maximum correlation R_i among $R_1, R_2, \dots, R_n$.

The first Cu content calculation module 208 is configured to calculate a predicted Cu content y_i based on an SLR model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_i .

The Cu emission line intensity-copper content ER model establishment module 209 is configured to use an ER equation to establish n ER models of Cu emission line intensity and Cu content of the test samples, and obtain correlations $R_{e1}, R_{e2}, \dots, R_{en}$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$.

The second maximum correlation obtaining module 210 is configured to obtain a maximum correlation R_{ej} among $R_{e1}, R_{e2}, \dots, R_{en}$.

The second Cu content calculation module 211 is configured to calculate a predicted Cu

content y_j based on an ER model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_{ej} .

5 The Cu emission line intensity-copper content MLR model establishment module 212 is configured to use an MLR method to establish n MLR models of Cu emission line intensity and Cu content of the test samples, and obtain a correlation R_d between the true Cu content y and a predicted content y_d .

The third Cu content calculation module 213 is configured to calculate the predicted Cu content y_d based on an MLR model of Cu emission line intensity and Cu content corresponding to the correlation R_d .

10 The multi-equation combination predicted content-true Cu content linear regression model establishment module 214 is configured to establish a linear regression model of multi-equation combination predicted content and true Cu content by using a linear regression method by taking Cu contents y_i , y_j and y_d as an input vector and the true content y as an output vector.

15 The fourth Cu content calculation module 215 is configured to determine Cu content in the rice leaf samples on the linear regression model of multi-equation combination predicted content and true Cu content.

Each example of the present specification is described in a progressive manner, each example focuses on the difference from other examples, and the same and similar parts between the examples may refer to each other. For a system disclosed in the examples, since it corresponds to the method disclosed in the examples, the description is relatively simple, and reference can be made to the method description.

20 In this paper, several examples are used for illustration of the principles and implementations of the present invention. The description of the foregoing examples is used to help illustrate the method of the present invention and the core principles thereof. In addition, those of ordinary skill in the art can make various modifications in terms of specific implementations and scope of application in accordance with the teachings of the present invention. In conclusion, the content of the present specification should not be construed as a limitation to the present invention.

What is claimed is:

1. A method for quantitatively detecting copper (Cu) in rice leaves, wherein the detection method comprises:

- 5 obtaining rice leaf samples;
 acquiring laser-induced breakdown spectroscopy (LIBS) data of the rice leaf samples;
 measuring a true Cu content y in the rice leaf samples by using inductively coupled plasma mass spectrometry (ICP-MS);
 obtaining a characteristic band with a highest correlation with the true Cu content from the
10 spectral data by using a characteristic variable screening method;
 quickly locating n Cu emission lines in the characteristic band, which are recorded as $\lambda_1, \lambda_2, \dots, \lambda_n$;
 using a simple linear regression (SLR) method to establish n SLR models of Cu emission line intensity and Cu content of the test samples, and obtaining correlations $R_1, R_2, \dots, R_n$
15 between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$;
 obtaining a maximum correlation R_i among $R_1, R_2, \dots, R_n$;
 calculating a predicted Cu content y_i based on an SLR model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_i ;
 using an exponential regression (ER) equation to establish n ER models of Cu emission line
20 intensity and Cu content of the test samples, and obtaining correlations $R_{e1}, R_{e2}, \dots, R_{en}$
 between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$;
 obtaining a maximum correlation R_{ej} among $R_{e1}, R_{e2}, \dots, R_{en}$;
 calculating a predicted Cu content y_j based on an ER model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_{ej} ;
25 using a multiple linear regression (MLR) method to establish n MLR models of Cu emission line intensity and Cu content of the test samples, and obtaining a correlation R_d between the true Cu content y and a predicted content y_d ;
 calculating the predicted Cu content y_d based on an MLR model of Cu emission line intensity and Cu content corresponding to the correlation R_d ;
30 establishing a linear regression model of multi-equation combination predicted content and true Cu content by using a linear regression method by taking Cu contents y_i, y_j and y_d as an input vector and the true content y as an output vector; and
 determining Cu content in the rice leaf samples on the linear regression model of multi-equation combination predicted content and true Cu content.

2. The method for quantitatively detecting Cu in rice leaves according to claim 1, wherein the obtaining rice leaf samples specifically comprises:

selecting plants with similar growth vigor for stress treatment in a CuCl_2 solution at different concentrations; collecting samples after 20 d of stress treatment, and washing, rapidly drying, grinding, sieving and tableting as samples to be tested.

3. The method for quantitatively detecting Cu in rice leaves according to claim 1, wherein the SLR model of Cu emission line intensity and Cu content of n test samples is specifically expressed as:

$y_1 = a_1 I\lambda_1 + b_1, y_2 = a_2 I\lambda_2 + b_2, \dots, y_n = a_n I\lambda_n + b_n, n = 1, 2, 3 \dots$, wherein $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ are intensities of the n Cu emission lines; $a_1, a_2, \dots, a_n$ are slopes of a fitting formula to fit the Cu emission line intensities and the true Cu content by using the SLR method; $b_1, b_2, \dots, b_n$ are intercepts of the fitting formula to fit the Cu emission line intensities and the true Cu content by using the SLR method.

4. The method for quantitatively detecting Cu in rice leaves according to claim 1, wherein the ER model of Cu emission line intensity and Cu content of n test samples is specifically expressed as:

$y_1 = a_1 I\lambda_1^{b_1}, y_2 = a_2 I\lambda_2^{b_2}, \dots, y_n = a_n I\lambda_n^{b_n}, n = 1, 2, 3 \dots$, wherein $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ are intensities of the n Cu emission lines; $a_1, a_2, \dots, a_n$ are slopes of a fitting formula to fit the Cu emission line intensities and the true Cu content by using the ER method; $b_1, b_2, \dots, b_n$ are exponents of the fitting formula to fit the Cu emission line intensities and the true Cu content by using the ER method.

5. The method for quantitatively detecting Cu in rice leaves according to claim 1, wherein the MLR model of Cu emission line intensity and Cu content of n test samples is specifically expressed as:

$y_d = f + f_1 I\lambda_1 + f_2 I\lambda_2 + \dots + f_n I\lambda_n, n = 1, 2, 3 \dots$, wherein $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ are intensities of the n Cu emission lines, and $f, f_1, f_2, \dots, f_n$ are coefficients corresponding to each intensity.

6. The method for quantitatively detecting Cu in rice leaves according to claim 1, wherein the linear regression model of multi-equation combination predicted content and true Cu content is specifically expressed as:

$$y = k + k_1 y_i + k_2 y_j + k_3 y_d$$

$= k + k_1 a_1 I\lambda_1 + k_1 b_1 + k_2 a_n I\lambda_n^{b_n} + k_3 f + k_3 f_1 I\lambda_1 + k_3 f_2 I\lambda_2 + \dots + k_3 f_n I\lambda_n$, wherein $I\lambda_1, I\lambda_2, \dots, I\lambda_n$ are intensities of the n Cu emission lines, k_1, k_2, k_3 are coefficients corresponding to y_i, y_j, y_d in the linear regression model, and $f, f_1, f_2, \dots, f_n$ are coefficients corresponding to each intensity.

7. The method for quantitatively detecting Cu in rice leaves according to claim 1, wherein the concentrations of CuCl_2 solution are 0 μM , 5 μM , 25 μM , 50 μM and 100 μM .

8. The method for quantitatively detecting Cu in rice leaves according to claim 1, wherein the characteristic variable screening method comprises one of interval partial least squares (iPLS), synergy interval partial least squares (Si-PLS), backward interval partial least squares (BiPLS), genetic algorithm (GA), successive projections algorithm (SPA), decision tree (DT), random forest (RF), regularized model, mean decrease in accuracy (MDA) and recursive feature elimination (RFE).

9. A system for quantitatively detecting Cu in rice leaves, wherein the detection system comprises:

a sample obtaining module, configured to obtain rice leaf samples;

an LIBS data acquisition module, configured to acquire LIBS data of the rice leaf samples;

a true Cu content determination module, configured to measure a true Cu content y in the rice leaf samples by using ICP-MS;

a characteristic band determination module, configured to obtain a characteristic band with a highest correlation with the true Cu content from the spectral data by using a characteristic variable screening method;

an emission line determination module, configured to quickly locate n Cu emission lines in the characteristic band, which are recorded as $\lambda_1, \lambda_2, \dots, \lambda_n$;

a Cu emission line intensity-copper content SLR model establishment module, configured to use an SLR method to establish n SLR models of Cu emission line intensity and Cu content of the test samples, and obtain correlations $R_1, R_2, \dots, R_n$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$;

a first maximum correlation obtaining module, configured to obtain a maximum correlation R_i among $R_1, R_2, \dots, R_n$;

a first Cu content calculation module, configured to calculate a predicted Cu content y_i based on an SLR model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_i ;

a Cu emission line intensity-copper content ER model establishment module, configured to use an ER equation to establish n ER models of Cu emission line intensity and Cu content of the test samples, and obtain correlations $R_{e1}, R_{e2}, \dots, R_{en}$ between the true Cu content y and predicted contents $y_1, y_2, \dots, y_n$;

a second maximum correlation obtaining module, configured to obtain a maximum correlation R_{ej} among $R_{e1}, R_{e2}, \dots, R_{en}$;

a second Cu content calculation module, configured to calculate a predicted Cu content y_j based on an ER model of Cu emission line intensity and Cu content corresponding to the maximum correlation R_{ej} ;

5 a Cu emission line intensity-copper content MLR model establishment module, configured to use an MLR method to establish n MLR models of Cu emission line intensity and Cu content of the test samples, and obtain a correlation R_d between the true Cu content y and a predicted content y_d ;

10 a third Cu content calculation module, configured to calculate the predicted Cu content y_d based on an MLR model of Cu emission line intensity and Cu content corresponding to the correlation R_d ;

a multi-equation combination predicted content-true Cu content linear regression model establishment module, configured to establish a linear regression model of multi-equation combination predicted content and true Cu content by using a linear regression method by taking Cu contents y_i , y_j and y_d as an input vector and the true content y as an output vector; and

15 a fourth Cu content calculation module, configured to determine Cu content in the rice leaf samples on the linear regression model of multi-equation combination predicted content and true Cu content.