Prediction of food additives based on grey prediction model and electrochemical analysis of gallic acid

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Abstract. In this paper, a grey prediction model was used to predict the future consumption of food additives, and then an electrochemical analysis method was combined to focus on the detection of food additives as an example of gallic acid, and to optimize the conditions that may affect the detection results. A series of standard curves describing the concentration of gallic acid (0.0005 μM - 200 μM) were obtained under optimal detection conditions. This study constructs a sensitive, short time-consuming and easy-to-operate assay system for the detection of gallic acid in food additives by electrochemical analysis, and provides a potential method for the quantitative determination of gallic acid in food additives in the future.

Keywords: Electrochemistry, Food additives, Gallic acid, grey prediction model.

1. Introduction

Nowadays, the search and development of food additive detection techniques that are both accurate, efficient and easy to use to ensure food safety is one of the most important future studies in the field of food science and engineering [1]. A food additive is a chemically synthesized or natural substance added to improve the quality, color and flavor of food, for preservative and processing purposes [2]. Under national standards, the use of food additives in the prescribed dosage and within the prescribed range can bring convenience and well-being to society. However, some unscrupulous businesses add food additives in excess of the dose and scope in food products circulating in the market for economic and other benefits. For example, sweetener in sorghum wine sold by Rice Wine Workshop in Northern Hunan was tested to exceed the standard, and aluminum residues in homemade doughnuts processed in Chuzhou City restaurant exceeded the national standard for food safety [3]. This can lead to excessive enrichment of additives within food, which ultimately poses a great safety risk to humans located at the top of the food chain and seriously endangers the lives and health of the general population [4]. Therefore, it is urgent to innovate and design a convenient and efficient low-cost method to detect food additives in the food market.

Currently, the methods used for the detection of food additives include liquid chromatography, UV-visible spectrophotometry, gas chromatography, ion chromatography, and atomic absorption spectrometry [5]. Although these methods can perform accurate and reproducible measurements to some extent, they also suffer from cumbersome sample pretreatment, lengthy testing time, complicated operational procedures, incomplete extraction and poor target recovery for multiple types and complex compositions of samples. In addition, most of these assays are matrix-specific and can only detect a few specific components in food additives, which are too fragmented and lack systematicity to meet the simultaneous determination of multiple classes of additives [6,7,8]. Therefore, there is an increasing demand for food additive detection methods with excellent performance and outstanding characteristics, and innovative designs are urgently needed to solve these problems.

To address these problems, in this paper, an electrochemical sensor with a double-layer niobium pentoxide/graphene oxide reduction (Nb2O5/rGO) loaded hollow nickel-cobalt nanorod modified glassy carbon electrode (GCE) was prepared to construct a detection system with high accuracy, short time and easy operation. And experimental conditions such as pH, molar ratio of monomer to template, number of polymerization circles and incubation time were optimized. In this paper, gallic acid in food additives was selected as the target. Gallic acid has good antioxidant properties and can help to

preserve and protect food. Therefore, it is important to investigate the detection method of gallic acid. A series of standard curves describing the concentration of gallic acid under optimal assay conditions were obtained and analyzed accordingly.

In addition, this paper also used a grey prediction model to correlate the available food additive production data, based on which a grey system model was constructed to predict the future changes in food additive production. The trend and extent of future food additive production changes not only illustrate the high market demand for food additives, but also the urgent need to develop technologies related to the detection of food additives. Therefore, this paper has a broad and far-reaching significance to investigate the electrochemical detection methods for food additives.

2. Future food additive production forecast

Grey analysis is a predictive analysis method made by combining grey systems. It can analyze the correlation between system factors, find out the pattern of system changes, and predict the status of the future development trend of things accordingly, with the characteristics of accuracy and rigor [9].

In this paper, we will make a relevant and reasonable analysis of food additive production through grey analysis, and use the grey model GM (1,1) model containing only one variable to make a quantitative forecast of food additive production in the Chinese food industry [10,11]. The raw data collected in this paper were obtained from the National Bureau of Statistics and are shown in Table.1.

Table 1. China's food additive production.

Time (Year)	**2016**	**2017**	**2018**	**2019**	**2020**	**2021**
Yield (10,000 tons)	851.75	851.39	687.96	837.93	1057	1197.15

Before building the grey prediction model GM (1,1), the yield series were tested for ratios. It was calculated that all the values of the ratios lie within the interval ($e^{-2/(n+1)}$, $e^{2/(n+1)}$), which indicates that the data are suitable for the construction of the grey prediction model [12].

Let the reference data $x^{(0)}$, $x^{(0)} = \{x^{(0)}(1), x^{(0)}(2), \ldots\ldots, x^{(0)}(n)\}$, make a cumulative addition to $x^{(0)}$ to obtain the sum series $x^{(1)} = \{x^{(1)}(1), x^{(1)}(2), \ldots\ldots, x^{(1)}(n)\}$, where $x^{(1)}(k) = \sum_{i=1}^{k} x^{(1)}(i)$. Substitute the collected food additive production data for 2016 - 2021, then:

$x^{(0)}$= (851.75, 851.39, 687.96, 837.93, 1057.00, 1197.15),

$x^{(1)}$= (851.75, 1703.14, 2391.10, 3229.03, 4286.03, 5483.15) .

Respectively solve for:

$d(k) = x^{(0)}(k) = x^{(1)}(k) - x^{(1)}(k-1)$, k = 2, 3, …, n.

$\boldsymbol{z}^{(1)}(k) = 0.5 \cdot x^{(1)}(k) + 0.5 \cdot x^{(1)}(k-1)$, k = 2, 3, …, n.

$$d(k) + a \cdot \boldsymbol{z}^{(1)}(k) = b \tag{1}$$

Using the least squares method, the estimated value of the development coefficient a is -0.122, and the estimated value of the grey effect amount b is 564.59.

Based on the above prediction model, solved with the help of SPSS 28, the expression for the predicted value of the yield series can be obtained:

$x^{(0)}(k) = 710.99 \cdot e^{0.122 \cdot (k-2)}$, k =2, 3, …, n, n+1, n+2, n+3, ….

The average relative error of the model is 7.95%, which is less than 10%, implying a good fit of the model, as shown in Table.2.

Table 2. Model fitting results.

k	Actual value	Predicted value	Residuals	Relative error
1	851.75	851.75	0	0.00%
2	851.39	710.99	140.4	16.49%
3	687.96	803.42	115.46	16.78%
4	837.93	907.86	69.93	8.35%
5	1057	1025.89	31.11	2.94%
6	1197.15	1159.25	37.9	3.17%

Based on the forecast value expression, it is clear that the forecast model produces approximately $e^{0.122}$ times the previous year's output in each year, or approximately 1.13 times, so the growth rate of the output series is approximately 13%. Substituting the corresponding parameters for 2022 - 2024 into the predicted value expression, the predicted values of food additive production in China for 2022 - 2024 are given in Table.3.

Table 3. Food additives forecast for China.

Time (Year)	2022	2023	2024
Yield (10,000 tons)	1309.953	1480.246	1672.678

The overall fit of the data is shown in Fig.1.

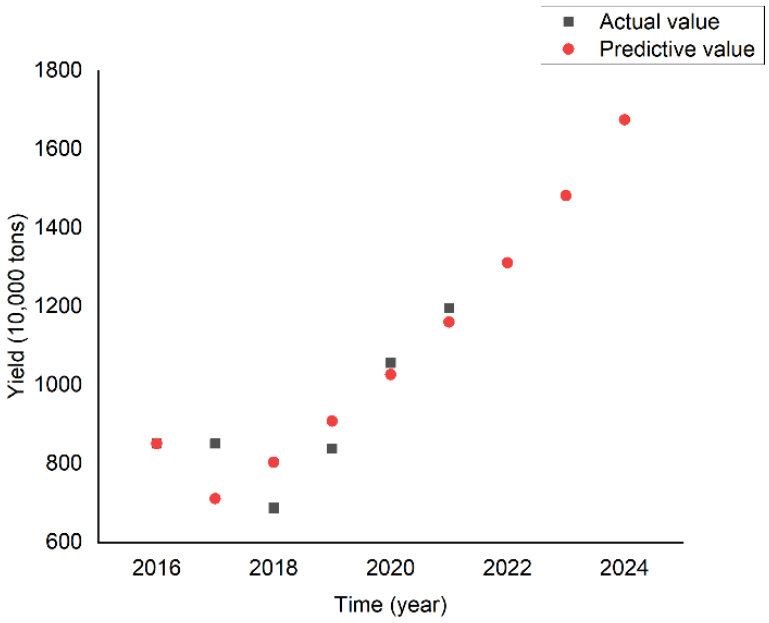

Figure 1. Forecasts for food additive production based on grey prediction model.

3. Construction of an electrochemical sensor for the detection of gallic acid

3.1. Apparatus and reagents

Apparatus: Electrochemical experiments were performed with the aid of CHI660E electrochemical workstation (Beijing Haiguang Instrument Company) and a three-electrode system, the working electrode was a 3 mm diameter glassy carbon electrode (GCE), the reference electrode was an Ag/AgCl (saturated KCl) electrode, the auxiliary electrode was a platinum wire electrode purchased from Beijing Zhong Han Instrument Company, a tube furnace (T1280A), an ultrasonic cleaner (SB-800DTD), timed magnetic stirrer (90-2), electronic analytical balance (BSA124S), high-speed frozen

centrifuge (HC-3018), platinum electrode (Pt), X-ray diffractometer (XRD), saturated mercury electrode, constant temperature water bath, electronic balance, frozen centrifuge, ultrasonic cleaner, freeze dryer, purchased from Beijing Bofei Instrument Company.

Reagents: gallic acid (≥99.5%), 4-vinylpyridine (≥99.5%), concentrated sulfuric acid (≥99.5%), concentrated nitric acid (≥99.5%), concentrated hydrochloric acid (≥99.5%), potassium persulfate (≥99.5%), sodium hydroxide (≥99.5%), methanol (≥99.5%), ethylene glycol (≥99.5%), anhydrous ethanol (≥99.5%) Acetic acid (≥99.5%), acetonitrile (≥99.5%), nickel acetate (≥99.5%), cobalt acetate (≥99.5%), the above reagents were purchased from Adamas brand.

3.2. Experimental methods

3.2.1. Synthesis of hollow nickel-cobalt nanorod composites

Synthesis of nickel hydrogen acetate: polyvinylpyrrolidone (PVP) and a certain amount of nickel acetate and cobalt acetate were taken, dissolved in about 90 mL of ethanol, and reacted at 80°C with continuous stirring. After the reaction, the mixture was processed by centrifugation and the precipitate was collected and washed five times with ethanol. The resulting product was placed in an oven and dried in an oven at 60 °C for 5 h, during which the amount of total Ni and Co obtained was kept constant, but making the Ni-Co ratio change. Ni-Co precursors with Ni-Co ratios of 1:1 and 1:2 was selected and set aside.

The above Ni-Co precursors were dissolved in ethanol and then dispersed by ultrasonic instrument, and the resulting mixture was heated and stirred at 80°C for 2.5 h. After the reaction was completed, the end products were collected by centrifugation, washed three times with ethanol to remove impurities, and all the products obtained were put into a drying oven and dried at 60°C for 2 h. The most suitable sample was selected and treated at high temperature under argon-filled conditions for 30 min. The effect of the heat treatment and the oxygen evolution reaction (OER) activity were checked, and a decontamination operation was performed to remove the oxides and hydroxides. Some of the resulting samples were taken and treated with sulfuric acid solution for 30 min, then washed with ethanol and dried.

3.2.2. Polymerization molecular imprinting on the surface of synthetic materials

Gallic acid and 4-vinylpyridine were dissolved in 10 mL of acetonitrile, and the modified electrode was placed in it, connected to the electrode system and connected to the instrument in the potential range of -0.4 - 1.2 V. The modified electrode with surface polymerization molecular imprint was obtained by scanning 20 turns at a scanning rate of 100 mV/s.

3.2.3. System construction and experimental conditions

In this paper, the electrochemical sensor of GCE modified with hollow nickel-cobalt nanorods loaded by double-layer Nb_2O_5/rGO was prepared. The experimental conditions such as pH, molar ratio of template to monomer, number of polymerizations turns, and incubation time were further optimized in order to achieve the best detection effect.

Regarding the molar ratio of monomer to template, the optimal molar ratio of monomer to template was selected by continuously adjusting the molar ratio of functional monomer to template molecule (gallic acid) and simultaneously testing the response of the system.

Regarding pH, this paper provides a series of different pH environments for the molecularly imprinted electrochemical sensor detection system. pH varies from 2.0 to 9.0, with a gradient of 1.0, to detect the response of the molecularly imprinted electrochemical sensor to gallic acid, and the pH corresponding to the best response is selected as the optimal detection pH.

Regarding the number of polymerizations turns, the response of the molecularly imprinted electrochemical sensor to gallic acid was examined in a gradient of 5 turns to select the most suitable number of polymerizations turns.

Regarding the incubation time, a series of different incubation times were used in this paper. The incubation time was varied from 0 - 120 min, and the response of the molecularly imprinted electrochemical sensor to gallic acid was examined to determine the optimal incubation time.

4. Results and Analysis

4.1. Optimization of experimental conditions

4.1.1. The molar ratio of functional monomer to template molecule

Gallic acid molecular blotting is directly related to the molar ratio of functional monomer to template molecule. As shown in Fig.2, the current response is positively correlated with the molar ratio in the range of 1:1 to 4:1. To the extent that the strongest peak current is obtained at a molar ratio of 4:1 of functional monomer to template molecule. And in the range of 4:1 to 6:1, the current response is negatively correlated with the molar ratio. This indicates that when the amount of functional monomer is small, the template molecule is completely bound to the functional monomer. When the optimal molar ratio is reached, the maximum number of molecularly imprinted cavities are formed, which can bind to more template molecules, resulting in the strongest current response. If more functional monomers are used, a dense membrane of non-molecularly imprinted polymer (NIP) is formed, which does not specifically recognize the template molecule and therefore the current response is greatly reduced. Therefore, the optimal molar ratio of functional monomer to template molecules is 4:1.

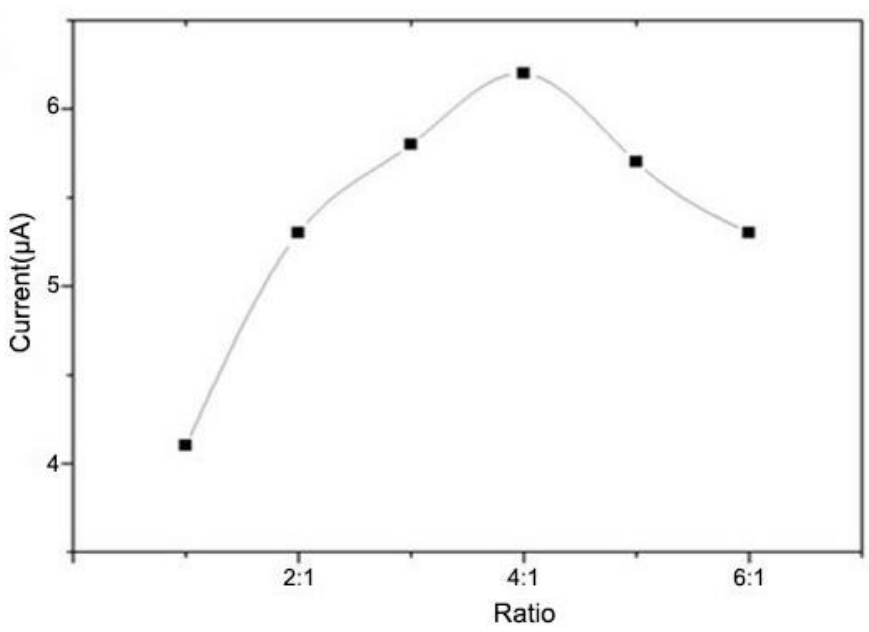

Figure 2. Effect of the ratio of template molecules to structural monomers on the detection system.

4.1.2. pH

The effect of pH on the peak current was investigated by using differential pulse voltammetry (DPV) in PBS containing 100 μM gallic acid as shown in Fig.3. The pH of the electrolyte has a significant effect on the binding of the target molecule to the molecular blotting cavity. The electrochemical response gradually increased as the pH increased from 4.0 to 7.0. And as the pH increases from 7.0 to 9.0, the peak current decreases significantly. This is because gallic acid binds to the molecularly imprinted polymer (MIP) recognition site with different strengths in different pH environments. The binding of the template molecule to the MIP depends on the interaction of functional groups between the template molecule and the MIP. And the functional groups have different dissociation degrees at different pHs, leading to changes in the interaction between the functional groups and thus in the binding strength of the template molecule to the MIP.

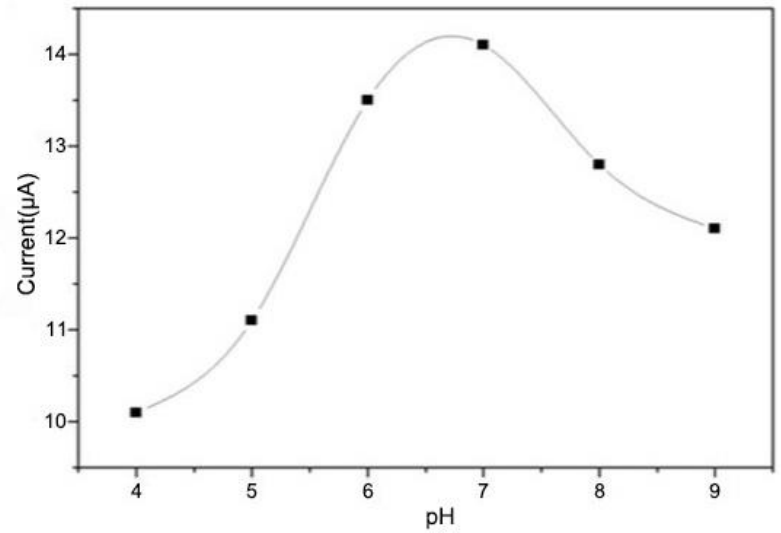

Figure 3. Effect of pH on the detection system.

4.1.3. The number of electropolymerization turns

According to previous studies, the number of turns of the electropolymerization cycle plays an important role in the system. As shown in Fig.4, the peak current increases gradually with the increase of the number of scanning turns. The strongest peak current occurs when the number of scan turns is 10, and thereafter the peak current decreases sharply. This indicates that the MIP film is too fragile to be electrodeposited on the electrode surface when the number of electropolymerization turns is small. And a large number of electropolymerization turns can lead to excessive electropolymerization, which prevents the eluate from fully extracting the template molecules. Therefore, the optimal number of scan turns is 10, when the strongest current response can be obtained.

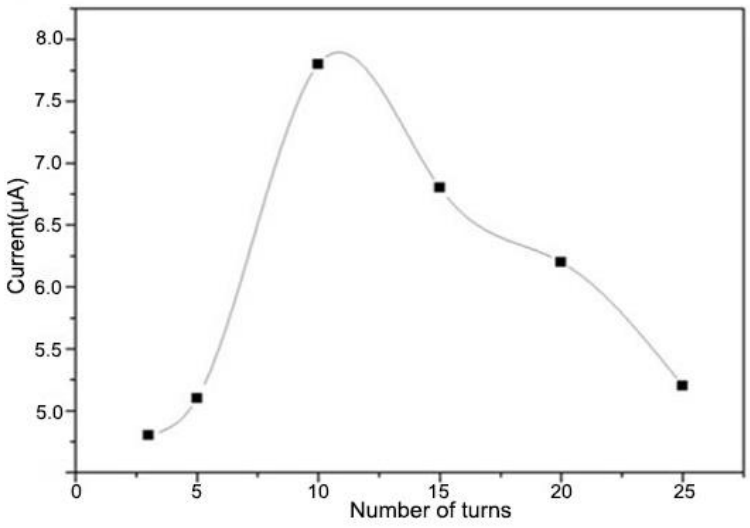

Figure 4. Effect of the number of electropolymerization turns on the detection system.

4.1.4. Incubation time

As shown in Fig.5, the current response of Ni-Co/MIP/GCE to gallic acid gradually increased from 0 - 20 min. After 20 min, the current response did not change significantly and the peak current was basically stable. The results showed that the current response increased with the increase of incubation time until the maximum adsorption of gallic acid by MIP membrane was reached. After the maximum adsorption amount was reached, the current response was basically stable. Therefore, the optimal incubation time required for the MIP membrane to be saturated with gallic acid was selected as 20 min.

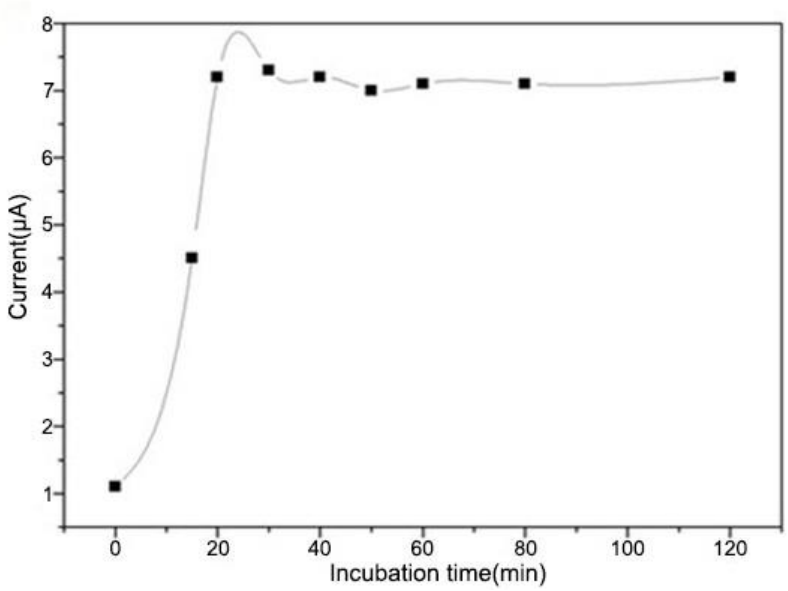

Figure 5. Effect of incubation time on the detection system.

4.2. Response of different gallic acid concentrations under differential pulse voltammetry (DPV)

By using DPV, the effect of gallic acid concentration on the peak current was investigated under the optimal detection conditions described above. The rate of gallic acid binding to the molecularly imprinted cavity varied for different concentrations. The electrochemical response gradually increased as the concentration gradually increased from 0.0005 μM to 200 μM. This is because the binding strength of gallic acid to the MIP recognition site varies at different concentrations. And the higher the concentration of gallic acid, the higher the binding probability of its template molecule to MIP, which led to the change of the binding intensity of the template molecule to MIP. As shown in Fig.6, the peak response of the detector was around 1.0 V, and the peak response increased gradually with the increase of gallic acid concentration, which indicates that the molecularly imprinted electrochemical sensor detection system constructed in this experiment has a good response effect on the detection of gallic acid.

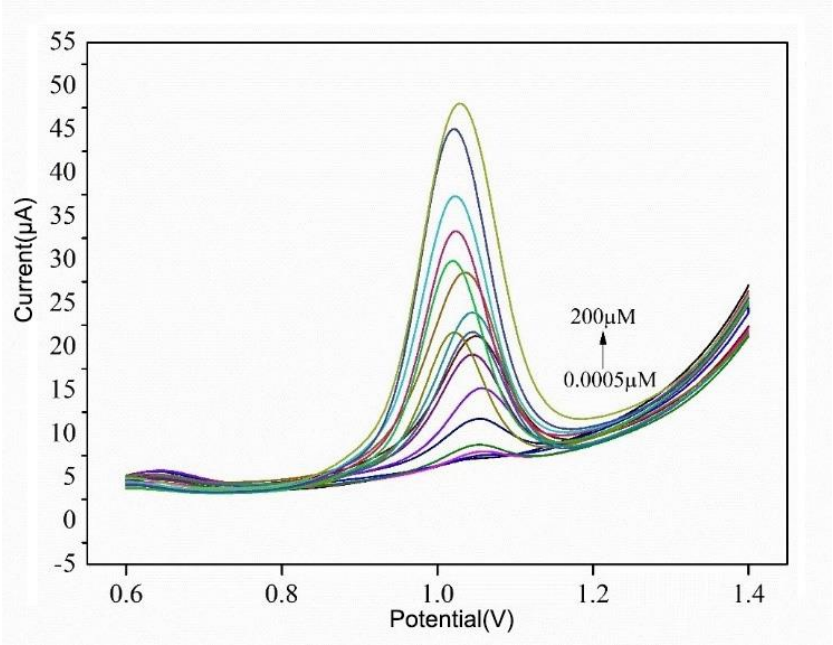

Figure 6. Gallic acid standard curves for concentrations from 0.0005 μM to 200 μM.

5. Conclusion

Through the grey prediction model, this paper predicts that the production of food additives will continue to grow steadily. Therefore, it is important to investigate the detection technology of food additives.

In order to achieve the best detection results, the optimization of relevant experimental conditions was first investigated in this paper. Then a series of voltammetric standard curves (0.0005 μM - 200 μM) for different concentrations of gallic acid were determined under the optimal conditions in combination with DPV in order to provide a reference for its application.

The detection method in this paper is accurate, sensitive, short time-consuming, low-cost and easy to operate, and provides a theoretical guide for the application of electrochemistry to food component testing, which has a broad and bright development prospect.

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