

Research Article

Determination of Benzylpenicillin Potassium Residues in Duck Meat Using Surface Enhanced Raman Spectroscopy with Au Nanoparticles

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A new method using surface enhanced Raman spectroscopy (SERS) with Au nanoparticles was established for the rapid detection of benzylpenicillin potassium (PG) residues in duck meat. Au nanoparticles were used as SERS enhancement substrate, and the maximum absorption peak of Au nanoparticles using the UV-Vis spectrophotometer was 548 nm. In the research, the SERS spectra of PG solutions and PG duck meat extract as well as their vibrational assignment were analyzed. The effects of Au nanoparticles addition, sample addition, NaCl solution addition, and adsorption time on the SERS intensities of PG duck meat extract were discussed. It is revealed that a good linearity can be obtained between the SERS intensities at 993 cm^{-1} and the PG residues concentrations ($0.5\sim 15.0\text{ mg}\cdot\text{L}^{-1}$) detected in duck meat extract. The linear equation was $Y = 831.68X + 1997.1$, and the determination coefficient was 0.9553. The determination coefficient of PG in duck meat extract between the actual values and the predictive values was 0.9757, and the root mean square error (RMSEP) was 0.6496 mg/L . The recovery rate of PG in duck meat extract was $90\sim 121\%$. The results showed that the method using SERS with Au nanoparticles could pave a new way for the rapid detection of PG residues in duck meat.

1. Introduction

Penicillin is a type of β -lactam antimicrobial drugs and, as one of the most output and the most widely used antibiotics, has been successfully applied to treat bacterial infections in both human and animals, such as gastrointestinal, urethra, and respiratory tract infections [1, 2]. Because of its high solubility, benzylpenicillin potassium (PG) is one of the most used penicillins and has been regarded as the best choice of treating duck diseases [2–4]. The penicillin residues are strictly controlled and limited in China, with a maximum residue limit (MRL) of penicillin residues in animal foods of $50\text{ }\mu\text{g}\cdot\text{L}^{-1}$, according to the regulation of China's Ministry of Agriculture [5]. If the amount of penicillin is not rationally used in the duck-raising process, violation residues in duck meat will be caused and the penicillin residues in duck meat would endanger human's health.

Currently, the main methods reported for the detection of penicillin residues in animal foods include the

high-performance liquid chromatography (HPLC) [1, 6], microbial method [7], enzyme-linked immunosorbent assay [8], and electrochemical immunosensor [5]. The advantages of these techniques are the sensitivity and practicality; however, these methods are also suffering several drawbacks, such as complex pretreatment and unsatisfactory cost-effectiveness. Therefore, it is very urgent to establish a new method for the simple, rapid, and accurate detection of penicillin residues in duck meat.

Surface enhanced Raman spectroscopy (SERS) is an interesting phenomenon that some molecules and functional groups were adsorbed onto the roughened surface of a suitable metal, such as gold, silver, or copper, and the intensities of their Raman signals can be greatly enhanced. This detection technique, which possesses many advantages such as convenient operation, high accuracy rate, fast testing velocity, and the portable instrument, has been widely applied in the biological engineering, medical, food detection, and

other research works [9–11]. Di Anibal et al. adopted a screening tool to detect Sudan I dye in culinary spices using SERS and multivariate analysis [12]. Tang et al. applied the alkaline silver colloid as SERS enhancement substrate to detect the melamine in milk [13]. Zhu used SERS to detect the nitrofurantoin antibiotics residues in chicken, fish, and shrimp meat [14]. In this research, Au nanoparticles were used as the SERS enhancement substrate and PG in duck meat extract was used as the research object, and a new method using SERS with Au nanoparticles was established for the rapid detection of PG residues in duck meat.

2. Materials and Methods

2.1. Reagents and Equipment. Duck was purchased from the vegetable market of Jiangxi Agricultural University. PG standard substance (99.8%) was purchased from standard substances network of China. Tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $M = 393.83$, its $\text{Au} \geq 49.0\%$) was purchased from Sigma-Aldrich. Trisodium citrate, sodium chloride, acetonitrile, and hexane were of analytical grade. Ultrapure water was also used.

QE65000 portable Raman spectrometer (Ocean Optics Co., Ltd.), T6 series UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.), laboratory ultrapure water machine (Kertong Water Co., Ltd.), wire coil heater (Beijing Yongxing Instrument Co., Ltd.), K-50B ultrasonic cleaner (Hefei Kinnic Machinery Co., Ltd.), FA1004B electronic balance (accuracy of 0.1 mg, Shanghai Flat Instrument Co., Ltd.), VORTEX-5 vortex mixer (Haimen, Jiangsu Province, Kylin-Bell Lab Instruments Co., Ltd.), HSC-24B termovap sample concentrator (Tianjin City Heng Austrian Science and Technology Development Co., Ltd.), JW-1024 low speed centrifuge (Anhui Jiaven Equipment Industry Co., Ltd.), and quartz sampling bottle (Beijing Cheng Teng Equipment Co., Ltd.) were used.

2.2. Experimental Methods

2.2.1. Pretreatment of Duck Meat Extract. The duck meat extract [6, 15]: 5 g of duck meat mud, 2 g of anhydrous sodium sulfate, and 25 mL acetonitrile were added into 50 mL polypropylene centrifuge tube. The mixture was oscillated for 1 min, followed by the ultrasonication treatment for 5 min. After centrifuging the mixture at 4200 r/min for 10 min, the supernatant of the mixture was removed. The above processes were repeated twice, and the supernatants were mixed. 4 mL of the supernatants with 8 mL of hexane saturated with acetonitrile was mixed, oscillated for 1 min, and centrifuged at 4200 r/min for 8 min. The hexane layer of the mixed solutions was removed, and the residual solutions were dried with nitrogen. The residue was dissolved in 4 mL ultrapure water, and the solutions were filtrated through a $0.45 \mu\text{m}$ filter membrane to remove lipids. The duck meat extract was obtained and stored under the environment of 4°C .

2.2.2. Synthesis of Au Nanoparticles. Au nanoparticles [16, 17]: 3 mL (1%) of auric chloride acid and 47 mL of ultrapure water were mixed in a 100 mL beaker, and the mixed solutions

were heated with wire coil heater. After the boiling had commenced, 2 mL (1%) of trisodium citrate solution was added rapidly into the above boiling solution under a glass rod stirring. After 5 min, the color of the mixed solution was changed to coffee. The synthesized Au nanoparticles were stored at the room temperature.

2.2.3. Standard Solution and Sample Solution. PG standard solution ($100 \text{ mg}\cdot\text{L}^{-1}$): 10 mg PG was dissolved in 100 mL duck meat extract. Sodium chloride standard solution ($0.1 \text{ mg}\cdot\text{L}^{-1} \text{ NaCl}$): 0.585 g of sodium chloride was dissolved in 100 mL ultrapure water.

The PG sample solution: the different volumes of PG standard solution were put into 10 mL centrifuge tube and the capacity was fixed to 5 mL using duck meat extract. Ultimately, the different mass concentrations of PG duck meat extract samples (0.5, 1.0, 2.0, 4.0, 6.0, 7.0, 9.0, 10.0, 12.0, and $15.0 \text{ mg}\cdot\text{L}^{-1}$) were obtained through the above method.

1 mL of Au nanoparticles, 20 μL of sample solution ($0.5\sim 15.0 \text{ mg}\cdot\text{L}^{-1}$), and 100 μL of NaCl solution ($0.1 \text{ mg}\cdot\text{L}^{-1}$) were sequentially added into the quartz sampling bottle. The mixture was well mixed, and then the SERS spectra were collected when the adsorption reaction lasted for 5 min.

2.3. Parameter Settings of Instruments. Raman spectrometer parameter settings: the spectrometer's power and the laser wavelength were 700 mW and 785 nm, respectively. The integration time of 10 s, the average integral number of 2, and the smoothness of 1 were applied.

UV-Vis spectrophotometer parameter settings: the display range and the scanning range were 0~2 s and 400~700 nm, respectively. The interval of 2 nm and the spectrophotometric mode of Abs were selected. Finally, the absorption spectra were collected under the fast scan speed.

3. Results and Discussion

3.1. UV-Visible Absorption Spectra of Au Nanoparticles and SERS Assignment of PG. In the formation of sodium citrate reduction of auric chloride acid, the sodium citrate, which was not directly reacted with the boiling solution of auric chloride acid, was firstly decomposed into the stable acetate and formic acid, and then Au nanoparticles were produced via the oxidation reaction between formic acid and auric chloride acid [18]. The sodium citrate was decomposed rapidly with electromagnetic heating, and the reactive substances were fused quickly [18]. Consequently, the smaller particle size and even distribution of Au nanoparticles could be synthesized. 500 μL of Au nanoparticles was diluted with 2 mL ultrapure water, and the UV-Visible absorption spectra were collected. As shown in Figure 1, the maximum absorption peak of Au nanoparticles was 548 nm and the half-peak width was about 79 nm. The results showed that the particle size of Au nanoparticle was somehow single and distributed uniformly [19].

The SERS spectra and structural formulas of PG were shown in Figure 2, and it can be seen that PG was mainly composed of the β -lactam ring, the thiazolidine ring, and the acyl side chain of the substituted benzene ring. As seen

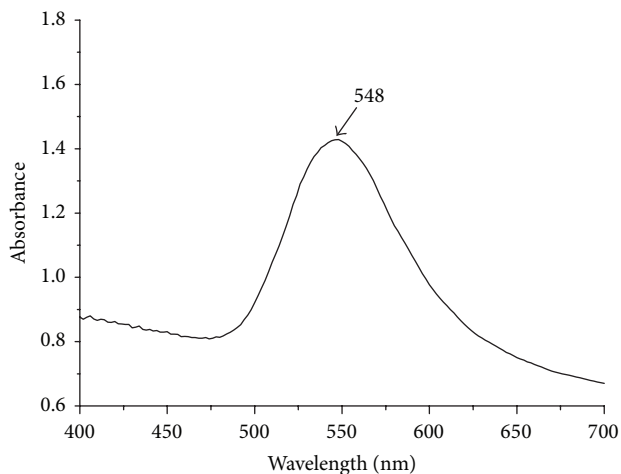


FIGURE 1: The UV-Visible absorption spectra of Au nanoparticles.

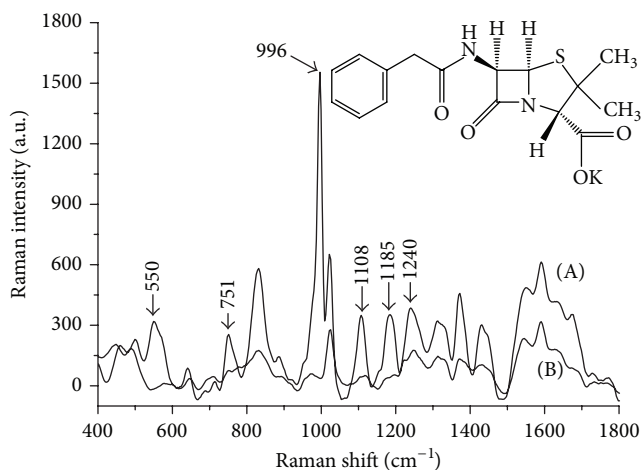


FIGURE 2: The SERS spectra and structural formulas of the PG: (A) Au nanoparticles + PG (7 mg/L), (B) Au nanoparticles.

from curves (A) and (B) in Figure 2, a visible difference was observed in the SERS spectra of Au nanoparticles and Au nanoparticles + PG at 550~1240 cm^{-1} , which indicates that some interaction was produced between PG and Au nanoparticles. As shown from curve (A) in Figure 2, the SERS peak at 550 cm^{-1} might result from the deformation vibration of thiazole ring and benzene ring, the SERS peak at 751 cm^{-1} might be ascribed to the CC stretching vibration, and the SERS peak at 996 cm^{-1} might be ascribed to the stretching vibration of benzene ring and the breathing vibration of triangle ring. The SERS peak at 1108 cm^{-1} was possibly due to CH_3 rocking vibration of plane and C-C-C bending vibration, the SERS peak at 1185 cm^{-1} was possibly due to CN stretching vibration and CH bending vibration of thiazole ring, and the SERS peak at 1240 cm^{-1} was possibly due to CH bending vibration and C-OH stretching vibration from curve (A) [20–23].

3.2. SERS Spectra of PG Solutions and PG Duck Meat Extract. The negative charge of Au nanoparticles resulted from many

anions of citrate self-assembled on Au nanoparticles surface. Because of electrostatic repulsion of Au nanoparticles, Au nanoparticles remained stable in aqueous solution [24]. When the NaCl solution was added, the negative charge of Au nanoparticles was neutralized by the reaction with Na^+ . The neutralizing reaction led to the disappearance of Au nanoparticles electrostatic repulsion and the aggregation of Au nanoparticles. As a result, the signal of resonance light scattering was enhanced. As shown in Figure 3(a), when the NaCl solution was added into the mixture of Au nanoparticles and PG solution (7 $\text{mg}\cdot\text{L}^{-1}$), the SERS signal of the mixture was further enhanced. In the comparison of curves (A) and (C) in Figure 3, the SERS peak of PG solution at 993 cm^{-1} was blue shifted about 3 cm^{-1} . It can be also seen that the SERS peaks of PG solution at 1492~1674 cm^{-1} were excited from curves (A) and (B). The SERS peak at 1492 cm^{-1} might result from the CH_3 bending vibration. The SERS peak at 1563 cm^{-1} might be attributed to double-peak vibration of degenerate ring, and the SERS peak at 1674 cm^{-1} might be ascribed to C=O stretching vibration of peptide bond, NH and CH bending vibration [20–23].

Some constituents of duck meat, such as protein and fat, could significantly interfere with the SERS signal of PG. Therefore, the acetonitrile was firstly used as the extraction solvent to precipitate the protein in duck meat. Secondly, the hexane saturated with acetonitrile was used to remove fat and other impurities. The remaining acetonitrile was dried with nitrogen, and the residue was dissolved in ultrapure water. Finally, the relatively pure duck meat extract was obtained. Au nanoparticles + duck meat extract + NaCl, Au nanoparticles + PG duck meat extract (7 $\text{mg}\cdot\text{L}^{-1}$) + NaCl, and Au nanoparticles + PG (7 $\text{mg}\cdot\text{L}^{-1}$) + NaCl were shown in Figure 3(b), and we could see that some SERS peaks of duck meat extract were the same with the SERS peaks of PG duck meat extract, such as 717 cm^{-1} , 1024 cm^{-1} , 1244 cm^{-1} , and 1369 cm^{-1} . The SERS spectra of PG duck meat extract presented the peaks at 993 cm^{-1} and 1492 cm^{-1} , while the SERS spectra of duck meat extract did not present peaks at 993 cm^{-1} and 1492 cm^{-1} . Meanwhile, the two SERS peaks of PG duck meat extract anastomosed with the SERS peaks of PG solution, which rendered a realistic basis for the detection of PG residues in duck meat.

3.3. Effect of Au Nanoparticles Addition on the SERS Intensity of PG Duck Meat Extract. The SERS effect is caused by the electromagnetic effect and the chemical effect, and the measured molecules are adsorbed onto the roughened surface of metal substrate. However, not all of the adsorbed molecules can produce the SERS effect on the surface of metal substrate. Most of the enhancement effect results from the portion of the adsorbed molecules on the positive surface of metal substrate. Therefore, the volume concentrations of Au nanoparticles are critical for the enhancement of SERS intensities [25, 26]. In this research, the volumes of PG duck meat extract (7 $\text{mg}\cdot\text{L}^{-1}$) and the NaCl solution (1 mol/L) were fixed to 50 μL and 100 μL , respectively, and then the SERS spectra of the mixture with the addition of 0.5, 0.7, 1, 1.2, and 1.5 mL of Au nanoparticles were collected, respectively.

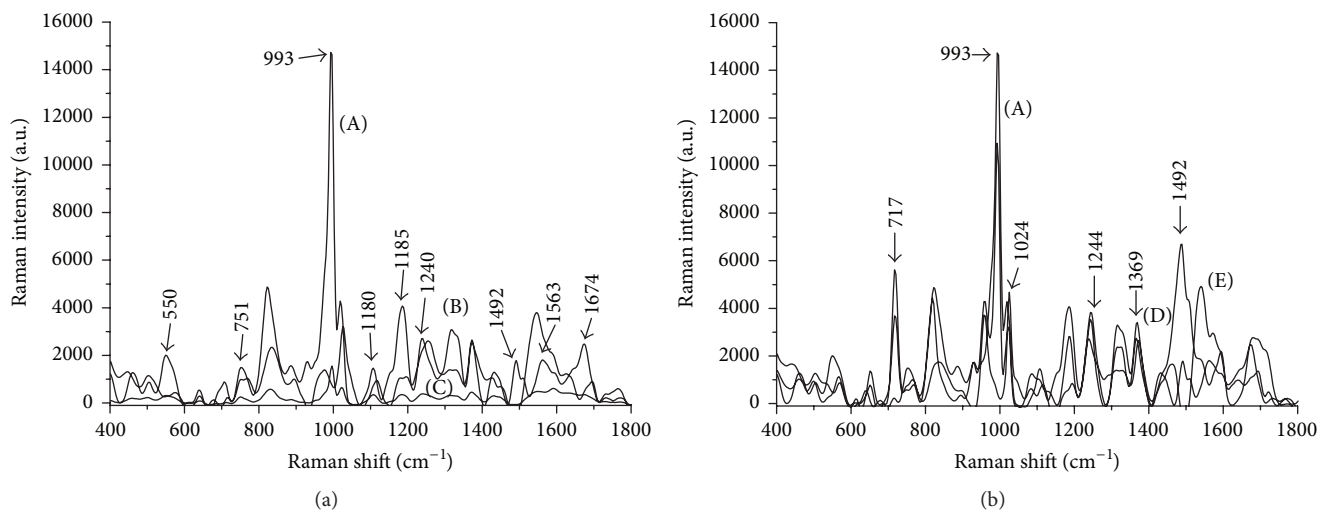


FIGURE 3: The SERS spectra of the PG solutions (a) and PG duck extract (b): (A) Au nanoparticles + PG (7 mg/L) + NaCl; (B) Au nanoparticles + NaCl; (C) Au nanoparticles + PG (7 mg·L⁻¹); (D) Au nanoparticles + PG duck meat extract + NaCl; (E) Au nanoparticles + duck meat extract + NaCl.

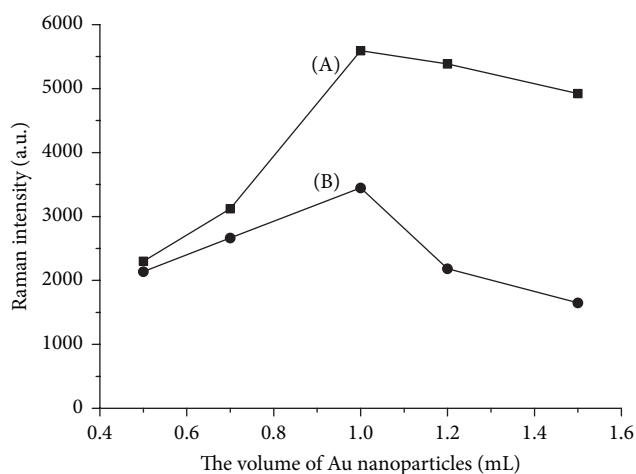


FIGURE 4: Effect of the Au nanoparticles addition on the SERS intensity of PG duck meat extract: (A) 993 cm⁻¹, (B) 1492 cm⁻¹.

As shown in Figure 4, the SERS intensities at 993 cm⁻¹ and 1492 cm⁻¹ were continuously strengthened with the increases of Au nanoparticles volume. However, when the volumes of Au nanoparticles exceeded 1 mL, the SERS intensities decreased gradually. It is speculated that Au nanoparticles firstly adsorbed PG and the adsorption effect enhanced the Raman signal with the increases of Au nanoparticles volumes. However, when the volumes of Au nanoparticles increased to a certain value, the neutralization of Na⁺ to Au nanoparticles could cover up the part of the PG adsorption effect and decreased the SERS intensities. Therefore, the Au nanoparticles addition was determined as 1 mL in the following experiment.

3.4. Effect of Sample Addition on the SERS Intensity of PG Duck Meat Extract. Owing to the portion of adsorbed

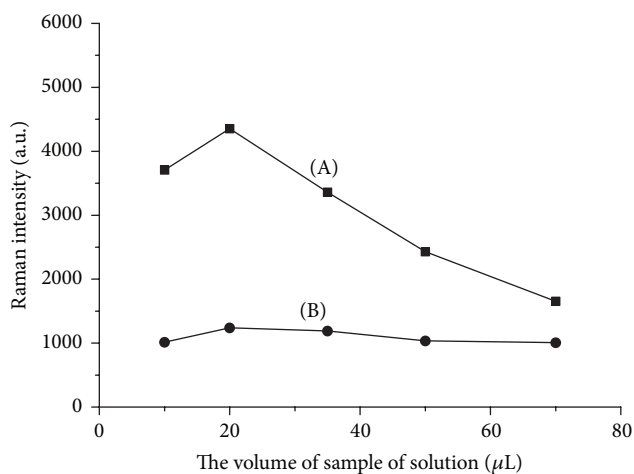


FIGURE 5: Effect of sample addition on the SERS intensity of PG duck meat extract: (A) 993 cm⁻¹, (B) 1492 cm⁻¹.

molecules on the positive surface of metal substrate, the volume concentration of the sample solution (7 mg/L) could impact the SERS intensity of PG duck meat extract. When Au nanoparticles and the NaCl solution were fixed, respectively, in this paper, the SERS spectra of the different volumes of the sample solutions (10, 20, 35, 50, and 70 μL) were collected and analyzed. As seen from Figure 5, when the volumes of the sample solutions increased from 10 μL to 20 μL, the SERS intensities at 993 cm⁻¹ and 1492 cm⁻¹ were enhanced. However, when the volumes were more than 20 μL, the SERS intensities decreased gradually. Therefore, the sample addition was selected as 20 μL in the following experiment.

3.5. Effect of NaCl Addition on the SERS Intensity of PG Duck Meat Extract. The larger particle size of aggregate, which was caused by the adsorbed PG on the surface of Au

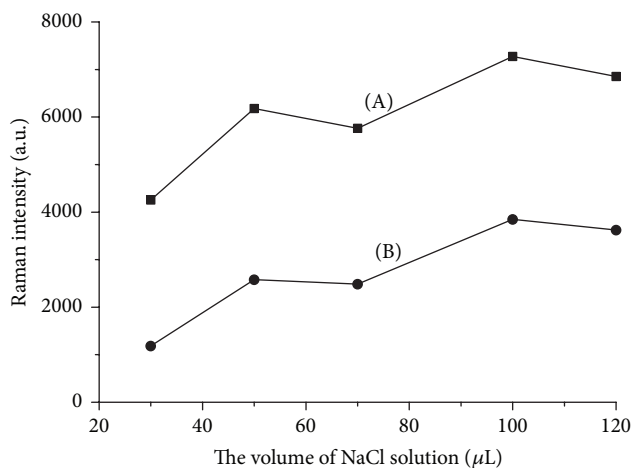


FIGURE 6: Effect of NaCl addition on the SERS intensity of PG duck meat extract: (A) 993 cm^{-1} , (B) 1492 cm^{-1} .

nanoparticles, would result in the local plasma resonance between PG and Au nanoparticles and the enhancement of SERS intensities [27]. When the NaCl solution was added into the mixture of Au nanoparticles + PG duck meat extract, Au nanoparticles would gather rapidly and the color of the mixture was changed from coffee to blue. The particle size of the above Au nanoparticles became bigger, which is manifested as the enhancement of the resonance light scattering, and the SERS intensities of PG duck meat extract were further enhanced. In order to investigate the effects of different volume concentrations of the NaCl solution on the SERS intensities of the mixture, 1 mL of Au nanoparticles and 20 μL of PG duck meat extract were firstly added into the quartz sampling bottle in turn. And, then, different volumes of the NaCl solution (30, 50, 70, 100, and 120 μL) were added, respectively, and their SERS spectra were collected. When the NaCl addition was 100 μL , the SERS intensities at 993 cm^{-1} and 1492 cm^{-1} reached the maximum value in Figure 6. The reason was probably that the proper volume of NaCl solution could have the effect of the activator, but the excess volume of the NaCl solution made the mixture produce the coagulation and resulted in the SERS intensities weakening [28]. The experimental results indicated that 100 μL of the NaCl solution was the optimum addition, so the NaCl addition was selected as 100 μL in the following experiment.

3.6. Effect of Adsorption Time on the SERS Intensity of PG Duck Meat Extract. When the volumes of Au nanoparticles, PG duck meat extract, and the NaCl solution were fixed, respectively, the adsorption time had some influences on the enhancement effect of SERS intensities. After 1 mL of Au nanoparticles, 20 μL of PG duck meat extract and 100 μL of the NaCl solution were mixed together, Au nanoparticles would gather, and then the aggregation of Au nanoparticles would produce the SERS spectra. When the adsorption times of the mixture were 1, 5, 10, 15, and 20 min, respectively, the SERS spectra of the mixture in different adsorption times were collected. As shown from curve (A) in Figure 7, the SERS

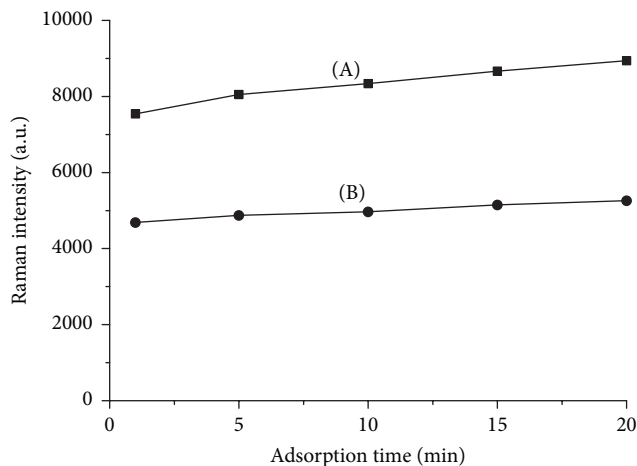


FIGURE 7: Effect of adsorption time on the SERS intensity of PG duck meat extract: (A) 993 cm^{-1} , (B) 1492 cm^{-1} .

intensities at 993 cm^{-1} were of larger increasing range at 1~5 min. Although the SERS intensities had some enhancement effect at 5~20 min, the enhancement extent was relatively stable. As seen from curve (B) in Figure 7, the SERS intensities at 1492 cm^{-1} were enhanced gradually at 1~20 min, but the enhancement extent did not change obviously. The above results might be because the PG molecules in duck meat extract could not be completely adsorbed on the surface of Au nanoparticles before 5 min, so the SERS intensities at 993 cm^{-1} and 1492 cm^{-1} were continuously enhanced. After 5 min, the PG molecules might be completely adsorbed on the surface of Au nanoparticles. Therefore, the SERS spectra were collected after the reaction for 5 min.

3.7. Prediction and Analysis Model. The proposed method based on SERS with Au nanoparticles was employed to determine PG residues in duck meat. The different mass concentrations of PG duck meat extract samples were prepared and the SERS spectra were collected under the optimum conditions. The research showed that when the concentration range of PG in duck meat extract was 0.5~15.0 $\text{mg}\cdot\text{L}^{-1}$, the SERS intensities at 993 cm^{-1} and 1492 cm^{-1} showed the enhancement trend with the increasement of PG concentrations. When the mass concentration of PG in duck meat extract was lower than 4 $\text{mg}\cdot\text{L}^{-1}$, the SERS peak at 1492 cm^{-1} was hardly observed. However, the SERS peak at 993 cm^{-1} could be observed under the same conditions when the mass concentration of PG in duck meat extract was 0.5 $\text{mg}\cdot\text{L}^{-1}$. Therefore, the PG duck meat extract samples (the concentration range of 0.5~15.0 $\text{mg}\cdot\text{L}^{-1}$) and the SERS intensities at 993 cm^{-1} were utilized for the quantitative analysis.

The calibration curve between the mass concentrations of PG in duck meat extract and the SERS intensities at 993 cm^{-1} was established using 6 samples, and 4 of the remaining samples were used to verify the accuracy of the calibration curve. As shown in Figure 8 and Table 1, when the concentration range of PG in duck meat extract

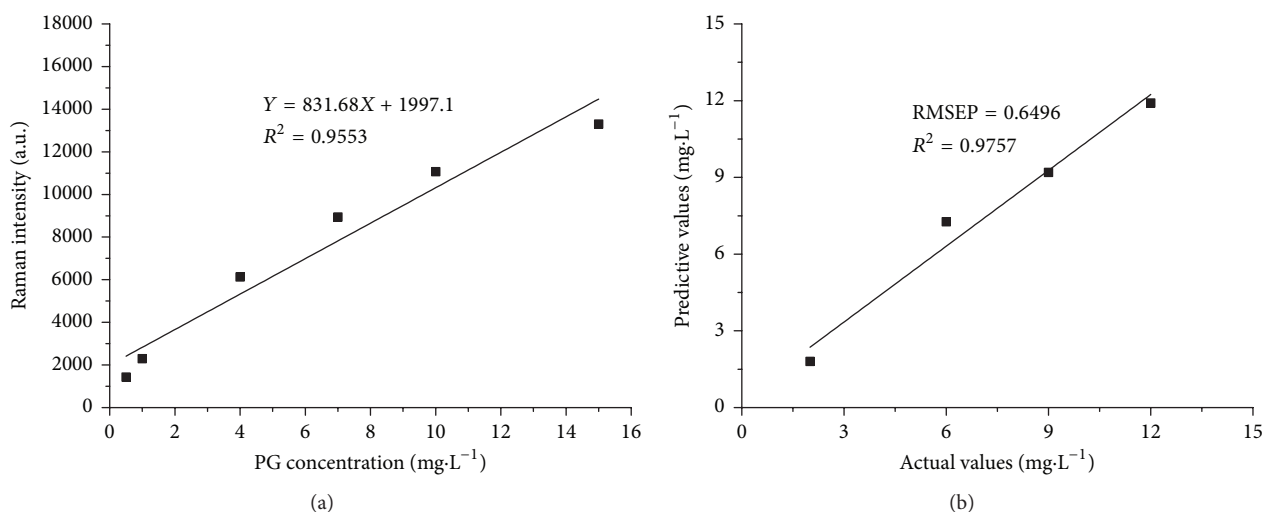


FIGURE 8: Linear equation of the PG duck extract (a) and the relationship of the prediction samples (b).

TABLE 1: Determined results of the recovery rate.

Sample number	Concentration of PG in duck meat extract/(mg·L ⁻¹)	Recovery amount/(mg·L ⁻¹)	Recovery rate/%
1	2	1.81	90.3
2	6	7.27	121.1
3	9	9.19	102.2
4	12	11.91	99.3

was 0.5~15.0 mg·L⁻¹, there was a good linear relationship between the concentrations of PG in duck meat extract and the SERS intensities at 993 cm⁻¹. The linear equation was $Y = 831.68X + 1997.1$, and the determination coefficient was 0.9553. The determination coefficient of PG in duck meat extract between the actual values and the predictive values was 0.9757, and the root mean square error (RMSEP) was 0.6496 mg·L⁻¹. The recovery rate of PG in duck meat extract was 90~121%. The result showed that the proposed method was feasible and relatively reliable using SERS with Au nanoparticles for the rapid detection of PG residues in duck meat.

4. Conclusions

Firstly, the absorption spectra of Au nanoparticles, the SERS spectra of PG solution, and PG duck meat extract and their vibrational assignment were analyzed, and these analyses could provide the realistic basis for the detection of PG residues in duck meat. Secondly, the effects of Au nanoparticles addition, sample addition, NaCl solution addition, and adsorption time on the SERS intensities of PG duck meat extract were discussed, respectively, and their optimal experimental conditions were determined, respectively. Finally, the SERS spectra of 10 samples with different mass concentrations of PG in duck meat extract were collected under the optimal conditions, and the model of PG residues in duck meat

extract was established and analyzed. The result showed that a good linearity was obtained between the SERS intensities at 993 cm⁻¹ and the concentrations of PG in duck meat extract in the range of 0.5~15 mg·L⁻¹, $Y = 831.68X + 1997.1$, and the determination coefficient was 0.9553. The determination coefficient of PG in duck meat extract between the actual values and the predictive values was 0.9757, the root mean square error (RMSEP) was 0.6496 mg·L⁻¹, and the recovery rate was 90~121%. The experimental results indicated that it was feasible that SERS with Au nanoparticles was used for the rapid detection of PG residues in duck meat.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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