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Highly sensitive and selective colorimetric detection of cartap residue in agricultural products

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ABSTRACT

The residue of pesticide has posed a serious threat to human health. Fast, broad-spectrum detection methods are necessary for on-site screening of various types of pesticides. With citrate-coated Au nanoparticles (Au NPs) as colorimetric probes, a visual and spectrophotometric method for rapid assay of cartap, which is one of the most important pesticides in agriculture, is reported for the first time. Based on the color change of Au colloid solution from wine-red to blue resulting from the aggregation of Au NPs, cartap could be detected in the concentration range of 0.05–0.6 mg/kg with a low detection limit of 0.04 mg/kg, which is much lower than the strictest cartap safety requirement of 0.1 mg/kg. Due to the limited research on the rapid detection of cartap based on Au NPs, the performance of the present method was evaluated through aggregation kinetics, interference influence, and sample pretreatment. To further demonstrate the selectivity and applicability of the method, cartap detection is realized in cabbage and tea with excellent analyte concentration recovery. These results demonstrate that the present method provides an easy and effective way to analyze pesticide residue in common products, which is of benefit for the rapid risk evaluation and on-site screening of pesticide residue.

1. Introduction

Cartap, an organonitrogen pesticide, has long been recognized as an analogue of nereistoxin since it was first introduced in Japan in1967 [1]. It acts against pests in target rice, sugarcane, fruit tree, vegetable and tea tree with multiple approaches, including contact, stomach and gaseous. Due to its low toxicity and high insecticidal activity, cartap has been widely used all over the world [2]. For example, cartap accounts for 19% of the insecticide usage in rice and rice–fish farms in the Mekong Delta, Vietnam [3], and it is also one of the most frequently used insecticides in rice and tea farms of China [4]. However, the overuse of cartap could lead to dangerous levels of residues, which enters the food supply chain and results in an unexpected hazard for human health. Therefore, maximum residue limits (MRLs) for cartap have been defined by food administrations. For example, the European Commission set a permissible limit of cartap at 0.1 mg/kg for tea [5], and China set the maximum level of cartap at 20 mg/kg and 0.1 mg/kg for tea and sugarcane, respectively [6].

In order to reduce the risk of cartap distribution in the environment and set the safe use standards of cartap, the quantitation of cartap level in contaminated materials is of great significance. Several analytical methods have been established for the determination of cartap, such as spectrophotometry [7], thin-layer chromatography [8], high performance liquid chromatography [9], gas chromatography (GC) [10,11], GC–mass spectrometry (GC–MS) [12], liquid chromatography–tandem mass spectrometry [13], and polarography [14]. However, most of the methods in published literatures are aimed for the qualitative and quantitative determination of cartap with tedious experimental procedures. Furthermore, cartap needs to be decomposed into nereid poison under alkaline condition before detection. Although GC with a microelectron capture detector could realize detection of cartap without decomposition, this analytical method is time-consuming and needs expensive instruments. Therefore, simple and convenient methods, such as using colorimetric sensors, for detection of cartap are still of significant need.

Due to several advantages of Au NPs, including extremely strong extinction coefficients [15–17], strong size- and distance-dependent optical properties [18,19], convenient immobilization of various functional molecules [20], capability of further amplification by silver stain [21,22], and their high quenching efficiency toward various fluorophores [23], Au NPs have been used as one

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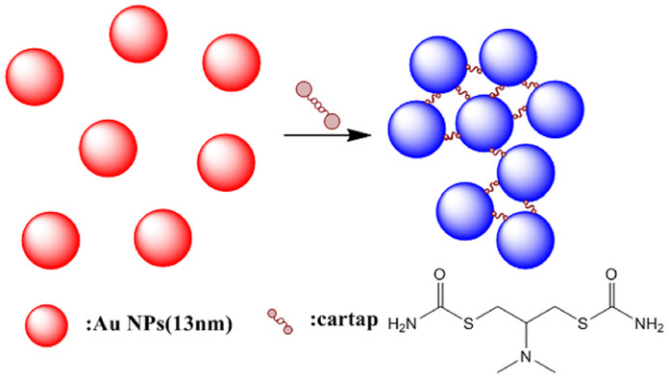

Scheme 1. Schematic representations of cartap-induced aggregation of Au NPs.

of the most advantageous nanomaterials for colorimetric reporting in chemical and biological detection. The controlled assembly-based Au NPs sensors have been proven to achieve high sensitivity in visual detection for all kinds of target molecules, including viruses [24,25], proteins [26,27], DNA [18,28], cancerous cells [29,30], metal ions [31], sugars [32], small molecules [33,34], and so on.

Given that electron-rich nitrogen exhibits much stronger binding ability/affinity to Au NPs, pyridine-like compounds are often used as phase transfer agents for Au NPs [35]. Cartap has two primary amine groups, so it offers a possibility to coordinate to Au NPs and cross-link Au NPs. As illustrated in the inset of Scheme 1, the positively charged amine groups of cartap show strong interaction with Au NPs, which decreases the stability of citrate-stabilized Au NPs against aggregation, thus causing obvious color changes and indicating the presence of cartap. The clearly distinguishable color change facilitates a simple sensor readout that can be performed by the naked eye, or be measured by spectrophotometry. Based on this principle, herein, we developed a simple colorimetry for the sensitive and selective detection of cartap.

2. Experimental

2.1. Chemicals

Cartap was obtained from Sumitomo Chemical (Japan). Other pesticides were purchased from China National Institute of Standardization (Beijing, China). Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 4H_2O$) and sodium bisulfate monohydrate ($NaHSO_4 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other chemicals were of analytical reagent grade and used as received. Distilled water was used in all experiments.

2.2. Synthesis of Au NPs

All the glasswares used in the procedures were soaked and cleaned in a bath of freshly prepared aqua regia, rinsed thoroughly in pure water, and dried in air prior to use. 13 nm Au NPs were synthesized by the reduction of $HAuCl_4$ with sodium citrate following a literature procedure [19]. Briefly, 100 mL of 1 mM $HAuCl_4$ (4 mL of 1% (w/w) $HAuCl_4$ solution dissolved in 96 mL of H_2O) was heated to reflux while stirring and then 10 mL of a 38.8 mM trisodium citrate (10 mL of 1.14% (w/w) trisodium citrate) solution was added quickly, which resulted in a color change of the solution from pale yellow to deep red. After the color change, the solution was refluxed for an additional 15 min and left to cool to room temperature. Then, the solution was stored at 4 °C for further study.

2.3. Detection of cartap

Typically, 10 mL of Au NPs solution was diluted with 30 mL of water to give a total volume of 40 mL as a stock liquid for the detection of cartap. 0.2 mL of sample solution was taken and added into 0.4 mL of Au NPs solution; then, the mixture was allowed to react for 5 min at room temperature. Absorbance spectra of the mixture solution were determined with a UV–vis spectrometer. The color change of the mixture solution was also recorded by a digital camera. The aggregating kinetics curves of Au NPs at different concentrations of cartap were obtained by the measurements of absorbance spectra at the interval of 0.5 min or 1 min with time up to 30 min. Furthermore, to increase the sensitivity of detection, the experimental condition was further optimized by adding $NaHSO_4$. Typically, 10 mL of original Au NPs solution was diluted with 29.68 mL of water and 0.32 mL of 0.1 M $NaHSO_4$ to give the mixture a total volume of 40 mL. Au NPs solution containing 0.9 mM $NaHSO_4$ was used as a stock liquid for the determination of cartap in real samples.

2.4. Pretreatments of real samples.

To measure cartap in real samples, green tea was pretreated by a method of multiple liquid–liquid extractions with alterations [10,11]. Typically, 5 g of tea powder and 40 mL of 0.05 M HCl were ultrasonicated for 40 min at 60 °C. The mixture was centrifuged at 4000 rpm for 5 min. During this step, cartap was protonated and extracted in the acidic aqueous with other soluble components. The nonionized organic compounds including acetamiprid remaining in solid residue were discarded. The resulted supernatant was washed with 30 mL of n-hexane and centrifuged at 4000 rpm for 5 min. The upper layer was discarded, and the lower layer was washed with another 30 mL of n-hexane again. This step was beneficial to decrease the content of amphiphilic molecules in the mixture. After that, the aqueous layer was carefully adjusted to pH 8.5–9.0 with 2 M NaOH. During this process, the amino groups of cartap were deprotonated, and the solubility of cartap in n-hexane was greatly increased. Then, 30 mL n-hexane was added into the aqueous layer to extract cartap from aqueous phase to organic phase. At the same time, the interference from inorganic salts could also be removed by this step because inorganic salts could not dissolve in n-hexane. The mixture was shaken for 1 min and centrifuged at 4000 rpm for 5 min. The organic layer was collected. Finally, 5 mL of water with pH 4.0 was added to the organic layer. Cartap was transferred to the aqueous layer by the protonation of amino groups in cartap again, and the obtained aqueous layer was used for cartap determination.

2.5. Instruments and measurements

The absorption spectra were recorded with a UV-2550 spectrophotometer (Shimadzu, Japan) at room temperature. Transmission electron microscopy (TEM) measurements were performed on a HT7700 (Hitachi, Japan) at 80 kV.

3. Result and discussion

3.1. Colorimetric sensitivity of Au NPs suspension

Electron-rich nitrogen could bind to the surface of Au NPs via Au–N bonds and shorten the average distance between Au NPs,

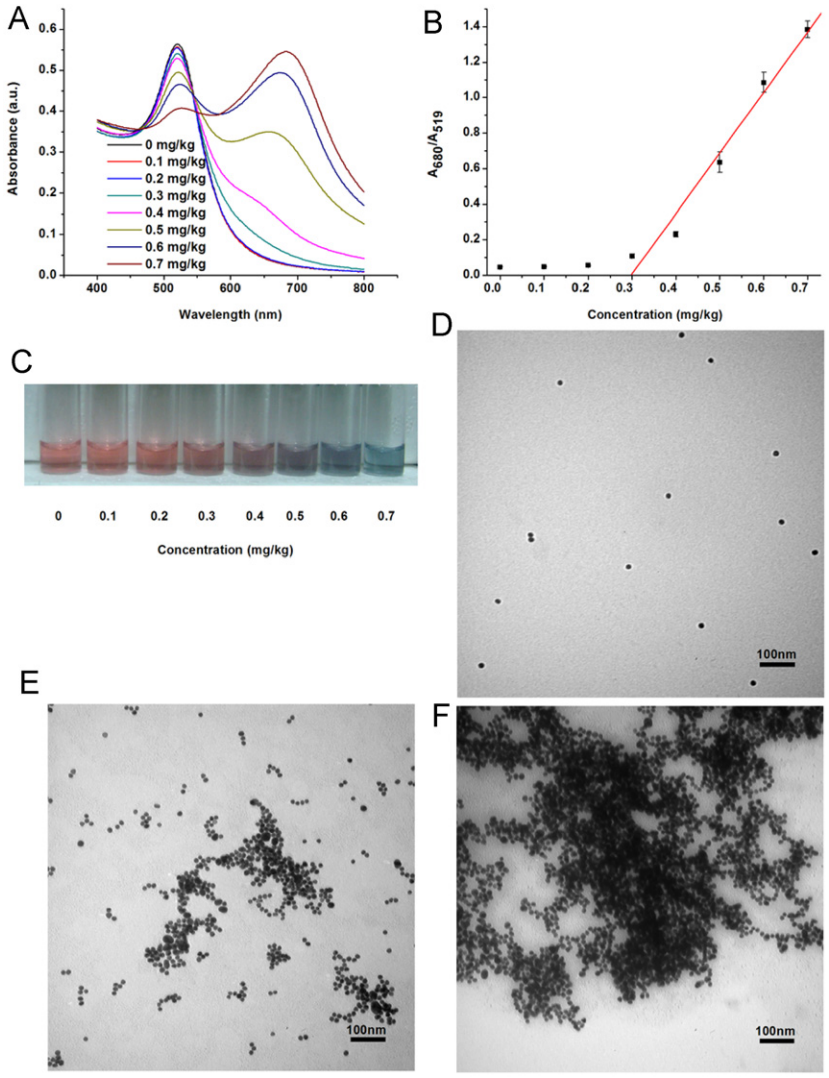

Fig. 1. (A) Visible absorption spectra of the Au NPs at different cartap concentrations; (B) Plots of A_{680}/A_{519} versus different cartap concentrations corresponding to (A); (C) visual color change of Au NPs corresponding to (A); TEM image of Au NPs with addition of (D) 0, (E) 0.3, and (F) 0.6 mg/kg cartap.

which results in the aggregation of the Au NPs, and is accompanied by a color change from red to blue [36]. Hence, target analytes with electron-rich nitrogen could be easily quantified by monitoring the ratio of aggregated to dispersed Au NPs [37]. As a representative of organonitrogen pesticide, cartap should be easily detected by Au NPs-based colorimetry. The aggregation of Au NPs induced by cartap is monitored by UV–vis spectroscopy (Fig. 1A). Upon the addition of cartap to the citrate-coated Au NPs system at the volume ratio of 1:2, a gradual decrease in the original plasmon absorption peak at 519 nm along with the increase of a new absorption band at 680 nm is observed. Furthermore, a typical plot of the extinction ratio (A_{680}/A_{519}) in the absence and presence of different concentrations of cartap is obtained. As shown in Fig. 1B, the extinction ratio increases slightly with the increase of cartap concentration in the low concentration range (< 0.3 mg/kg), whereas a significant extinction ratio increase is observed in the concentration range higher than 0.3 mg/kg, while the extinction ratio and cartap concentration over the range of 0.3–0.7 mg/kg exhibits a linear correlation with an R of 0.9875. Simultaneously, the color of the mixture solution changes from wine-red to purple and finally to blue progressively (Fig. 1C). Clear color changes are observed from wine red to deep red at a cartap concentration as low as 0.3 mg/kg, which indicates that the proposed method could be used to detect cartap by visual evaluation. Visual evaluation of pesticides without the use of instruments is of particular importance because of its convenience [38,39]. In order to know the morphology feature of the Au NPs before and after the occurrence of spectral and color changes, TEM characterization is performed. The as-prepared Au NPs are well-dispersed with uniform particle size (Fig. 1D). However, after addition of 0.3 and 0.6 mg/kg cartap, the Au NPs aggregate together (Fig. 1E and F, respectively). The results of TEM analysis confirm directly the experimental observations discussed above, which well agree with the results of visible absorption spectra. These experimental phenomena are consistent with the reported finding on the aggregated Au NPs cross-linked by other molecules, such as melamine [40] and cationic thiocholine [34].

3.2. Optimization of experimental conditions

In order to meet the strictest cartap safety requirement of 0.1 mg/kg, experimental conditions should be optimized. As pointed out earlier, sensitivity and dynamic range of the colorimetry are dependent on the resistance of Au NPs to aggregation and can be adjusted by changing the buffer composition of the Au NPs [41]. To increase the detection sensitivity, the effect of $NaHSO_4$ is investigated. It's well known that SO_4^{2-} anions could destroy the stability of citrate-capping metal NPs colloids by

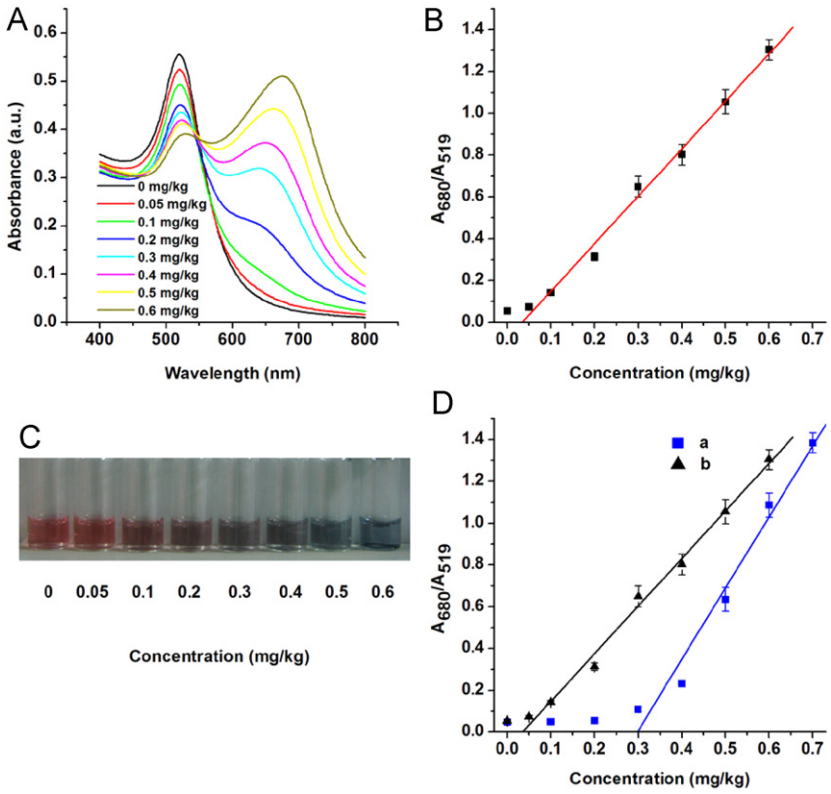

Fig. 2. Optimized sensitivity of Au NPs with $NaHSO_4$. (A) Visible absorption spectra of the Au NPs at different cartap concentrations; (B) Plots of A_{680}/A_{519} versus different cartap concentrations corresponding to (A); (C) visual color change of Au NPs corresponding to (A) and (D) the evolutions of A_{680}/A_{519} values of Au NPs with different cartap concentrations before (a) and after (b) the addition of 0.9 mM $NaHSO_4$.

occupying the surface of metal NPs [42,43]. The acidity of HSO_4^- salt further promotes destabilization of Au NPs [33]. Previous studies have shown that the addition of $NaHSO_4$ improves the sensitivity of Au NPs [5,33]. Here one-factor-at-a-time methodology is used to optimize the experimental conditions. Fig. 2A shows the VIS spectra of Au NPs solution containing 0.9 mM $NaHSO_4$ and different concentrations of cartap after a mixing time of 5 min. With the addition of cartap from 0 to 0.6 mg/kg, the absorbance of Au NPs solution at 519 nm decreases gradually and the absorbance around 680 nm increases obviously. The extinction ratio (A_{680}/A_{519}) is calculated based on the data shown in Fig. 2A, and a good linear relationship between the value of A_{680}/A_{519} and concentration of cartap is observed in the range of 0.05–0.6 mg/kg (Fig. 2B). At the same time, the colors of the solutions change from wine-red to purple and finally to blue (Fig. 2C). When the concentration of cartap reaches 0.1 mg/kg, the change in color can be evaluated visually, whereas a color change occurs at 0.3 mg/kg cartap without $NaHSO_4$. Furthermore, the extinction ratio (A_{680}/A_{519}) change of Au NPs solution before and after the addition of $NaHSO_4$ is compared with different cartap concentrations. As shown in Fig. 2D the A_{680}/A_{519} ratios for $NaHSO_4$ optimized Au NPs in the presence of 0.05–0.6 mg/kg cartap are obviously larger than the corresponding ratio for original Au NPs, which indicates that aggregation degree of Au NPs increases with $NaHSO_4$. The calibration curve after the addition of $NaHSO_4$ displays an excellent linearity in the range from 0.05 to 0.6 mg/kg with the detection limit of 0.04 mg/kg. Although there is still a gap between our method and other chromatographic methods (0.01–0.05 mg/kg) [10,12,13] in terms of detection limit, the method developed in present work does not require sophisticated instrumentation. Considering the permissible limits of cartap residue (0.1 mg/kg for tea in EU), the optimized detection well meets with all requirements of rapid detection and is also very simple in implementation. Thus, the method provides a convenient and easy way for qualitative and semi-quantitative determination of cartap in screening [44].

3.3. Aggregation kinetics of AuNPs with cartap

Kinetics is an important aspect of chemical processes, which will benefit to understand the rate, equilibrium and mechanism of chemical processes. Generally, the reaction rate needs to be estimated because a colorimetry with fast response at room temperature is highly preferred for on-site and real-time detection in real sample [45]. Therefore we examine the aggregation kinetics of unmodified Au NPs in the presence of different cartap concentrations by measuring the temporal evolution of A_{680}/A_{519} at the interval of 0.5 min or 1 min with time up to 30 min. Since cartap with higher concentration (>0.8 mg/kg) leads to the rapid precipitation of Au NPs during the mixing of cartap with Au NPs, the kinetic aggregation could not be accurately characterized by UV–vis spectroscopy. Therefore, four typical concentrations of cartap (0.3, 0.4, 0.5 and 0.6 mg/kg) are used to evaluate the aggregation kinetics (Fig. 3A). As anticipated, these curves almost exhibit a rapid increase of extinction ratio in the initial stage, followed by a much slower increase over the following time. In the case of 0.6 mg/kg cartap, the extinction ratio increases very rapidly from 0.05 to 1.03 during the first 3 min, and a slow increase to a maximum value of 1.08 is observed after 5 min. In the case of 0.5 mg/kg cartap, the extinction ratio exhibits a quick increase from 0.05 to 0.50 in the first 2 min, and a slow enhancement to 0.70 in the succeeding 6 min. When the concentration of cartap is further reduced to 0.4 mg/kg or 0.3 mg/kg, however, extinction ratio increases in the first few minutes and reaches a plateau, which means the free cartap molecules are almost exhausted in a shorter time. The aggregation of Au NPs should

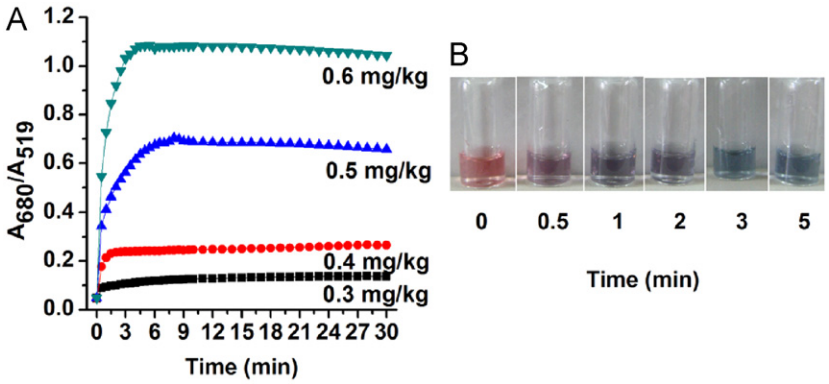

Fig. 3. (A) Plots of A_{680}/A_{519} versus time at different cartap concentrations and (B) the color change of Au NPs with time after the addition of 0.6 mg/kg cartap.

be attributed to the ligand exchange between cartap and citrate ligands at the surface of Au NPs. These detailed observations further suggest that cartap has a strong binding ability with Au NPs, and results in the crosslink of Au NPs. Considering that most of reactions could be completed within 5 min, the temporal evolution of A_{680}/A_{519} is used in the following experiments for the concentration determination of cartap. In addition, the color change of Au NPs with time after addition of 0.6 mg/kg cartap is also observed. As shown in Fig. 3B the wine red of Au NPs solution promptly changes into light purple within 0.5 min, purple within 1 min and finally blue within 3 min after the addition of cartap. The corresponding extinction ratios are about 0.55, 0.73 and 1.03. These results provide a possibility to develop a gold nanoparticle-based rapid detection kit for cartap detection for real samples.

3.4. Interference studies

One disadvantage of the current optical chemosensors is that they are easily disturbed by other analytes [46]. On the other hand, colorimetry based on unmodified Au NPs has been desired under critical conditions owing to its lesser tolerance to interference than that of ligand-stabilized Au NPs [34]. To explore the specific detection of cartap in food using the proposed colorimetry, the selectivity of the sensing system must be tested. Ten kinds of compounds, including omethoate, aldicarb, amitraz, dichlorvos, methamidophos, imidacloprid, triazophos, methomyl, carbaryl and acetamiprid, which are the most common insecticides used in agriculture, are detected by the present method to demonstrate its selectivity. The typical extinction ratio (A_{680}/A_{519}) is still used to estimate the selectivity. The results are shown in Fig. 4. Among the chemicals, cartap exhibits the greatest extinction ratio, and 0.2 mg/kg cartap results in a rapid aggregation of Au NPs. No obvious change of extinction ratio is observed when the other interferences (except acetamiprid) are added. even the concentration of interferences are increased to 3 mg/kg, which is 15 times higher than that of cartap. In addition, their presence did not lead to the distinct color change of Au NPs solution. The results indicate that most insecticides could not disturb the selective detection of cartap in this method. The reason could be attributed to the high affinity of flexible, positively charged molecules to unmodified Au NPs but much less affinity of rigid, negatively charged ones [47]. This difference in affinity could be transformed to the difference in stability of Au NPs in concentrated solutions of salts and finally converted to color change signals. Although the purified acetamiprid with concentration as low as 0.5 mg/kg has serious interference, the effect of acetamiprid in the real sample detection was very small because the pretreated process of real samples described in Section 2.4 was specific for the extraction of alkyl amine. These results confirm

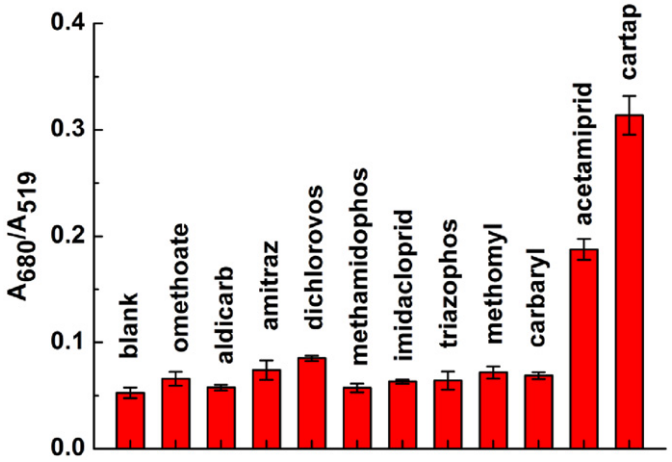

Fig. 4. Corresponding A_{680}/A_{519} ratios of Au NPs with different analytes. The concentrations of cartap and acetamiprid are 0.2 mg/kg and 0.5 mg/kg, respectively, while those of the others are 3 mg/kg.

that the developed strategy has sufficient specificity and cartap can be identified with high selectivity. And also, the high specificity would be achieved by removing the interference through suitable pretreatment process as well as by using modified Au NPs [34,37,48].

3.5. Analysis of cartap in spiked sample

To validate the reliability of the proposed method, the proposed colorimetry and GC were used to detect the amount of cartap in cabbage and tea, respectively. Confirmed cartap-negative samples were spiked with different concentrations of cartap (0.1, 0.3 and 0.5 mg/kg) and pretreated according to the procedure described in Section 2. The calibration curve in Fig. 3B was used for the quantitative determination of cartap in the pretreated samples. At the same time, the pretreated samples were also examined by GC [10]. The results for the spiked 0.1, 0.3 and 0.5 mg/kg samples are displayed in Table 1. The colorimetric determination results of these practical samples are satisfactory, and the recovery is 71.8–104% with the variation coefficient of 4.5–10.7%. The cartap account of the spiked samples detected by the present method and GC is in good accordance, which indicates the method is reliable and practical.

As we mentioned above, the MRLs of cartap in tea are legally regulated at 0.1 and 20 mg/kg by the European Commission and Chinese government, respectively. Therefore, the present method can be used to detect cartap in real sample both with naked eyes observation and a UV–vis spectrometer within 5 min.

Table 1
Detection results of cartap residue in tea and cabbage.

Samples	Added concentration (mg/kg)	GC measured concentration (mg/kg, n=3)	Observed concentration (mg/kg, n=3)	Recovery (%)	C V (%)
Tea 1	0.1	0.073 ± 0.006	0.081 ± 0.008	81.4	9.7
Tea 2	0.3	0.247 ± 0.019	0.216 ± 0.018	71.9	8.1
Tea 3	0.5	0.382 ± 0.024	0.374 ± 0.040	74.7	10.7
Cabbage 1	0.1	0.092 ± 0.005	0.104 ± 0.008	104	8.1
Cabbage 2	0.3	0.311 ± 0.021	0.281 ± 0.017	93.8	6.1
Cabbage 3	0.5	0.439 ± 0.017	0.412 ± 0.019	82.3	4.5

Although the accuracy of rapid method is a little lower than that of GC, whose recovery is 76–103% with the variation coefficient less than 10%, many advantages provided by our method, such as easy sample pretreatment, rapid and visual analysis, high sensitivity, low cost, and low requirement of professional techniques, could facilitate future development of rapid detection of cartap residues. This colorimetry might be used in the alarm system, and would provide promising properties for the possible practical applications.

4. Conclusion

In conclusion, we have developed a simple and sensitive colorimetry for the detection of cartap residue in agricultural products by the direct use of as-prepared or optimized unmodified Au NPs as colorimetric probe. Two amine groups of cartap molecule are demonstrated to be the key factor for the aggregation of Au NPs. The developed method could detect cartap within 5 min by visual assessment, which can tell us a "Yes or No" answer without the aid of any advanced instrument and the need of any complex derivation. With the help of a UV–vis spectrometer, the proposed method can be used to detect cartap with a detection limit of 0.04 mg/kg, which meets the MRLs of cartap in China and EU. The proposed method is simple, fast and cost-effective, which realizes a promising approach toward using nanomaterials for pesticide residue analysis.

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