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One-component Model Approach for Sensing the Sweetness, Sourness and Astringency of Rice

Lin Lu[1,2], *Xianqiao Hu*[2], *Zhiwei Zhu*[2], *Shiyi Tian*[1,*], *Zhongxiu Chen*[1,*]

[1] School of Food Science and Biotechnnology, Zhejiang Gongshang University, Hangzhou 310018, China
[2] China National Rice Research Institute, Hangzhou 310006, China
[*]E-mail: zhxchen@zjgsu.edu.cn (Z. Chen), tianshiyi@zjgsu.edu.cn (S. Tian)

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This paper deals with a new one-component model approach for sensing the sweetness, sourness, and astringency of rice. Chemical indexes of rice were analyzed, and the sensory score was obtained by sensory evaluation. It was resulted that dominant components for sweetness, sourness and astringency of rice were sucrose, acidity and tannic acid, respectively. A multi-metal sensor was used to quantify the taste perception of sweetness, sourness and astringency through taste stimuli corresponding to dominant components. Continuous Wavelet Transform (CWT) was applied to transform the original voltammetric signal into CWT coefficient curve. The one-component (OC) model with the accuracy of 81.5% was established via neural network method, and used to predict the gustatory values of rice. The correlation analysis between sensory score and gustatory value was applied to clarity the ability of OC model. It was concluded that one-component model approach could accurately sense the sweetness, sourness, astringency of rice.

Keywords: Dominant component; Taste; Sensory evaluation; Multi-metal sensor

1. INTRODUCTION

Rice is the main grain crop in the world, for which people's demand has risen to a higher level. The taste quality of rice reflects its market value and the degree of consumer preference. The researches on flavor compounds in rice have focused on volatile components. Rice odor consists of complex mixtures of various active compounds, in which a large number of components and several main aromatic components have identified [1,2]. Griglione et al. [3] reported that the main volatile fractions of aromatic and non-aromatic rices included 2-acetyl-1-pyrrolidine, 3-methyl-1-butanol, 1-octene-3 alcohol, 2-octenal and 2-ethylhexanol. Among those, 2-acetyl-1-pyrrolidine is considered to be a characteristic component, which presents not only the fragrance of popcorn, but also the fragrance of leaves or flowers [4]. However, flavor compound in rice is not the key to determine its taste quality.

In the sensory evaluation of rice, the sweetness is more prominent, occasionally accompanied with sourness or astringency. Generally speaking, sourness is caused by hydrogen ions in organic acids [5], and bitterness or astringency comes from specific stimuli. Rice contains a large amount of starch which cannot affect its taste, but the contribution of geranyl acetate and ionone to the sweetness has been reported [6]. However, the soluble sugar in rice is considered as the most likely explanation for the sweetness of rice. The taste perception in rice is not clearly caused by which kinds of compounds.

In recent years, with the demand for non-destructive, fast and intelligent detection technology, the research about sensory bionics technology such as electronic tongue, electronic nose has gradually become a hot topic pursued by many scientists, which has been applied in food, agriculture and other fields [7-11]. Although bionic sensory instrument has been introduced to differentiate the rice and analyze its eating quality [12-14], taste response of rice is barely studied. Due to the limit of manual sensory evaluation, the sensor is considered to be the proper tool which can perform taste response of rice.

In this study, a one-component model approach was developed for multi-metal sensor to quantitatively predict the sweetness, sourness and astringency of rice. Chemical analysis and sensory evaluation were utilized for the establishment and verification of the developed approach. The approach was expected as a rapid and simple one for sensing the sweetness, sourness and astringency of rice.

2. MATERIAL AND METHODS

2.1. Rice samples and treatment

Five Oryza sativa subsp. xian rice (numbered as X1, X2, X3, X4, X5) and five Oryza sativa subsp. geng rice (numbered as J1, J2, J3, J4, J5) were collected for this study. These rice samples from different provinces in China have large acreages and wide distributions. After drying, rice samples were hulled to brown rice with husking machine, then milled and ground into flour by a cyclone with a 0.42 mm sieve.

2.2. Taste stimuli and formulation

Taste stimuli i.e. sucrose, citric acid, and tannic acid were respectively selected for sweetness, sourness, astringency, according to subsequent chemical analysis. People in different countries have different recognition thresholds and difference thresholds for taste stimuli [15]. In this study, the thresholds of Chinese were considered to be the low concentration of stimuli, and the concentrations of taste stimuli were set in Table 1.

Table 1. The recognition thresholds and concentrations of taste stimuli.

Taste stimulus	Recognition threshold (mM, %)	Concentration (mM)					
		1	2	3	4	5	6
Sucrose	12.6 (0.431%)	3	8	13	18	25	30
Citric acid	0.246 (0.0047%)	0.05	0.1	0.25	0.5	1	1.5
Tannic acid	0.4 (0.075%)	0.1	0.2	0.4	0.6	0.8	1

The mixtures were all the possible combinations of taste stimulus at the highest, the lowest and the third concentrations (close to recognition thresholds). In this study, there were 54 mixtures including 27 mixtures with two stimuli and 27 mixtures with three stimuli. The control sample is deionized water with dilute lye.

2.3. Sensor and voltammetric measurement

The sensor was a standard three-electrode system consisted of six metal electrodes (Au, Ag, Ni, Pd, Pt, Ti) as working electrodes, an Ag/AgCl electrode as the reference electrode and a Pt electrode as the auxiliary electrode. Cyclic voltammetry (CV) was conducted in multichannel potentiostat (CHI1040C, CH Instruments Inc., USA) with the multi-metal sensor (Scheme 1). CV scanned from -1V to 1V with potential gap of 0.005V, the scanning rate of 0.05 $V \cdot s^{-1}$, and the sensitivity of 1e-4. For each measurement, all signal points of the sample were saved and output.

4.0 g rice flour and 100 mL boiling deionized water were put into beaker, then stirred evenly to make flour fully immersed in boiling water. After cooling to room temperature, the mixture was filtered and the filtrate was collected. 15 mL filtrate was measured using the sensor. Before testing, the sensor must be electrochemically cleaned. Each sample was measured three times.

2.4. Chemical analysis

The soluble sugars of rice samples such as sucrose, glucose, fructose and maltose were determined via ion chromatography method. A total of 0.5 g rice flour was weighed to 15mL centrifugal tube, then added with 10.0mL 50% ethanol solution, and oscillated in shaking table for 30 min. The supernatant was obtained by the centrifugation with a speed of 3000 r/min for 15 min, and put into plug tube. Immediately, the centrifugal tube with sediment was added 10.0mL ethanol solution for repeated operation. The supernatant was filtered via microporous membrane after mixing, and analyzed by ion chromatography. In ion chromatography, sugar ion exchange column (Metrosep Carb 1, 5.0 μm, 150mm × 4.0mm) was used as chromatographic column, and pulsed ampere detector with gold working electrode and was employed. The injection volume was 10 μL, the flow rate of mobile phase was 1 mL/min. The content of sucrose, glucose, fructose and maltose of rice sample was quantified by the curve of standard solution mixed with four sugars.

The acidity of rice sample was determined by alkali titration. The supernatant obtained above was added with phenothalin, and titrated using 0.01 mol/L KOH until the color became red. The titration volume of KOH was used for the calculation of the acidity value. Soxhlet extraction method was applied for the determination of fat content. The decrease of rice flour was used to calculate the fat content by the extraction for 6h with petroleum ether.

Tannic acid was quantified through spectrophotometry. The filtrate of rice sample obtained in Section 2.3. A series of standard tannic acid solutions was prepared, and then their absorption values at 276 nm were recorded. The content of tannic acid in rice sample was calculated by its absorption value putting into the standard curve.

2.5. Sensory evaluation

Sensory evaluations of the sweetness, sourness, astringency of rice samples were conducted by a group of eight skilled panelists. The cooked rice was prepared for evaluation, and the preparation was as followed: a total of 150g milled rice were washed and soaked in 240 g water for 30 min, and then steamed for 25 min, ultimately cooled for 30 min at room temperature. The cooked rice was placed in eight ceramic bowls for each panelist, which were presented in random sequence. Panelists scored the sweetness, sourness, astringency of each rice sample with different intensities. For the sweetness, there were five intensities corresponding to 1-5 points, the higher intensity the higher score. For the sourness and astringency, there were three intensities corresponding to 1-3 points, the higher intensity the higher score. The sensory score (SSc) of sweetness, sourness, astringency was calculated as the average score of eight scores from panelists for each rice sample.

2.6. Data processing

2.6.1. Continuous wavelet transform

Continuous wavelet transform (CWT) has been widely used in signal denoising and resolution of overlapping peaks [16,17]. The simple expression of the wavelet function [18] is as followed:

$$\psi(t) = (1 - t^2)\exp(-\frac{t^2}{2})$$

In case of *f(t)* as a one-dimensional discrete signal composed of 1 to n, CWT of *f(t)* is its projection on Mexican hat wavelet:

$$W_f(a,b) = \frac{1}{\sqrt{a}}\int_{-\infty}^{+\infty} f(t)\psi(\frac{t-b}{a})dt$$

Where a is the scale value; b is the translation factor. In the stationary scale, each coefficient value $W_f(a, b)$ of b from 1 to n can be calculated. The coefficients of a certain scale can be plotted into a curve i.e. CWT coefficient curve from which useful information about the original signal can be caught.

In this study, original voltammetric signal of sample was transformed to CWT coefficient curves. The continuous wavelet coefficients were obtained in the oxidation and reduction processes of voltammetric signal, that is, one original signal can be converted into two CWT coefficient curves.

2.6.2. Extraction of feature value

All extreme points (maximum points and minimum points) from CWT coefficient curve of each electrode were taken as characteristic points. Each characteristic point had potential value (p) and current value (c). The characteristic points of one curve were arranged into a group of values (p1, c1, p2, c2,...) from -1V to 1V in order of Pt, Au, Pd, Ag, Ni, Ti electrode. Two group of values from two CWT coefficient curves of each sample were combined into a set of feature values.

2.6.3. Neural network algorithm

Artificial neural network simulates biological neural network, which is an adaptive non-linear dynamic system composed of a large number of neurons. Each neuron unit has a certain number of real input and produces a single real output. Back Propagation neural network (BpNN) model was applied in this study. During training, the activation function of hidden layer and the transfer function of output layer were Tansig and Purelin functions, respectively. The other parameters were as followed: the maximum epoch of training was 500, the goal of training precision was 0, and the minimum gradient was 1e-5. The variable gradient algorithm function Trainglm was used as the training function, and the gradient descent threshold with momentum factor function Learngdm was used as the learning function. In this study, the input variables of BpNN model were feature values of stimuli mixtures, and the target variables were the concentrations of each stimulus in the mixture.

Each gustatory value of rice sample was obtained by converting the predicted concentration of corresponding stimulus via BpNN model into the value according to recognition threshold, which was recorded as *LZ*. The formula is as followed:

$$LZ = \frac{Cp}{Rt}$$

Where *Cp* is the predicted concentration; *Rt* is the corresponding recognition threshold.

2.6.4. Accuracy calculation of prediction

The predicted concentration of each stimulus in the mixture was compared with the actual concentration. For the concentration of signal stimulus, when the relative error (Re) is less than 5%, the prediction is correct, or when the actual concentration is 0, the prediction is not more than 0.5. When the concentrations of all stimuli in the mixture are predicted correctly, the prediction of the mixture is correct, of which the ratio is the accuracy A.

$$\mathrm{Re} = \frac{|Cp - Cr|}{Cr} \times 100\%$$

$$A = \frac{Ntr}{N} \times 100\%$$

Where *Cp* is the predicted concentration; *Cr* is the actual concentration; *Ntr* is the correct number of stimuli mixture; *N* is the total number of stimuli mixture.

3. RESULTS AND DISCUSSION

3.1. Chemical analysis and sensory evaluation

Chemical analyses for rice samples were launched for the confirmation of dominant component leading to the sweetness, sourness and astringency through the comparison with sensory evaluation. The contents of sucrose, glucose, fructose and maltose in all rice samples were in the range of 0.315%-0.701%, 0.032%-0.201%, 0.0031%-0.0102%, 0.004%-0.094% respectively. For each sample, the content of sucrose was the highest than glucose, fructose and maltose, and fructose was the lowest, which was 10^{-3} times lower than sucrose. The comparison of the contents of soluble sugars and SScs from sensory evaluation was shown in Fig.1.

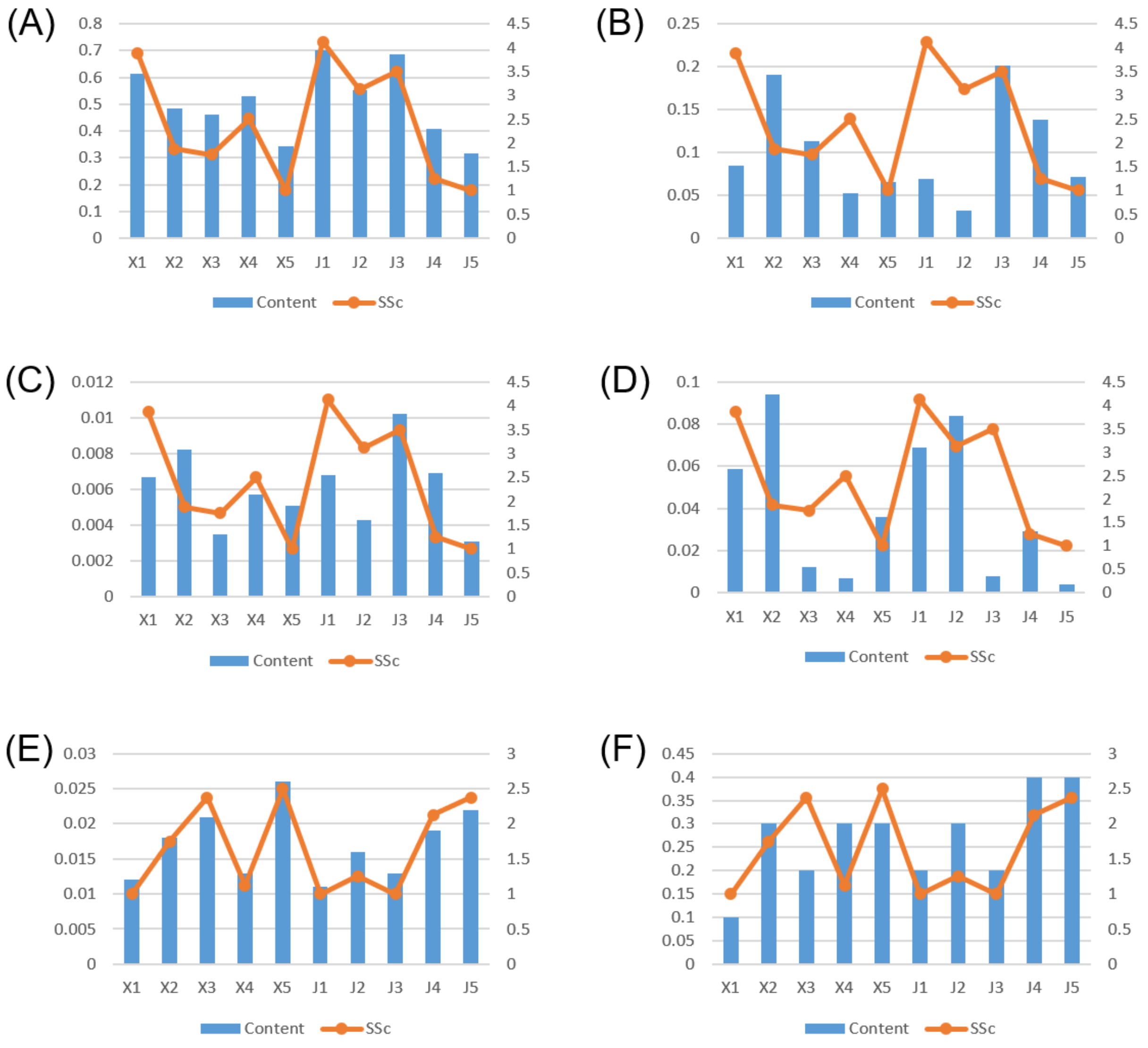

Figure 1. The comparison of the contents of soluble sugars, acidity, fat and SScs from sensory evaluation. (A) sucrose; (B) glucose; (C) fructose; (D) maltose; (E) acidity; (E) fat.

The tendency of sucrose was closest to that of sweetness, and obvious similarity could not be displayed for other three sugars. Soluble sugar contributes most to the sweetness of rice. Sucrose is the temporary storage form of photosynthesis products in leaves, and also the output form of assimilates between plant tissues and organs [24]. Moreover, fructose is a major component of carbohydrate hydrolysis, which can provide energy [25]. The content of sucrose in most samples exceeded its recognition threshold, however, glucose and maltose had the lower sweetness grades which cause to higher recognition thresholds. Owing the highest sweetness grade, fructose had super low content so that it could not contribute to the sweetness of rice. Therefore, the sucrose was the dominant component leading to the sweetness of rice, and selected as the taste stimulus for sensing the sweetness.

Table 2. Sensory scores and gustatory values of the sweetness, sourness, astringency of all rice samples.

Sample number	Sensory score (SSc)			Gustatory value		
	Sweetness	Sourness	Astringency	Sweetness	Sourness	Astringency
X1	3.875	1.000	1.125	1.3	0.5	0.3
X2	1.875	1.750	1.250	1.2	0.7	0.2
X3	1.750	2.375	2.750	1.0	1.1	1.2
X4	2.500	1.125	1.000	1.2	0.5	0.0
X5	1.000	2.500	1.500	0.9	1.5	0.1
J1	4.125	1.000	1.000	1.7	0.5	0.1
J2	3.125	1.250	1.000	1.3	0.5	0.2
J3	3.500	1.000	1.250	1.6	0.4	0.1
J4	1.250	2.125	2.250	0.8	0.9	1.1
J5	1.000	2.375	1.250	0.7	1.2	0.0

As for the SSc of the sourness (Table 2), X5 had the highest, followed by X3, J5, and X1, J1, J3 had the lowest. The acidity values had the difference among rice samples, which showed the similar pattern to sensory evaluation in Fig.1. But there was only a little difference for fat contents of all samples, and no tendency was present, so it was resulted that the acidity mainly contributes to the sourness of rice. Though the acidity of rice may be caused by hydrogen ions from fatty acid, citric acid was the alternative taste stimulus due to the complexity of fatty acid. For the astringency, X4, J1, J2 had the lowest SSc, followed by X1 and J5, and X3, J4 had high SSc. Except for X3 and J4, the content of tannic acid in the rest samples was in the range of 0.011%-0.029%, which was under its recognition threshold. Analogously, the SScs of astringency of X3 and J4 were high, and that of the rest samples were all lower than 1.5. Tannic acid was considered as the dominant component for the astringency.

3.2. Signal processing and feature extraction

The comparison of original CV signals from Pt electrode towards citric acid and corresponding CWT coefficient curves in different scales was present in Fig.2. No significant peak appeared in oxidation and reduction curve of CV, illustrating that original voltammetric response of stimulus at the concentration as low as recognition threshold was weak. Signal processing and enhancement access to feature data were needed in order to close to tongue perception, thus transformation of original voltammetric response was utilized in this study. CWT possessing the advantage in signal decomposition compared to traditional transform [19,20] can obtain the coefficients which correspond to the original data. The absolute position of peak in CWT changes little when the appropriate wavelet basis is chosen.

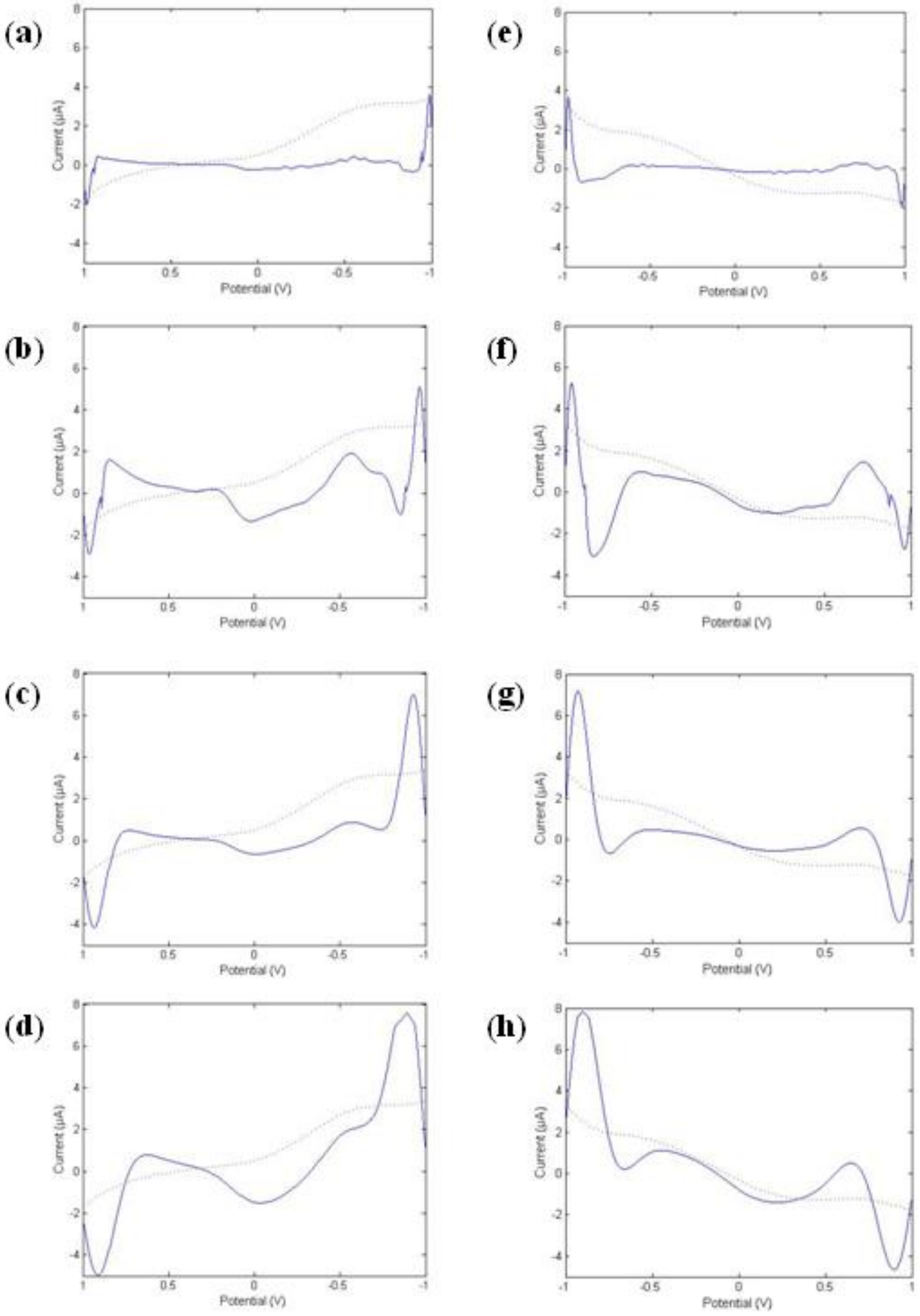

Figure 2. The comparison of original CV signals (dashed curves) from Pt electrode towards citric acid at 0.25mM and corresponding CWT coefficient curves (solid curves) in different scales (a, e - scale 4; b, f - scale 8; c, g - scale 16; d, h-scale 24) for the reduction (a～d) and the oxidation part (e～h).

In CWT, scale value determines the degree of compression or stretching for the wavelet. Low scale value compresses the wavelet and correlate with high frequency, and high scale value stretches it and correlate with low frequency. The high and low scale for CWT coefficient respectively performs their coarse-scale and fine-scale features in the input signal vector. The scale of CWT affects the separation degree and position recognition of signal [21], which can be selected by observing the curve. The front and the end pseudo peak of CWT coefficient curve shown in Fig.2 were not considered, causing by boundary effect of the wavelet transform [18]. In the low scale, the coefficient curve changes little, of which baseline oscillation is fierce in the high scale. As observed, the curves in the scale of 4 were similar to horizontal baselines without obvious peaks or points, and in the scale of 16, 24 distorted seriously leading to the cover of weak signal peak. Thus, the scale of 8 was selected because of stable baseline, high resolution and significant signal peak. Similarly, feature values of all stimuli mixtures were extracted from CWT coefficient curves in the scale of 8.

3.3. Establishment of one-component model

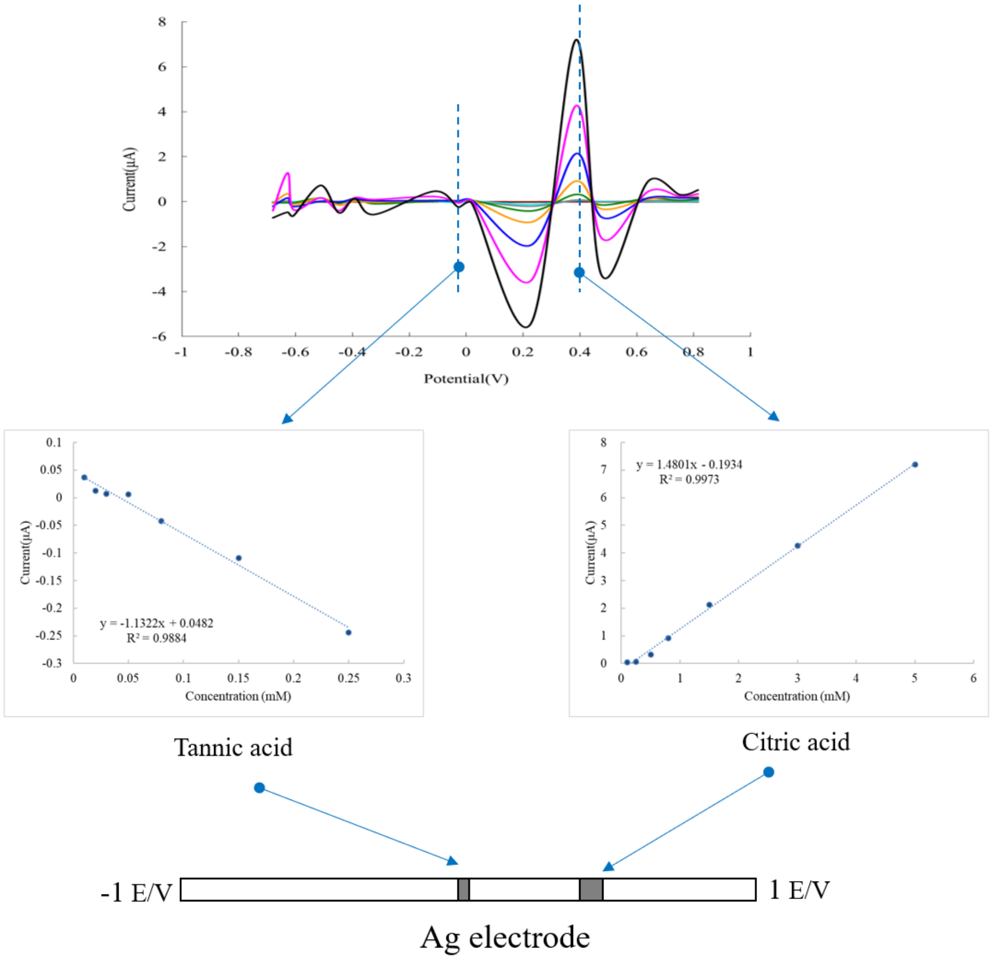

Figure 3. The process of obtaining linear sensing areas in Ag electrode.

Each electrode in the sensor determined a series of single taste stimulus with gradient concentration, and linear regression was used to investigate the applicability of the sensor. For tannic acid at different concentrations, the current values of certain characteristic points from CWT coefficients curve measured by Pt, Ag, Ni, Ti electrode respectively showed a linear trend. The similarity occurred in the determination of other taste stimuli with different electrodes. Good correlation coefficient exceeded 0.95 was achieved via linear regression made between the current value of characteristic point and corresponding concentration, which was the index of linear sensing area for taste stimulus. Six electrodes have different linear sensing areas located at potential: Pt: -0.790±0.042V for sucrose, -0.320±0.042 V for tannic acid; Au: 0.110±0.029V for sucrose; Pd: 0.185±0.012V for citric acid; Ag (Fig.3): -0.020±0.011V for tannic acid, 0.400±0.051V for citric acid; Ni: 0.220±0.026V for citric acid, 0.820±0.066V for tannic acid; Ti: 0.690±0.036V for tannic acid. Compared to the previous study [23], these linear sensing areas in this study were similar to the response areas on former metal sensor. It was indicated that the sensor with multi-metal electrodes could be applied for the quantification of taste stimulus, and feature values embodies the linear information for establishing a taste model.

The input variables of one-component (OC) model were feature values of 54 taste stimuli mixtures, which were used to train the OC model using BpNN and also to verify its predictive ability. The accuracy of the model was 81.5%, revealing that the established model had good ability of prediction for gustatory value. Besides, the high accuracy confirmed that linear and nonlinear data coexisted in the feature value for taste quantification.

3.4. Correlation of taste prediction and sensory evaluation

For the prediction of OC model for rice sample, the feature values of samples were used as input variables for the model to obtain the gustatory values of sweetness, sourness, astringency (Table 2). The results showed that J1 had the highest sweetness, followed by J3; J3 had the highest sourness but the lowest astringency, both of X3 were high; except for X3 and J4, the astringency of the rest was not evident. It was demonstrated that the predictive ability of the OC model was greater than sensory ability of human because of the gustatory values lower than recognition threshold.

Correlation of taste prediction and sensory evaluation for rice was analyzed by the linear regression between gustatory values and SScs of sweetness, sourness, astringency. The slopes, intercepts and correlation coefficients were calculated for the linear regression. It had been reported that the correlation coefficient and the slope of the optimum model should be close to 1, and the intercept close to 0 [22]. Good correlation coefficients ($R > 0.9$) were achieved for all taste, as seen in Fig.4, indicating that the prediction of model was equivalent to the result of sensory evaluation. Consequently, one-component model approach could be ultimately developed for quantitatively sensing the sweetness, sourness, astringency of rice.

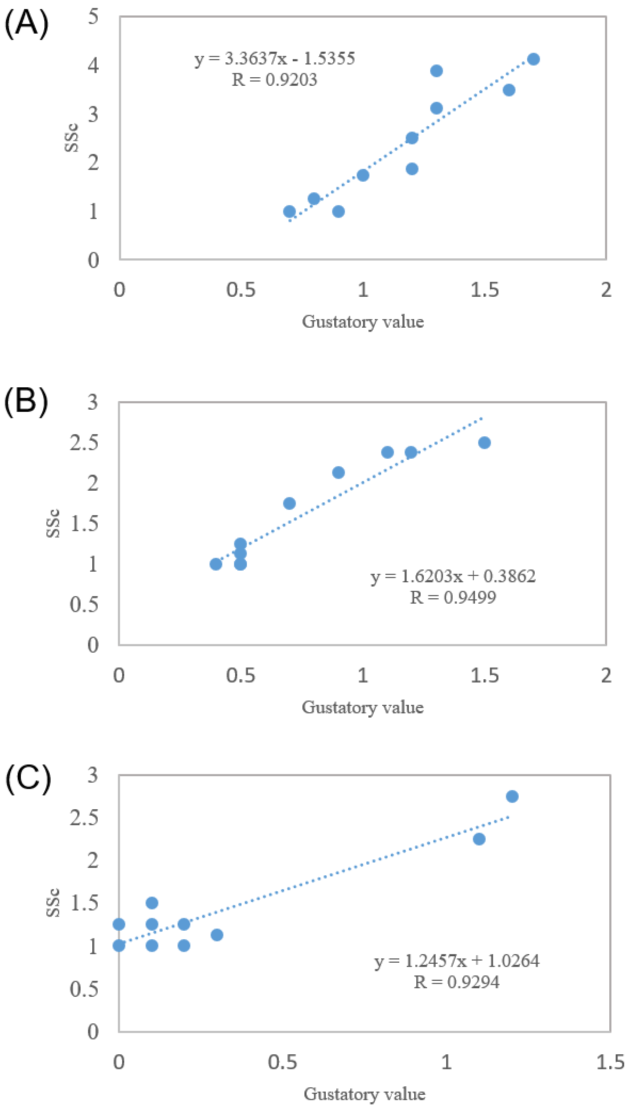

Figure 4. The linear regression between gustatory values and SScs of sweetness (A), sourness (B), astringency (C).

4. CONCLUSION

In this paper, the sweetness, sourness and astringency of rice were determined via sensor measurement, sensory evaluation and chemical analysis. The chemical indexes such as soluble sugars, acidity, fat, and tannic acid in rice were analyzed. The sensory scores of rice samples were obtained by sensory evaluation. The comparison of chemical index and SSc of rice was launched, confirming that dominant components for sweetness, sourness and astringency were sucrose, acidity and tannic acid respectively. The original voltammetric signal of stimulus was transformed by CWT in which the feature value was extracted. Neural network algorithm was used to establish the OC model with feature values of stimuli mixtures, and its high accuracy confirmed the effectiveness of the model. The gustatory values of rice samples were successfully predicted. The correlation analysis between sensory score and gustatory value was applied to clarity the ability of one-component model approach. It was concluded that the developed approach could accurately sense the sweetness, sourness and astringency of rice.

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