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Overlapping of Second Order Scattering and Frequency Double Scattering Spectra Method and Resonance Rayleigh Scattering Method for the Determination of 6-Benzyladenine in Bean Sprout

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Abstract In this work, second order scattering (SOS), frequency double scattering (FDS), the overlapping method of the two (SFOM), and resonance Rayleigh scattering (RRS) method had been developed for sensitive determination of trace 6-benzyladenine (BA) in bean sprout samples. In pH 1.6 HCl-NaAc medium, Pd(II) reacted with BA to form a 1:1 chelate complex, and then, the complex further self-aggregated into nanoparticles $[Pd(II)\text{-}BA]_n$. This resulted in a remarkable enhancement of resonance Rayleigh-scattering (RRS), second-order scattering (SOS), and frequency-double scattering (FDS) spectra. The maximum wavelengths were located at 312 nm (RRS), 632 nm (SOS), and 323 nm (FDS), respectively. The increments of scattering intensities ΔI were directly proportional to the concentration of BA in certain ranges. The detection limits were 7.0 nmol L^{-1} (0.79 μg/kg, RRS), 10.3 nmol L^{-1} (1.16 μg/kg, SOS), 39.4 nmol L^{-1} (4.44 μg/kg, FDS), and 8.6 nmol L^{-1} (0.96 μg/kg, SFOM). In addition, the optimum conditions of the reaction, and the effects of coexisting substances were investigated. The results showed that these methods exhibited a high selectivity. The reaction mechanism and the reasons for the enhancement of scattering were also discussed. Moreover, the feasibility for the SFOM method was illustrated in this paper. The proposed method had been successfully applied to determine a trace amount of BA in bean-sprout samples with the recoveries of 97.0–103.0 %.

Keywords Overlapping method · Second order scattering · Frequency double scattering · Resonance Rayleigh scattering · 6-benzyladenine · Bean sprout

Introduction

Advances in the food and agricultural industry in the past century have allowed many vegetables to be planted with a variety of pesticides and phytohormones in order to enhance their yield. Unfortunately, many of the pesticides and phytohormones pose a potential risk to human health, especially if they are excessively consumed. For this reason, safety data, such as the acceptable daily intake, based on toxicological studies on experimental animals and human clinical studies, have been repeatedly determined and evaluated by Food and Agricultural Organization (FAO) and World Health Organization (WHO) (Liu et al. 2011). 6-Benzyladenine (BA), the first artificially synthesized plant growth regulator, which is also classified as pesticide, has been widely used around the world in horticulture, farming, and fruits growing. It can inhibit the decomposition of chlorophyll, nucleic acid, and protein in plant leaves to prevent the aging of fruits and vegetables to keep them fresh (Tavares and Kende 1970). Additionally, it is effective in accelerating the growth of fruits and grains and increasing their output by stimulating cell division (Wismer et al. 1995; Pan and Xu 2011; Gurmani et al. 2011). Based on the above functions of BA, at present, some market traders add a large amount of BA to bean sprout during cultivating processes to improve their shelf-life, organoleptic quality, and production to get a high rate of interest. The results of toxicology and accumulated experiments indicate that BA is of low toxicity, and its cumulative toxicity to mice is weak (Chen

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1987). However, an excessive intake of BA can cause damage to esophageal and gastric mucosa, and some symptoms such as sicchasia and emesia may occur sequently (Li et al. 2005). In fact, it has been banned to add any pesticides during cultivating processes in sprout vegetables in many countries. For example, in China, hygienic standards for uses of food additives GB2760-1996 (Ministry of Health, People's Republic of China 1996) has regulated that the maximum allowable amount and the maximum residue limit for BA in bean sprout are 0.01 g/kg and 0.2 mg/kg, respectively. But GB2760-2011 (Ministry of Health, People's Republic of China 2011) has banned its use as a kind of food additive. The Korea Food and Drug Administration (KFDA) has set a maximum residue limit for BA at 0.1 mg kg^{-1} for fruits (Korea Food and Drug Administration 2009). And residual pesticides should not be detected in the case of sprout vegetables in Korea (Lee et al. 2013). Therefore, it is essential to establish a simple, sensitive, and rapid approach to administrate BA to ensure the safety of food for consumers.

Several methods have been proposed for the analysis of BA, such as spectrophotometry (Wu and Li 1998), high-performance liquid chromatography (HPLC) (Jin et al. 2007), pyrolysis mass spectrometry (PyMS) (Kim and Liu 2009), electrochemistry (Li 2006; Zhao et al. 2003; Zhang et al. 2012; Tarkowská et al. 2003), etc. Among them, spectrophotometry is widely used in pesticide analysis owing to its simplicity and cheapness, but its sensitivity is not high enough for trace analysis. Although HPLC and PyMS methods have low detection limit and are very useful for the determination of trace BA in some complicated samples, they are at high cost and require costly instrument and skillful operators. Electrochemical technique offers advantages of sensitivity, selectivity, and mechanical stability, yet it is tedious and time consuming to fabricate functionalized electrodes. Hence, it is of great significance to develop a new, convenient, rapid, and sensitive method to detect a trace amount of BA.

Resonance Rayleigh scattering (RRS), second order scattering (SOS), and frequency double scattering (FDS) spectra have been paid more and more attention due to their convenience, simplicity, and high sensitivity. As reliable analytical techniques, they have been widely applied for the determination of metal ions (Kong et al. 2011; Fu et al. 2012; Jiang, et al 2009), protease (Cai et al. 2011), pharmaceutics (Chen et al. 2010, 2014), viruses (Zou et al. 2012), and so on. In recent years, it also has been used to the analysis of hazardous substances in various food and environmental samples (Song et al. 2011; Zhu et al. 2014; Luo et al. 2014; Lin et al. 2013). In addition, with the development of nanotechnology, analyzing aggregation systems at the nanogram level (Jiang et al. 2006, 2008; Xu et al. 2012) in the RRS technique have been an obvious attraction for many researchers.

To the best of our knowledge, the RRS technique is proved to be sensitive enough to study trace substances, but RRS signals are generally restricted in single-wavelength responses, which suffer from poorly quantified or variable factors such as the apparatus response, probes' concentration, and environment around the probes (Hao et al. 2009). To solve these problems, triple-wavelength overlapping method (Hao et al. 2009) and dual-wavelength overlapping method (Cui et al. 2011) have been developed and successfully applied to the determination of dextran sulfate sodium and chondroitin sulfate, respectively. However, so far, the feasibility for analysis of multi-wavelength overlapping RRS method signals still has not been illustrated.

Compared to RRS method, although SOS and FDS methods usually show lower signals, it provides higher stability. Thus, to develop their advantages and compensate for these defaults, herein, for the first time, we propose a SOS and FDS overlapping method which also can conquer variable apparatus and environmental factors. Furthermore, the feasibility for this method is elaborated in this paper. The method is proved to be sensitive and selective. It has been successfully applied to the determination of BA in bean sprout samples. Additionally, this method extensively enriches the research contents of RRS and will bring new energy to the application of RRS method.

Experimental

Apparatus and Reagents

A F-2,500 spectrofluorophotometer (Hitachi Company, Japan) was used for recording the RRS, SOS, and FDS spectra and measuring the scattering intensities. The slits (EX/EM) were 5.0/5.0 nm for RRS and 10.0/10.0 nm for SOS and FDS. The PMT voltages of spectra were all 400 V. A UV-2,450 spectrophotometer (Shimadzu, Japan) was used to acquire absorption spectra. A Hitachi S-4,800 scanning electron microscope (SEM) (Tokyo, Japan) was used to observe the morphology. A pHS-3C meter (Shanghai Scientific Instruments Company, China) was used to measure the pH values of the solutions.

A stock solution of 2.0×10^{-3} mol L^{-1} BA (Sanland Chem International Inc. China) was prepared by dissolving 0.0451 g BA with 10.0 mL 1.0 N HCl, and appropriate amounts of 1.0 mol L^{-1} NaOH was used to adjust the pH value to nearly neutral. The above solution was diluted in a 100-mL volumetric flask with water and stocked at 4 °C. The working solution was obtained by diluting the stock solution to 2.0×10^{-5} mol L^{-1}. A stock solution of 1.0×10^{-2} mol L^{-1} $PdCl_2$ (Shanghai Reagent Factory, China) was prepared by dissolving 0.1773 g $PdCl_2$ in 0.5 mL concentrated hydrochloric acid and diluting to 100 mL in a volumetric flask with water. The working solution was prepared by diluting the stock solution of $PdCl_2$ to 2.0×10^{-4} mol L^{-1} .HCl-NaAc buffer solution was

prepared by mixing 1.0 mol L^{-1} NaAc and 1.0 mol L^{-1} HCl according to a suitable proportion and was adjusted with a pH meter. All reagents were analytical reagent grade (A.R), and doubly distilled water was used throughout.

General Procedure

HCl-NaAc buffer solution 1.0 mL with pH 1.6, 1.0 mL of 2.0×10^{-4} mol L^{-1} Pd(II), and an appropriate volume of the BA solution were added in a 10.0-mL calibrated flask. The mixture was diluted to the mark with doubly distilled water at room temperatures (25±5 °C). After the reaction for 8 min, the RRS spectra of the system was recorded with synchronous scanning at $\lambda_{ex}=\lambda_{em}$ in the range of 220~800 nm; then, SOS and FDS spectra were recorded by scanning at $\lambda_{ex}=1/2\lambda_{em}$ and $\lambda_{ex}=2\lambda_{em}$, respectively. RRS, the scattering intensities, I_{RRS}, I_{SOS}, and I_{FDS} for the system and for the reagent blank I^0_{RRS}, I^0_{SOS}, and I^0_{FDS}, were measured at their own maximum wavelengths, $\Delta I=I-I^0$.

Results and Discussion

RRS Spectra

The RRS spectra of reaction systems are shown in Fig. 1. From Fig. 1a, it could be seen that the RRS intensities of Pd(II) and BA are very faint under the measurement condition. When Pd(II) reacted with BA to form a chelate complex, the RRS intensity was enhanced greatly, and the maximum scattering wavelengths was located at about 312 nm. Fig. 1b shows the linear relationship of BA concentration with RRS intensity. So, the RRS method could be used to the determination of BA.

SOS and FDS Spectra

The SOS and FDS spectra of Pd(II), BA, and Pd(II)–BA systems are shown in Figs. 2 and 3. It could be seen that under the experimental conditions, the FDS and SOS intensities of Pd(II) and BA systems were very weak, but the Pd(II)–BA system had strong SOS and FDS intensities. Their maximum wavelengths ($\lambda_{ex}/\lambda_{em}$) were located at 316 nm/632 nm (SOS) and 646 nm/323 nm (FDS). The enhancement intensities of FDS and SOS were directly proportional to the concentration of BA in certain ranges. Hence, the SOS and FDS methods could be applied to the determination of a trace amount of BA.

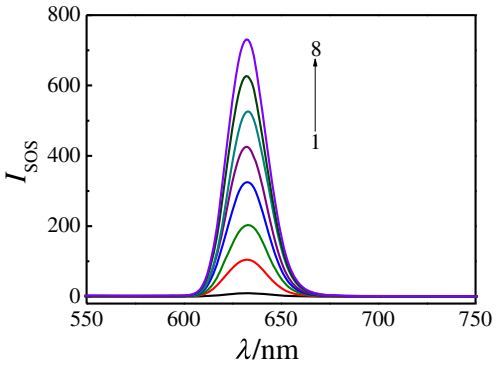

Fig. 2 SOS spectra of Pd(II)–BA system. *1* indicates Pd(II), *2–8* indicates Pd(II)–BA, and *1–8* indicates c_{BA} which are follows: 0, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0 ($\times10^{-6}$)mol L^{-1}; $c_{Pd(II)}=2.0\times10^{-5}$ mol L^{-1}, pH=1.6

Optimum Conditions of the Reaction

Effect of Acidity

Three buffer solutions, BR, HCl-NaAc, and Na_2HPO_4-citric acid, were used to investigate the effects of acidity on RRS, SOS, and FDS intensities. The results showed that in HCl-NaAc buffer solution, the sensitivities and stability of the system were the best. So, HCl-NaAc buffer solution was selected to adjust the pH of the solutions. It could be seen from Fig. 4 that the optimal pH range of HCl-NaAc buffer solution are 1.0~2.2 (RRS), 1.5~2.5 (SOS), and 1.5~2.0 (FDS). Therefore, 1.0 mL of pH 1.6 HCl-NaAc buffer solution was chosen for the reaction.

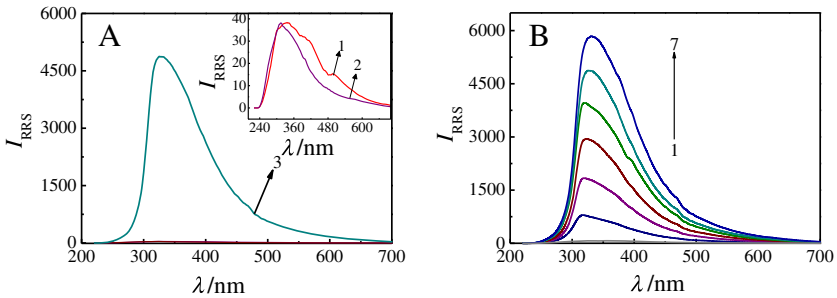

Fig. 1 RRS spectra. **a** *1* indicates Pd(II), *2* indicates BA, and *3* indicates Pd(II)–BA; $c_{Pd(II)}=2.0\times10^{-5}$ mol L^{-1}, $c_{BA}=1.0\times10^{-5}$ mol L^{-1}, pH=1.6. **b** *1* indicates Pd(II), *2–7* indicates Pd(II)–BA, and *1–7* indicates c_{BA} which are as follows: 0, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0 ($\times10^{-6}$) mol L^{-1}; $c_{Pd(II)}=2.0\times10^{-5}$ mol L^{-1}, pH=1.6

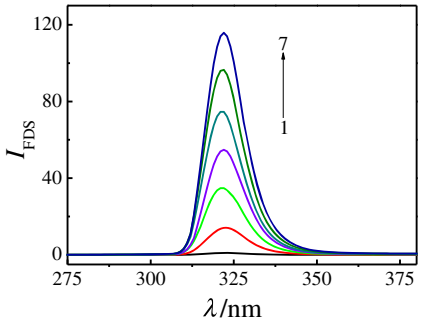

Fig. 3 FDS spectra of Pd(II)–BA system. *1* indicates Pd(II), *2–7* indicates Pd(II)–BA, and *2–7* indicates c_{BA} which are follows: 0, 2.0,4.0, 6.0,8.0,10.0,12.0 ($\times 10^{-6}$)mol L^{-1}; $c_{Pd(II)}=2.0\times10^{-5}$ mol L^{-1}, pH=1.6

Effect of Pd(II) Concentration

The effects of different metal ions such as Zn(II), Cu(II), Fe(III), Hg(II), Cd(II), Co(II), Ni(II), Pt(II), and Pd(II) on the RRS intensity of the reaction were tested. The results showed that Co(II), Ni(II), Zn(II), Cu(II), Cd(II), Fe(III), and Pt(II) could not lead to the enhancements of RRS. The sensitivity of Pd(II) as a reaction reagent was much higher than that of Hg(II). Therefore, Pd(II) was selected as a reaction reagent. The influences of the concentration of Pd(II) on the RRS, SOS, and FDS intensities of the Pd(II)–BA system were also investigated. The experiment results showed that at first, ΔI enhanced gradually with the increase of Pd(II) concentration; then, it reached the maximum and remained stable in the range of 1.0×10^{-5}~4.0×10^{-5} mol L^{-1} (RRS), 1.0×10^{-5}~3.0×10^{-5} mol L^{-1} (SOS), and 1.0×10^{-5}~2.5×10^{-5} mol L^{-1} (FDS). And it would decrease if a higher amount of Pd(II) was added to the Pd(II)–BA system. So, we chose 2.0×10^{-5} mol L^{-1} Pd(II) as a suitable concentration.

Effect of Ionic Strength

The effects of ionic strength on RRS, SOS, and FDS intensities of the Pd(II)–BA system were examined. They were obtained by changing the NaCl concentration while keeping the Pd(II) and BA concentrations and the pH constant. The experiment showed that when the NaCl concentration was lower than 0.01 mol L^{-1}, ΔI almost kept unchanged, but it would gradually decrease if the concentration of NaCl continues to increase.

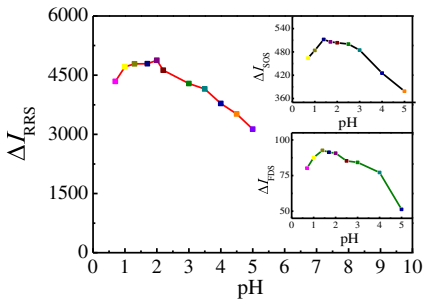

Fig. 4 Effect of acidity. $c_{Pd(II)}=2.0\times10^{-5}$ mol L^{-1}, $c_{BA}=1.0\times10^{-5}$ mol L^{-1}

Effects of Temperature and the Stability of the Reaction

The effects of temperature on RRS, SOS, and FDS intensities were investigated. The results showed that the ΔI_{RRS} reached the maximum and kept constant over the range of 10~30 °C. At the optimum temperature, the reaction completed in 5 min, and ΔI would remain stable for 2 h. So, all samples were determined after the reaction for 8 min at room temperature (25±5 °C).

Calibration Graphs

Under optimum conditions, the different concentrations of the BA solution reacted with Pd(II), and the I_{RRS}, I_{SOS}, and I_{FDS} intensities were measured at 312 nm, 632 nm, and 323 nm, respectively. The calibration graphs of the enhanced scattering intensity ΔI versus the BA concentrations were constructed. Linear regression equation, correlation coefficient, linear ranges, and detection limits were listed in Table 1. It could be seen from Table 1 that the detection limits were 7.0 nmol L^{-1} (RRS), 10.3 nmol L^{-1} (SOS), 39.4 nmol L^{-1} (FDS), and 8.6 nmol L^{-1}(SFOM). The sensitivities of the four methods were all very high. Among the four methods, the RRS method was the most sensitive, and SFOM was comparable to it. Analytical features of some typical methods employed for BA determination are shown in Table 2. Also, the results of the comparison for the analysis of BA in bean sprout with some other methods are listed in Table S1. From Table 2 and Table S1, it could be seen that the detection limits of the RRS and SFOM methods are lower than or comparable to that of other common analytical methods. Therefore, more suitable methods for the determination of a trace amount of BA had been developed.

The Formation of the Chelate Complex and the Reasons for RRS Enhancement

When Pd(II) reacted with BA, it not only resulted in the obvious enhancement of RRS, SOS, and FDS but also aroused the changes of absorption spectra (as shown in Fig. 5). As seen in Fig. 5, Pd(II) had a very faint absorption while BA had a strong peak at 284 nm. When Pd(II) associated with BA, the maximum absorption wavelength shifted to 294 nm. Both the changes of RRS and absorption

Table 1 Related parameters of calibration curves

Method	λ (nm)	Linear equation (c, μmol L^{-1})	Linear range (c, μmol L^{-1})	R	Detection limit (nmol L^{-1})
RRS	312	ΔI=−232.7+505.7c	0.46~12.0	0.9995	7.0
SOS	632	ΔI=−7.2+52.3c	0.14~14.0	0.9993	10.3
FDS	323	ΔI=−7.2+10.2c	0.71~12.0	0.9998	39.4
SFOM	632+323	ΔI=−16.0+62.8c	0.71~12.0	0.9993	8.6

Table 2 Analytical features of some typical methods employed for BA determination

Method*	Linearity (μmol L^{-1})	Detection limit (nmol L^{-1})	Remarks
FL (Li et al. 2013)	0.2~66.6	75.5	Rapid, effective, and selective, but the sensitivity is lower
RRS (Li et al. 2013)	0.2~66.6	36.4	
EC(Li 2006)	0.05~2.5	20	Low-cost and sensitive yet require much time and several complicated steps to fabricate functionalized electrodes
(Zhao et al. 2003)	0.04~10.0	5.0	
(Zhang et al. 2012)	1~30	900	
HPLC-MS (Jin et al. 2005)	0.22~8.88	66	Effective and selective, but need expensive equipments; using toxic organic solvents
SFMO	0.71~12.0	8.6	Sensitive, selective, simple, rapid, and no need for toxic organic solvents
RRS (Present work)	0.46~12.0	7.0	

FL fluorsecence, *EC* electrochemistry, *HPLC-MS* high-performance liquid chromatography-mass spectrum

spectra indicated that a new complex had formed. The composition ratio of the chelate complex was established by molar ratio method and Job's method (Fig. 6). The results showed that the ratio of BA to Pd(II) was 1:1. The reaction mechanism for the Pd(II)–BA system is speculated in Fig. 7. BA may be associated with Pd(II), and they formed a stable five-membered ring chelate complex. Furthermore, the complex would self-aggregate to form dispersed nanoparticles, which was confirmed by the SEM (Fig. 8).

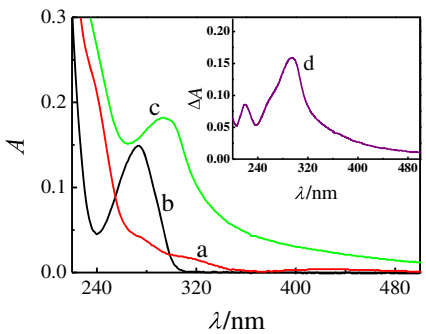

Fig. 5 Absorption spectra of Pd(II)–BA system. **a** Pd(II); **b** BA; **c** Pd(II)–BA; **d** Pd(II)–BA; $c_{Pd(II)}=2.0\times10^{-5}$ mol L^{-1},$c_{BA}=1.0\times10^{-5}$ mol L^{-1}, pH=1.6; **a**, **b**, and **c** were determined by using water as blank; **d** was determined by using BA as blank

The reasons for RRS enhancement were also discussed. There were two related reasons for the enhancement. Firstly, resonance enhanced scattering effect. To our knowledge, RRS was a scattering–absorption–rescattering process produced by the resonance of scattering and absorption, so RRS spectra should be closely related to the absorption spectrum (Fig. 9). The comparison between the absorption spectrum and RRS spectrum clearly demonstrated that RRS peak (312 nm) was close at its absorption peak (294 nm). Therefore, RRS was significantly enhanced. Secondly, the formation of nanoparticles not only enhanced the hydrophobicity of the aggregates (Wang et al. 2013; He et al. 2005) but also enlarged the volume of the scattered molecules. It was the main reason of the enhancement of RRS.

The Feasibility Analysis

Twelve blank solutions were measured to determine the standard deviation of a population, and the results were as follows: σ_{RRS}=1.1757, σ_{SOS}=0.1794, and σ_{FDS}=0.1340. From the data, we would know that the standard deviation of FDS was close to that of SOS, which was a drastic testimony that the data of FDS and SOS could overlap with each other. The overlapping result is shown in Fig. 10. The detection limit was

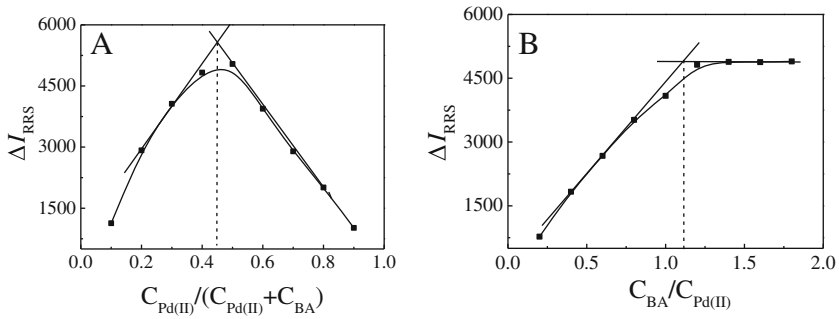

Fig. 6 The composition ratio of BA with Pd(II). **a** Job's method $c_{Pd(II)}+c_{BA}=2.0\times10^{-5}$ mol L^{-1} and pH=1.6. **b** molar ratio method $c_{Pd(II)}=1.0\times10^{-5}$ mol L^{-1}, pH=1.6

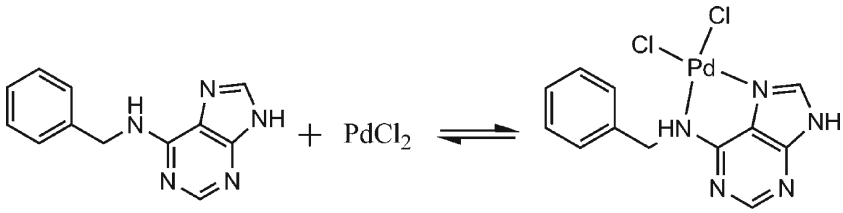

Fig. 7 The reaction mechanism for Pd(II)–BA system

calculated according to the larger standard deviation (σ_{SOS}= 0.1794), and it was 8.6 nmol L^{-1}.

Selectivity of the Method

Under optimum conditions, the effects of some coexisting substances on the determination of the BA of 4.0×10^{-6} mol L^{-1}, such as inorganic compounds, saccharides, cationic surfactants, and amino acids, were investigated, and the results are given in Table 3. As shown, most of the common metal ions, vitamins, saccharines, and amino acids did not interfere with the determination of BA, but cationic surfactants, Hg^{2+} and I^-, interfered. Fortunately, the amounts of these substances were extremely low in bean sprout samples. Also, 60 times of Hg^{2+} did not interfere after being masked. Hence, the method had a good selectivity and could be applied to the determination of BA in bean sprouts.

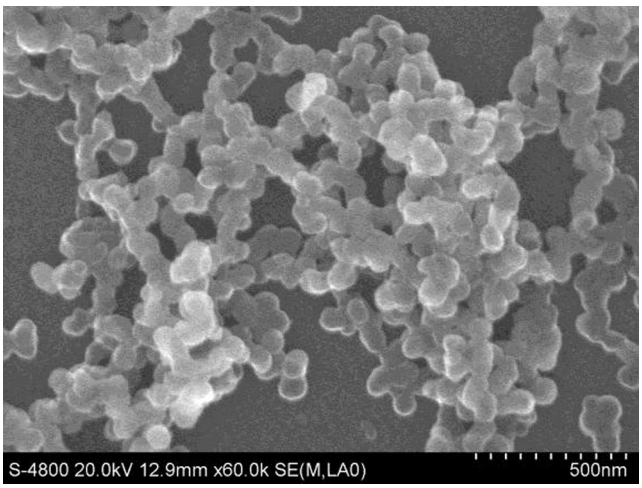

Fig. 8 SEM image of $[PdCl_2\text{-}BA]_n$ nanoparticles

Analytical Applications

To determine the BA in bean-sprout samples, we chose the SFOM and RRS methods for analytical applications since the RRS method had the highest sensitivity, and SFOM was comparable to it. Three bean-sprout samples were obtained from three different supermarkets in Chongqing, China. As

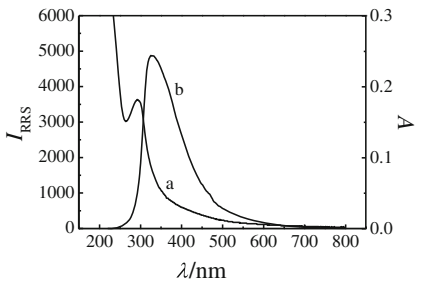

Fig. 9 Comparison between absorption (**a**) and RRS (**b**) spectra of Pd(II)–BA system. c_{BA} 1.0×10^{-5} mol L^{-1}, $c_{Pd(II)}$ 2.0×10^{-5} mol L^{-1}, and pH=1.6

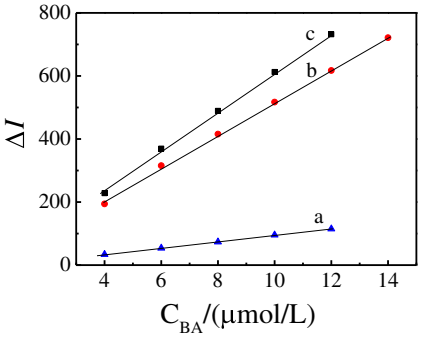

Fig. 10 Calibration graph of SOS, FDS, and SFOM of Pd(II)–BA system. *a* indicates FDS, *b* indicates SOS, and *c* indicates SFMO

reported (Jin et al. 2007), for each sample, 1.0 g of the chopped bean sprout was spiked with an adequate amount of BA as an internal standard, and then, 25.0 mL acidified ethyl alcohol was added. The above samples were partially immersed into a KQ 250DB ultrasonic cleaning bath (Kunshan Ultrasonic, Jiangsu, China) adjusted at 200 W. After a set time (30 min), the extract was transferred into a centrifuge tube and centrifuged for 15 min at 7,800 rpm for protein precipitate separation. Then, the supernatant was concentrated to 5.0 mL. The resulting solution was mixed with Pd(II) and NaAc–HCl buffer as described above. Then, the concentration of BA was determined, and the recovery was tested by using the standard addition method. The results are listed in Table 4. It could be seen that the methods had a good accuracy (recovery was from 97.0 % to 103.0 %) and repeatability (RSD was from 1.2 % to 3.6 %). The results were consistent with the literature method (Wu and Li 1998). Therefore, the methods could be applied to the determination of BA in bean-sprout samples.

Table 3 Effects of coexisting substances (c_{BA}=4.0×10^{-6} mol L^{-1})

Coexisting substance	Concentration (μmol L^{-1})	Relative error (%)	Coexisting substance	Concentration (μmol L^{-1})	Relative error (%)
$NaNO_3$	2,000	0.5	KNO_3	380	−3.4
NH_4Cl	100	4.8	Glucose	400	1.3
KBr	400	4.5	Saltose	1,000	−2.7
$MgSO_4$	20	4.2	Sucrose	400	−2.5
$CuSO_4$	1,200	2.4	L-Tyrosine	200	−2.3
$ZnCl_2$	600	0.3	Phenylalanine	100	−0.7
$CaCl_2$	2,000	−4.9	L-Arginine	2,000	−4.0
$MnSO_4$	2,000	4.8	L-Aspartic acid	400	1.3
$NH_4Fe(SO_4)_2$	400	4.7	β-cyclodextrin	200	−4.6
NaF	500	0.5	Vitamin A	200	−2.8
$HgCl_2$	3, 60[a]	3.7, 3.5[a]	Vitamin B1	50	3.3
cis-platinum	600	2.8	Vitamin K	280	−4.3
$NiSO_4$	800	−2.1	Vitamin C	80	2.4
$CoSO_4$	800	−3.2	CPB	5.0	−4.5
$CdCl_2$	600	4.5	CTAB	4.5	−4.7
KI	2.0 ,	4.6			

[a] Added 5.0×10^{-3} mol L^{-1} citric acid sodium 0.5 mL

CPB cetylpyridinium bromide, *CTAB* cetyltrimethylammonium bromide

Table 4 Determination of BA in bean-sprout samples

Sample	Found (mg/Kg)			Added (mg/Kg)	Total found (n=5) (mg/Kg)			RSD (n=5) (%)			Recovery (%)		
	RRS	SFOM	UV[a]		RRS	SFOM	UV	RRS	SFMO	UV	RRS	SFMO	UV
No.1	ND	ND	ND	2.0	1.94	2.02	2.12	2.2	1.2	1.9	97.0	101.0	106.0
No.2	ND	ND	ND	6.0	6.18	5.92	5.90	3.6	3.4	3.9	103.0	98.6	98.3
No.3	ND	ND	ND	10.0	9.89	10.02	10.24	1.6	2.6	2.4	98.9	100.2	102.4

[a] Ultraviolet spectrophotometry

ND not detected

Conclusion

A new, simple, rapid, and sensitive method for the determination of BA with Pd(II) by SFOM was successfully developed, and also the feasibility for this overlapping method had been firstly illustrated. Under optimum conditions, Pd(II) could react with BA to form a 1:1 chelate complex of Pd(II)-BA, which would self-aggregate to form $[PdCl_2\text{-}BA]_n$ nanoparticles. This resulted in the enhancements of SOS, FDS, and RRS. The analytical results demonstrated that the sensitivity of SFOM was comparable to the RRS method, but it was more stable and selective since it could compensate many variable factors from the apparatus, environment, and the probes. In general, SFOM was a promising method which also extensively enriched the research contents of the applications of RRS.

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Conflict of Interest Xiaoli Hu declares that she has no conflict of interest. Man Qiao declares that she has no conflict of interest. Jidong Yang declares that he has no conflict of interest. Shaopu Liu declares that he has no conflict of interest. Zhongfang Liu declares that she has no conflict of interest. Jinghui Zhu declares that he has no conflict of interest. This article does not contain any studies with human or animal subjects.

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