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An Electronic Nose Technology to Quantify Pyrethroid Pesticide Contamination in Tea

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Abstract: The contamination of tea with toxic pesticides is a major concern. Additionally, because of improved detection methods, importers are increasingly rejecting contaminated teas. Here, we describe an electronic nose technique for the rapid detection of pyrethroid pesticides (cyhalothrin, bifenthrin, and fenpropathrin) in tea. Using a PEN 3 electronic nose, the text screened a group of metal oxide sensors and determined that four of them (W5S, W1S, W1W, and W2W) are suitable for the detection of the same pyrethroid pesticide in different concentrations and five of them (W5S, W1S, W1W, W2W, and W2S) are suitable for the detection of pyrethroid pesticide. The models for the determination of cyhalothrin, bifenthrin, and fenpropathrin are established by PLS method. Next, using back propagation (BP) neural network technology, we developed a three-hidden-layer model and a two-hidden-layer model to differentiate among the three pesticides. The accuracy of the three models is 96%, 92%, and 88%, respectively. The recognition accuracies of the three-hidden-layer BP neural network pattern and two-hidden-layer BP neural network pattern are 98.75% and 97.08%, respectively. Our electronic nose system accurately detected and quantified pyrethroid pesticides in tea leaves. We propose that this tool is now ready for practical application in the tea industry.

Keywords: electronic nose; tea; pyrethroid pesticide; BP neural network technique

1. Introduction

Awareness of the importance of food safety is growing [1–3]. In China, the contamination of tea with toxic pesticides has become a major concern. Additionally, improved methods for the detection of these contaminants have enabled increased testing [4], the stringency of tests, and the rejection of contaminated foods by importers. As the world's largest producer of tea leaves, exporting ~3 million tons annually, Chinese producers and authorities should be focused on avoiding tea leaf contamination [5]. However, this problem has been largely ignored [6–9].

Among the pesticides applied to tea crops, pyrethroids are widely used to control smaller green leafhopper, blackthorn whitefly, and aphid pests [10,11]. Gas chromatography (GC), high-performance liquid chromatography (HPLC), and ultra-high-performance liquid chromatography-tandem mass spectrometry are typically used for the detection of pyrethroids contamination in tea products [12–16]. However, these methods are expensive and technically challenging, and therefore are not widely applied.

Electronic nose methods are bionic detection methods that simulate biological olfactory systems. Following further development, these methods are now regarded as fast, simple, and cheap approaches, and they are being adopted in food quality and safety settings, principally in the detection of agricultural residues in fruits and vegetables [17–20]. Electronic nose methods have not yet been applied to the discovery of pesticide residues in tea.

Here, we investigate the possibility of using electronic nose technology to detect pyrethroid pesticides contamination in tea. We propose an easy-to-use electronic nose system that can detect, differentiate, and quantify three pyrethroid pesticides (cyhalothrin, bifenthrin, and fenpropathrin), which we believe is now ready for industry use.

2. Materials and Methods

2.1. Test Materials

The raw materials of tea tree for test were from antaishan agricultural Co., Ltd. of Taian City, Shandong Province. The samples used in the experiment were fresh tea leaves with one bud and two leaves, which had not been previously sprayed with pesticides. These samples were sprayed with cyhalothrin (2.5% effective content, Nuopuxin Agrochemical Co., Ltd., Shenzhen, China.), bifenthrin (10% effective content, Langfang Pesticide Pilot Plant of the Plant Protection Institute of Chinese Academy of Agricultural Sciences, Langfang, China.), or fenpropathrin (20% effective content, Meilan Agricultural Development Co., Ltd., Haikou, China.). The electronic nose tests were performed immediately after spraying.

2.2. Selection and Optimization of the Electronic Nose Sensor

In the test, the spraying concentration was the maximum residue limit concentration of pesticides in tea, as specified in the three national drug standards (GB 2763-2019) [21]. To test the convenience and accuracy of sampling, this test used a quantitative sampling method, where 3 mL of pesticide was sprayed onto 5 g of tea samples at a time. The erlenmeyer flask was placed in an oven for drying before the start of the test. The drying temperature was 120 degrees, and the drying time was 30 mins. After drying, the absorbent paper and Na_2CO_3 (use after drying) were put in the bottle to absorb the water in the bottle. Immediately after picking, the tea samples were placed in a conical flask and sealed with tin foil, and the gas detection analysis was performed using the PEN3 portable bionic electronic nose system (PEN3, Airsense Analytics GmbH, Schwerin, Germany) by headspace aspiration method.

In reference [22], sample quality was controlled at (5.0 ± 1.0) g, the volume of gas collector was 50 mL, headspace preheating temperature was 30°C, headspace time was 30 min, electronic nose detection parameters were sensor cleaning time of 100s, automatic zero setting time was 10 s, sample preparation time was 5 s, sample determination interval time was 1s, internal flow rate was 300 mL/min, and injection flow rate was 300 mL/min. The method described in reference [22] with the parameters of the headspace aspiration method modified was used: the headspace time was 10 min, the volume of the container was 50 mL, and the headspace temperature was 25 °C. The laboratory temperature was about 25°C, the humidity was about 50%, and the atmospheric pressure was 101.325 kpa. The electronic nose detection parameters were sensor cleaning time, 120 s; auto-zero time, 10 s; sample preparation time, 5 s; sample measurement interval, 1 s; internal flow, 300 mL/min; injection flow, 300 mL/min; measurement time, 150 s; and the signal at 145–147 s was used as the time point for sensor signal analysis. The sensor was cleaned and standardized before and after each measurement. Screening and optimization of sensors were performed using load-loading analysis.

2.3. Test Design

As the standards, we used the maximum pesticide residue limit for tea pesticides specified in the national standard [21], and four treatments were set for each pesticide. Cyhalothrin was set at 5, 15, 30, and 60 mg/kg, and bifenthrin and fenpropathrin were set at 2, 5, 10, and 20 mg/kg. Distilled water was

used as the control group. Samples were measured using the PEN3 electronic nose system, and each group was repeated five times.

2.4. Data Extraction, Processing, and Model Establishment

2.4.1. Extraction of Data Eigenvalues of the Electronic Nose Sensor

The following electronic nose sensor response value expression method was used: $R_i = G/G_0$, where R_i was the signal ratio of the i-th sensor input, G was the resistance (Ω) of the sensor after contacting the sample volatiles, and G_0 was the resistance of the sensor in zero gas (the gas was filtered by standard activated carbon) (Ω).

2.4.2. Data Processing

Loading analysis (LA) was done using the Winmuster software for electronic nose systems. SPSS 16.0 software was used to perform the Principal Component Analysis (PCA) of the optimized sensor response characteristic values, and a Partial Least Squares Regression Algorithm (PLS) was used to establish a prediction model for the concentration of pyrethroids and pesticides. One-way ANOVA analysis by LSD method and t-tests were applied. The BP neural network technology was used to distinguish the types of pyrethroid pesticides.

2.4.3. Model Establishment and Verification

Four concentration gradients were used for each pesticide category, five samples were selected for each concentration gradient, and five samples were selected for the control group (so that 25 samples were used to establish multiple concentration prediction models for the same pyrethroid pesticide). Additionally, 25 samples were randomly selected to verify the correctness of the model. SPSS 16.0 software was used to establish a linear regression model for the concentration gradient discrimination of the same pesticide. By comparing the predicted value of the model with the measured value, we were able to establish the accuracy of the prediction model.

3. Results

3.1. Optimization of the Electronic Nose Sensor

There were 10 metal oxide sensors in the PEN3 electronic nose (designated as W1C, W5S, W3C, W6S, W5C, W1S, W1W, W2S, W2W, and W3S) (Table 1). Loading analysis (LA) was used to investigate the effect of sensors on the spatial distribution of the PCA data, and the sensors' pesticide distinguishing abilities were determined. Generally, the farther the coordinate value of a sensor was from the origin (0,0), the larger the contribution it had [22]. In LA analysis of three kinds of single pesticides, W5S, W1S, W1W, and W2W sensors were far from the origin, followed by the W2S sensor, while W1C, W3C, W6S, W5C, and W3S sensors were close to the origin (Figure 1a–d). According to the LA analysis, the W5S, W1S, W1W, and W2W sensors made a substantial contribution to the concentration gradient differentiation of cyhalothrin, bifenthrin, and fenpropathrin (Figure 1a–c).

To further verify the accuracy of these sensors, four sensors were used to analyze three pesticides at various concentrations. The W5S, W1S, W1W, and W2W sensors could effectively distinguish the different types and levels of pesticide (Figure 2a–c). Based on this data, we propose that the sensors W5S, W1S, W1W, and W2W could be used as an metal oxide sensor array for concentration discrimination.

Table 1. Sensor sensitivities of the PEN3 e-nose.

Sensor Name	Performance Description
W1C	Sensitive to aromatic compounds
W5S	Very sensitive to oxynitride
W3C	Sensitive to ammonia and aromatic compounds such as benzene
W6S	Sensitive to hydrogen
W5C	Sensitive to alkane such as propane and aromatic compounds
W1S	Sensitive to methane
W1W	Sensitive to sulfur compounds such as hydrogen sulfide
W2S	Sensitive to alcohols and aldehydes and ketones
W2W	Sensitive to aromatic compounds and organic sulfur compounds
W3S	Sensitive to alkane such as methane

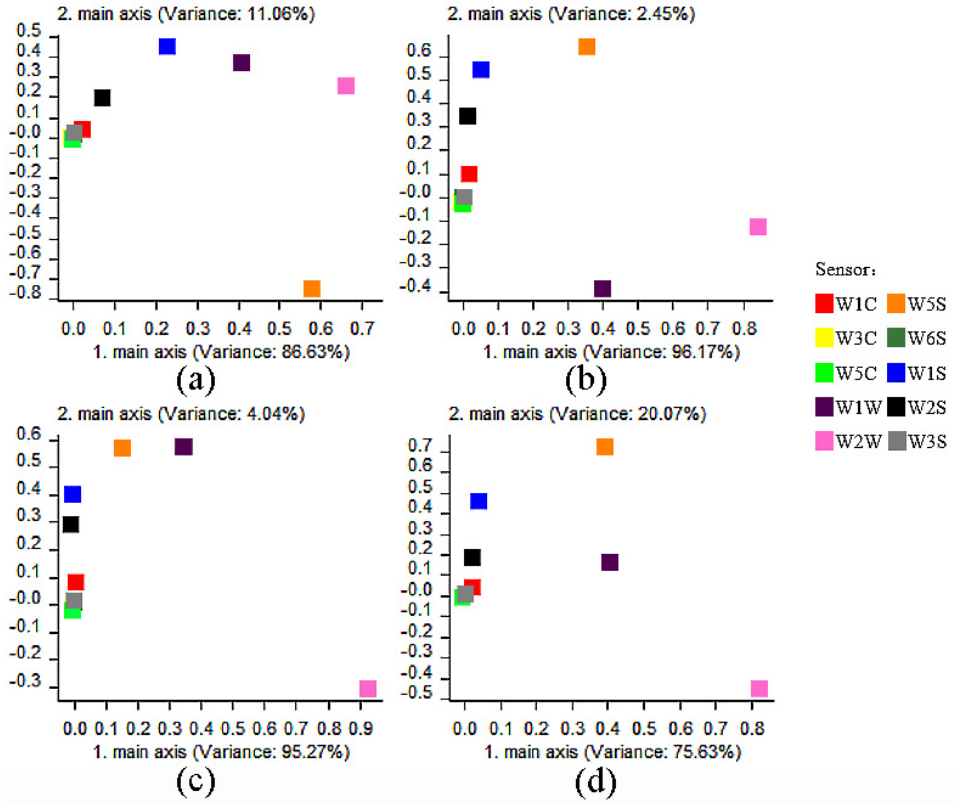

Figure 1. Loadings analysis (LA) of 10 sensors for different kinds of pesticides. (**a**–**d**) are the load loading analysis of three pyrethroids, i.e., cyhalothrin, bifenthrin, fenpropathrin, and mixture.

Regarding the classification of the three tested pesticides, the sensors W5S, W1S, W1W, and W2W had a larger contribution rate (Figure 1d). To increase the recognition of the sensor, the sensor W2S was added to the observation to distinguish the mixed types. Using PCA analysis to verify the performance of the sensor array, it was found that the overlap area of bifenthrin and fenpropathrin after adding the sensor W2S (Figure 2d) was smaller than that without adding (Figure 2e). Therefore, sensors W5S, W1S, W1W, W2S, and W2W were selected as the sensor arrays for the mixed types.

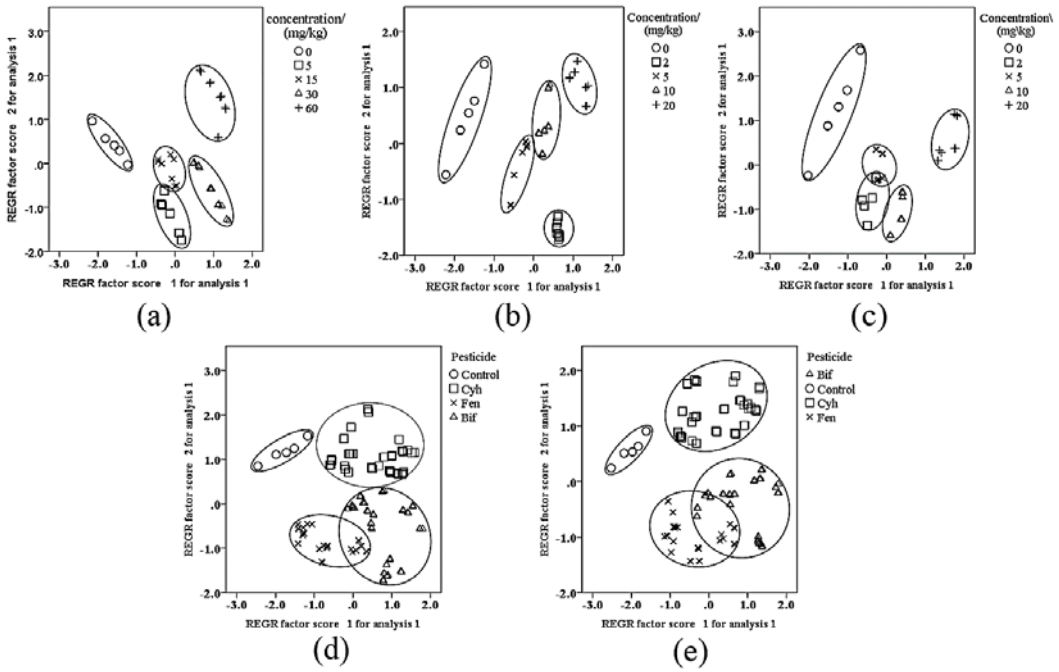

Figure 2. Principal component analysis (PCA) of odor data of electronic nose at 145-147s. This figure is the principal component analysis of the odor data of electronic nose at 145-147s. (**a**–**c**) are PCA analysis charts of cyhalothrin, bifenthrin, and fenpropathrin, respectively. (**d**) is PCA analysis diagram of pyrethroid pesticide types with sensors W5S, W1S, W1W, W2S, and W2W as main sensors. (**e**) is PCA analysis diagram of pyrethroid pesticide types with sensors W5S, W1S, W1W, and W2W as main sensors. Control group with distilled water instead of pesticide, Cyh—Cyhalothrin, Fen—Fenpropathrin, and Bif—Bifenthrin.

3.2. Establishment of A Concentration Prediction Model of Pyrethroids

Those sensors with larger response values (W5S, W1S, W1W, and W2W) were selected, and a prediction model of different concentration gradients of the same pesticide was established by the partial least square method (PLS).

Model I (Cyhalothrin): $Y_1 = -10.361 + 4.214\ G/G_{0\ W5S} - 2.951\ G/G_{0\ W1S} + 0.58\ G/G_{0\ W1W} + 1.15\ G/G_{0\ W2W}$

Model II (Bifenthrin): $Y_2 = -2.459 + 0.038 G/G_{0\ W5S} + 2.351 G/G_{0\ W1S} - 4.271 G/G_{0\ W1W} + 2.364 G/G_{0\ W2W}$

Model III (Fenpropathrin): $Y_3 = -5.3.74 + 3.462 G/G_{0\ W5S} - 2.423 G/G_{0\ W1S} + 1.386 G/G_{0\ W1W} - 0.334 G/G_{0\ W2W}$

In the formula, $G/G_{0\ W5S}$, $G/G_{0\ W1S}$, $G/G_{0\ W1W}$, and $G/G_{0\ W2W}$ represent the signal response values of the W5S, W1S, W1W, and W2W sensors at the detection time of 145–147 s, respectively. Bringing the sensor response value into the above formula, the Y value obtained was judged as the specific concentration of the pyrethroid pesticide. By Anova, the p-values of models I, II, and III were all less than 0.001 (Table 2), indicating that the PLS regression models were extremely significant.

Table 2. Analysis of variance of concentration prediction model of pyrethroids. Model I—Cyhalothrin; Model II—Bifenthrin; Model III—Fenpropathrin.

Prediction Model	Item	Square Sum	df	Mean Square	F	P
Model I	Regression	34268.483	4	8567.121	879.946	0.000
	Residue	681.517	70	9.736		
	Total	34950.000	74			
Model II	Regression	3741.735	4	935.434	759.061	0.000
	Residue	86.265	70	1.232		
	Total	3828.000	74			
Model III	Regression	3765.806	4	941.451	1059.609	0.000
	Residue	62.194	70	0.888		
	Total	3828.000	74			

3.3. Validation of the Content Prediction Model

The accuracies of models I, II, and III were verified using 25 samples of the same pesticide at different concentrations (Table 3). The accuracies of the three models were 96%, 92%, and 88%, respectively. These data show that the model could accurately predict the concentration of pyrethroid pesticide residues in tea leaves.

Table 3. Validation of the prediction model of tea pyrethroid pesticide content. Model I—Cyhalothrin; Model II—Bifenthrin; Model III—Fenpropathrin. * Means greater difference between the predicted and measured values.

Sample	ModelI (Cyhalothrin)	ModelII (Bifenthrin)	ModelIII (Fenpropathrin)	Actual Concentration (Model I\II\III)
1	−0.29	0.54	−0.78	0\0\0
2	0.77	−0.23	0.51	0\0\0
3	0.72	−0.32	0.50	0\0\0
4	−0.253	2.34 *	−0.53	0\0\0
5	0.723	−0.47	−0.44	0\0\0
6	3.25	2.33	−0.05 *	5\2\2
7	3.78	2.54	1.56	5\2\2
8	3.56	2.13	2.54	5\2\2
9	6.08	2.57	2.41	5\2\2
10	4.47	2.33	2.62	5\2\2
11	15.62	4.32	5.24	15\5\5
12	15.50	6.45	4.74	15\5\5
13	15.03	5.87	8.32 *	15\5\5
14	15.59	5.38	6.12	15\5\5
15	14.52	4.76	5.98	15\5\5
16	31.83	7.22 *	10.73	30\10\10
17	31.79	10.04	10.98	30\10\10
18	30.93	9.61	12.04 *	30\10\10
19	29.33	9.76	9.17	30\10\10
20	29.68	9.95	9.03	30\10\10
21	61.99	20.33	19.25	60\20\20
22	60.67	19.44	20.97	60\20\20
23	60.93	20.27	20.82	60\20\20
24	63.13 *	19.98	19.70	60\20\20
25	60.11	19.15	19.59	60\20\20
Accuracy rate:	96%	92%	88%	\

3.4. Identification of Pesticides by BP Neural Network

The response values of the five characteristic sensors (W5S, W1S, W1W, W2S, and W2W) were used as the eigenvectors of the BP network. The three-hidden-layer BP neural networks of 6-10-10-10-4 (Figure 3a) and the two-hidden-layer BP neural networks of 6-10-10-4 (Figure 3b) were constructed. The topological structure is shown in Figure 3.

Each processing sample extracts 50 sample feature parameters to normalize the principal component data of sample features. Cross-stored input variables X6 × 200 were used as inputs for three different networks (the sample data of each variety were stored into the input variable X, one by one), and the output variable Y4 × 200 was the variety of the sample corresponding to the input variable X. The network was trained using the momentum descent method and the adaptive learning rate gradient descent method. After 10,000 loop iterations, the characteristic data obtained from the analysis were used to test the trained BP neural network. There was no misrecognition event in the untrained samples in two different BP neural network models, and the number of misrecognition events of training samples when using the three-hidden-layer model was less than that with the two-hidden-layer model (Table 4). Therefore, the method performed the best at the identification of three pyrethroid pesticides.

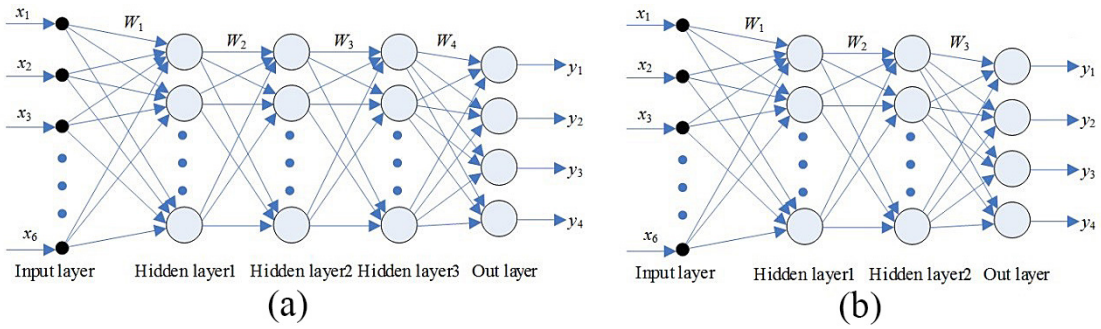

Figure 3. Back propogation (BP) neural network structure diagram. (**a**) is the three-hidden-layer BP neural network pattern structure diagram and (**b**) is the two-hidden-layer BP neural network pattern structure diagram.

Table 4. Neural network recognition of three kinds of pyrethroid pesticides.

BP Neural Network Model	Amount of Samples	Number of Training Samples	Number of Untrained Samples	Number of Training Sample Error Recognition	Number of Untrained Sample Error Recognition	Recognition Accuracy/%
Three-hidden-layer	240	200	40	3	0	98.75
Two-hidden-layer	240	200	40	7	0	97.08

4. Discussion

So far, electronic nose methods have been mostly limited to the detection of organic phosphorus pesticides [17–19] and organic chloride pesticides [20] in fruits and vegetables, achieving detection rates of 80–100%.

Here, we describe an electronic nose system to detect contaminating pyrethroid pesticides in tea leaves. The detection data were analyzed using PCA and BP neural networks, and models were developed to quantify and differentiate among the pyrethroid pesticides. By this approach, optimized electronic nose sensor system could accurately quantify the levels of cyhalothrin, bifenthrin, and fenpropathrin contamination (success rates of 96%, 92%, and 88%) and differentiate among these three pyrethroids (success rates of 98.75% and 97.08% when using three-hidden-layer and two-hidden-layer models, respectively).

During optimization of the electronic nose system, we identified four sensors (designated as W5S, W1S, W1W, and W2W) with higher response values for cyhalothrin, bifenthrin, and fenpropathrin.

Although, according to the loading analysis, the characteristic response values of the sensors W2S were all around 0.2–0.3, and the response values were small. However, in the PCA chart without the W2S sensor, the overlap area of bifenthrin and fenpropathrin was larger than that added, so the sensors W5S, W1S, W1W, W2S, and W2W were selected as the primary sensors for better discrimination (Figure 2).

The analysis of the data from the sensor array was divided into two steps: feature extraction and model classification. The feature extraction step describes the entire evolution of the sensor response signal, thus obtaining detailed information about the test sample. The second step relies on classification modeling, an approach that allows robust and reliable inferences to be made for the characteristics of the measured samples [23,24]. However, the current analysis of the latest sensor array data was still not in the created model maintain universality and plasticity [25]. Because the model was strictly related to the sensor, it needed to be replaced or added to the existing primary sensor array [26] for calibration [27]. Therefore, the W2S sensor was selected as one of the primary sensors for the discrimination test of pyrethroid pesticides in this test.

Tea is rich in aromatic substances [28], with more than 80 kinds of volatile aroma substances in fresh tea leaves [29]. Additionally, after picking and spreading, the aromatic substances in tea leaves transform continuously [30–33]. These naturally occurring volatile aroma substances in tea leaves might interfere with the detection of contaminating pesticides by an electronic nose. Furthermore, current electronic nose systems are susceptible to interference from changes in ambient temperature, humidity, and atmospheric pressure [34]. In this test, the temperature, humidity, and atmospheric pressure of the laboratory were controlled at 25 °C, 50%, and 101.325 kpa, respectively. The picked fresh leaves were tested immediately after treatment to shorten the in vitro time, in order to reduce the interference of fresh leaf odor and environmental changes on the sample.

Therefore, in future work, we intend to test fresh tea leaves using multiple spreading times, analyze the influence of aroma components of fresh leaves on pesticide detection, further optimize the sensor detection system, shorten the measurement time difference between samples, and improve the efficiency of the electronic nose test. These further works will enhance the stability and accuracy of electronic nose technology in tea residue detection. Additionally, we will expand the scope of testing, increase the number of pesticides tested, and use our electronic nose technology to establish a traceability system for pesticide residues in tea.

5. Conclusions

Here, we describe an easy-to-use electronic nose system that can detect, differentiate, and quantify pyrethroid pesticides, which we believe is now ready for industry use. This system is based on four sensors (designated as W5S, W1S, W1W, and W2W) and could quantify cyhalothrin, bifenthrin, and fenpropathrin concentrations, achieving success rates of 96%, 92%, and 88%. Based on five sensors (W5S, W1S, W1W, W2W, and W2S), the BP neural network recognition technology was used to identify the three pesticides. The newly developed three-hidden-layer model and two-hidden-layer model were used to identify the three pesticides, with accuracies of 98.75% and 97.08%, respectively.

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