Microchim Acta (2015) 182:401–408
DOI 10.1007/s00604-014-1347-x

ORIGINAL PAPER

Colorimetric and visual determination of total nereistoxin-related insecticides by exploiting a nereistoxin-driven aggregation of gold nanoparticles

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Received: 28 May 2014 / Accepted: 26 August 2014 / Published online: 3 September 2014

Abstract We describe a method for the visual and colorimetric determination of total nereistoxin-related insecticide residues. It is based on the nereistoxin-induced aggregation of gold nanoparticles (AuNPs). The nereistoxin-related insecticides are first converted to nereistoxins in a pretreatment step that involves liquid–liquid extraction and hydrolysis for sample clean-up. Next, the interaction between nereistoxins and AuNPs provides a possibility to visually semi-quantify or accurately quantify nereistoxins because it is associated with a color change from red to blue. The interaction between nereistoxins and AuNPs is caused by the electrostatic interactions and the strong Au–S covalent bonds. The photometric assay is performed by measuring the ratio of absorbances at 660 and 519 nm, respectively. It has a detection range from 50 to 250 μg kg^{-1} and a detection limit of 40 μg kg^{-1} to for the total quantity of nereistoxin-related insecticides. The visually detectable color change to blue occurs in the 50 to 100 μg kg^{-1} concentration range, and this enables a fast visual test on whether or not the concentration of total nereistoxin-related insecticides exceeds the tolerated level of 100 μg kg^{-1}. The method was applied to the analysis of nereistoxin-related insecticides in agricultural products.

Keywords Colorimetric detection · Nereistoxin-related insecticides · Residue · Gold nanoparticles

Introduction

Increasing attention has been given to the detection of pesticide residues in crops and environment matrices because pesticide residues could enter the food supply chain and result in an unexpected hazard for human health. Nereistoxin insecticides as new biomimetic insecticides were developed in the 1960s [1]. A family of synthetic modification of nereistoxin has been known as commercial insecticides for decades, including cartap, bensultap, thiocyclam, thiosultap, and monosultap. They have been widely used for the control of lepidoptera, coleoptera and diptera insects, at almost all developmental stages, on many crops, including rice, potato, vegetables, and fruit field [2]. Although nereistoxin derivatives are considered as insecticides with low toxicity, the overuse of nereistoxin-related insecticides has led to increased environmental problems and public health risk. Therefore, several international organizations and countries have set the maximum residue limit (MRL) for nereistoxin-related insecticides residues, for example, the European Commission sets a permissible limit of cartap at 100 μg kg^{-1} for tea (EC No 396/2005), Japan sets the maximum level of cartap, thiocyclam, and bensultap as total at 100 μg kg^{-1} for potato (Japan's Positive List System), China sets the maximum level of cartap at 0.1 and 100 μg kg^{-1} for rice and sugarcane, thiosultap and thiocyclam at 100 and 200 μg kg^{-1} for rice, respectively (GB 2763-2012).

Presently, limited analytical methods have been reported for the determination of nereistoxin-related insecticides, most of which are instrument analysis. For example, simultaneous

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Electronic supplementary material The online version of this article (doi:10.1007/s00604-014-1347-x) contains supplementary material, which is available to authorized users.

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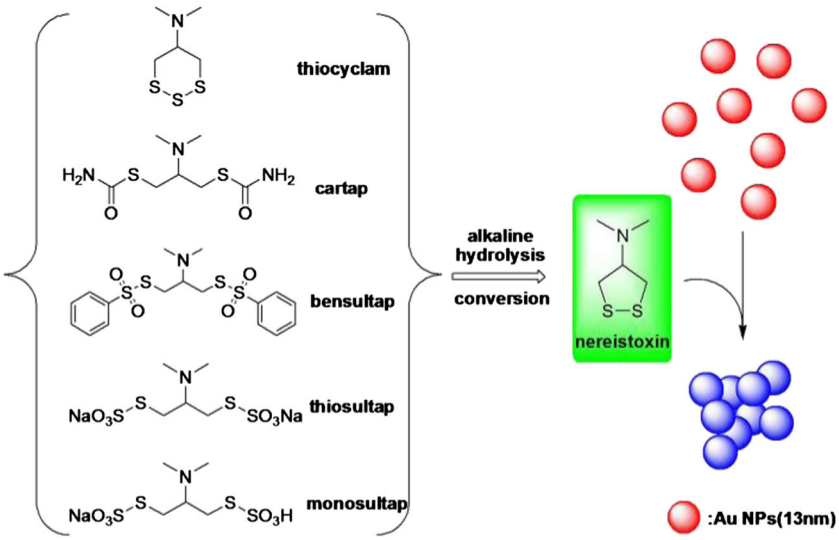
detection of both nereistoxin and dihydronereistoxin using π reversed-phase, ion-pair HPLC with electrochemical detection [3], the monosultap sodium residue analysis in tomato and soil using GC-FPD method [4] by conversion into nereistoxin with alkaline hydrolysis, the analysis of nereistoxin and its metabolites in human serum using a modified GC-MS method [5], the determination of thiosultap sodium, thiocyclam, and nereistoxin in pepper by LC-MS/MS [6]. Although instrumental analysis is chosen as the official detection method due to its high sensitivity and accuracy, the expensive instrument and specially trained person requirement, and time-consuming cleaning up procedure limit their application for the rapid and on-site detection. With respect to the foregoing, it is necessary to develop simple and convenient methods such as colorimetric sensors to prevent the risk of nereistoxin-related insecticides pollution.

Gold nanoparticles (Au NPs) based colorimetric assays are of particular interest because molecular events can give rise visible color changes and no sophisticated instruments are required but bare eyes for signal acquisition. The color change is influenced not only by the size, shape, capping agents, medium refractive index, but also by the aggregation state of Au NPs [7, 8]. Indeed, sensors with aggregation-induced color change of Au NPs have been proved to achieve high sensitivity in visual detection for all kinds of target molecules including viruses [9, 10], proteins [11, 12], DNA [13, 14], cancerous cells [15, 16], metal ions [17–20], sugars [21, 22], small molecules [23–25], and so on. Au NPs based colorimetric methods for organophosphorus pesticides [26, 27] have been also developed in the past decade, especially, an attractive non-destructive detection of dithiocarbamates using Au NPs has been reported by combining the benefits of solid phase extraction [28], while colorimetric assay for the determination of other pesticides still lack sufficient applications.

Herein, a new approach is designed for visual and colorimetric detection of total nereistoxin-related insecticides residues based on nereistoxin-induced aggregation of Au NPs. According to the official standard of Japan and European Commission, total nereistoxin-related insecticides residue is the sum of nereistoxin hydrolyzed by cartap, bensultap, thiocyclam, thiosultap, and monosultap in agriculture products. Considering nereistoxin containing amine and thiol groups, the developed assay provides an easy way to detect nereistoxin by the aggregation of Au NP due to the strong interaction of nereistoxin with Au NP. The detailed detection principle is illustrated in Scheme 1. Nereistoxin-related insecticides are firstly transformed into nereistoxins according to the general alkaline hydrolysis method and confirmed by the official instrument analytical methods of Japan and European Commission [29, 30]. The obtained nereistoxins could cause the aggregation of Au NPs due to its special molecule structure. On the one hand, positively charged amino group of nereistoxin inclines to adsorb onto the surface of negatively charged Au NPs via electrostatic interactions at acidic medium, on the other hand, thiol group of nereistoxin prefers to substitute the citrate onto the surfaces of Au NPs. As a result, crosslinking and aggregation of Au NPs would occur due to the electrostatic interactions and the strong Au–S covalent bonds. The aggregation degree of Au NPs is dependent on the concentration of nereistoxin in the system, and accordingly, the distinguishable color change facilitates the simple signal readout of nereistoxin that can be performed by the bare eye, or be measured by spectrophotometry, which could be further transferred to the total amount of nereistoxin-related insecticides.



Scheme 1 Schematic representations of aggregation of Au NPs by nereistoxin-related insecticides

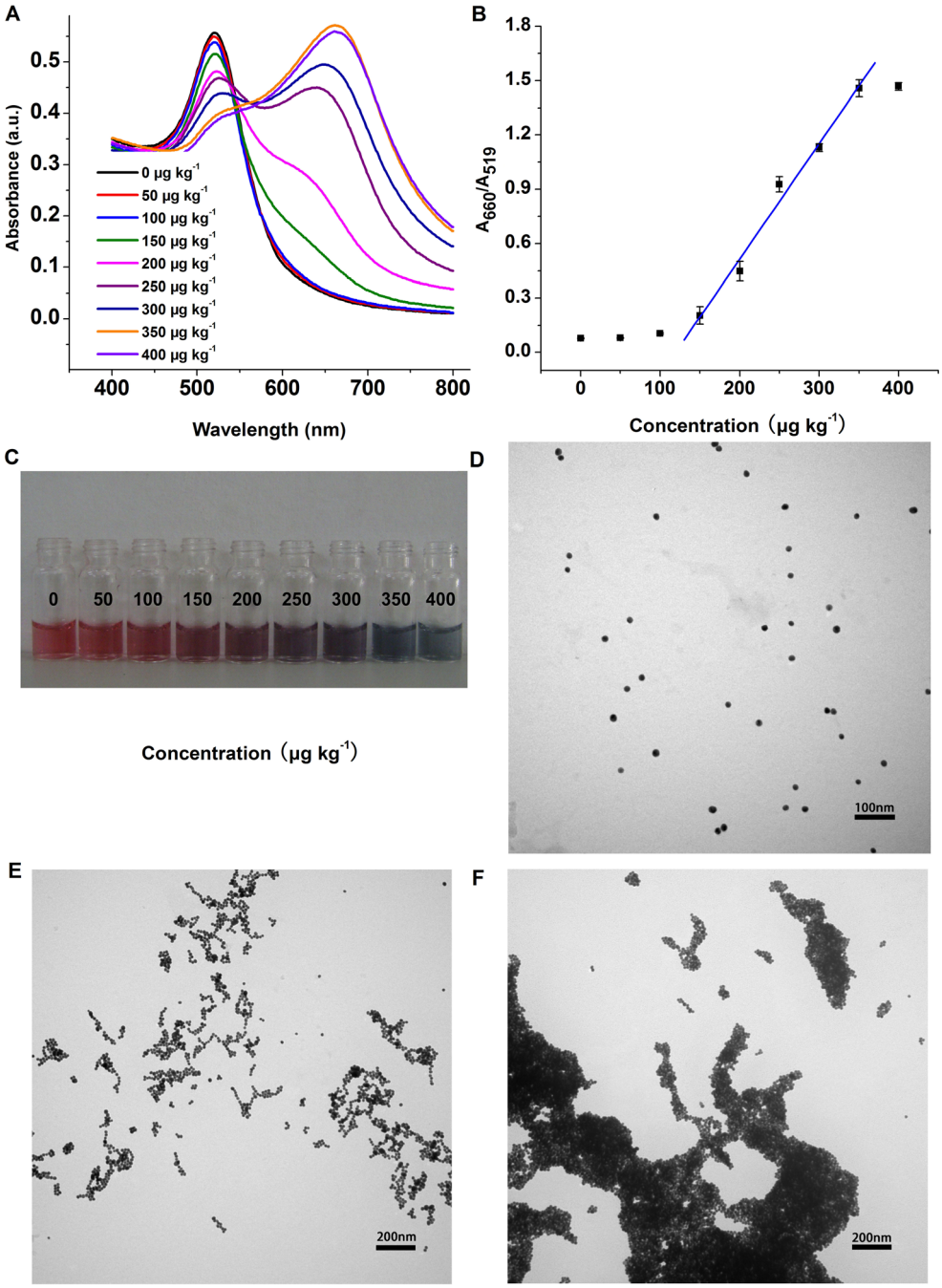


Fig. 1 **a** Visible absorption spectra of Au NPs at different nereistoxin concentrations; **b** plots of A_{660}/A_{519} versus different nereistoxin concentrations corresponding to **a**; **c** visual color changes of Au NPs corresponding to **a**; TEM images of Au NPs with nereistoxin addition of **d** 0, **e** 150, and **f** 350 μg kg^{-1}, respectively

Experimental

Chemicals and materials

Nereistoxin and other pesticides were purchased from China National Institute of Standardization (Beijing, China. www.ncrm.org.cn). Hydrogen tetrachloroaurate (Ш) hydrate ($HAuCl_4 \cdot 4H_2O$), sodium cloride (NaCl) and sodium bisulfate monohydrate ($NaHSO_4 \cdot H_2O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China. www.reagent.com.cn). Other chemicals were of analytical reagent grade and used as received. Distilled water was used in all experiments.

Instruments and measurements

The absorption spectrum was recorded with a UV-2550 spectrophotometer (Shimadzu, Japan) at room

temperature. Transmission electron microscopy (TEM) measurements were performed on an HT 7700 (Hitachi, Japan) at 80 kV.

Synthesis of Au NPs

All the glass used was 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 [13].

Detection of nereistoxin

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 nereistoxin. 0.2 mL of sample solution was taken and added into 0.4 mL of Au NPs solution, then, the mixture was shaken for 1 min and allowed to stand for another 2 min at room temperature. Absorbance spectra of the mixture solution were determined with UV–vis spectrometer.

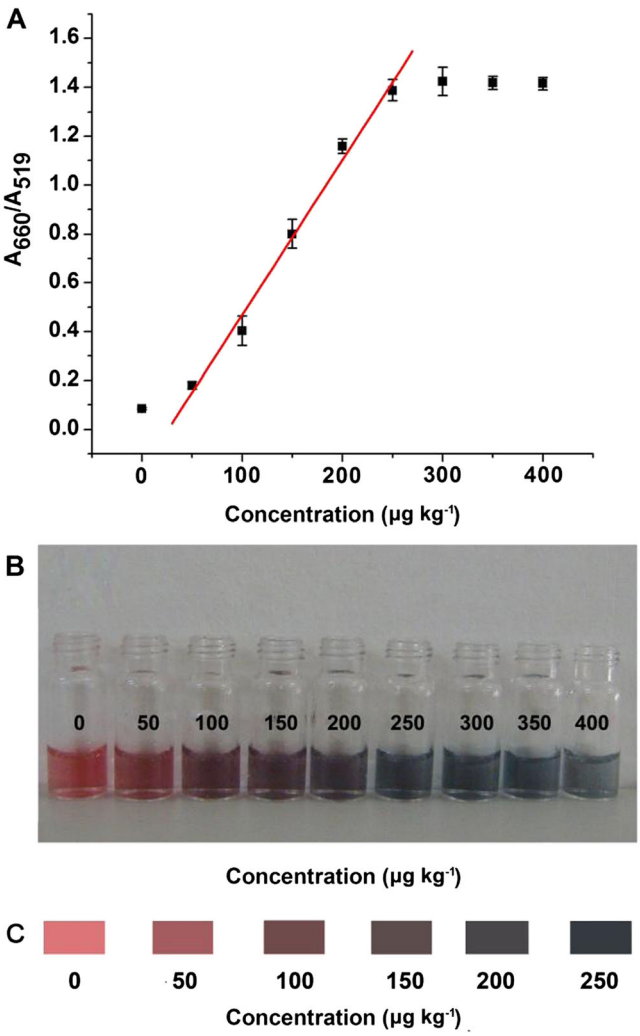


Fig. 2 Detection of nereistoxin under optimal conditions. **a** Plots of A_{660}/A_{519} versus different nereistoxin concentrations; **b** visual color changes of Au NPs corresponding to **a**; **c** standard colorimetric card

Pretreatments of real samples

To measure total nereistoxin-related insecticides residue in real samples, agricultural products (tea, kiwifruit, rice and cabbage) were pretreated according to the previous method [4] with minor alterations. Typically, a representative 5 g portion of previously homogenized sample was weighted in a 50 mL centrifugation tube. Then 20 mL of 0.1 M HCl was added and the mixture was ultrasonicated for 40 min at 60 °C. Afterwards, the mixture was centrifuged at 4,000 rpm for 5 min to remove organic compounds of matrix. The resulted supernatant was washed with 15 mL of n-hexane and centrifuged at 4,000 rpm for 5 min. The upper layer was discarded, and the lower layer was washed with another 15 mL of n-hexane again. This step was beneficial to decrease the content of amphiphilic molecules in the mixture. The aqueous layer was carefully adjusted to pH 8.5–9.0 with 2 M NaOH, then 2 mL of 0.2 M Na_2S was added and the mixture was held for 2.5 h at 70 °C. During this process, nereistoxin-related compounds were conversed to nereistoxin. After that, the mixture was then cooled down to room temperature and 20 mL of chloroform was added to extract nereistoxin 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 chloroform. The mixture was vigorously shaken for 1 min and centrifuged at 4,000 rpm for 3 min. Then 20 mL of chloroform was added for a second extraction. Finally, the combined organic layer was evaporated, and redispersed in 5 mL of water (pH 4) for further analysis.

Table 1 RGB values of the Au NPs solution with different concentrations nereistoxin

Nereistoxin concentrations (μg kg^{-1})	Red	Green	Blue
0	220	116	120
50	165	92	94
100	112	75	76
150	92	77	74
200	72	70	73
250	52	58	63

Table 2 Comparison of different analytical methods for the determination of nereistoxin related insecticides

Methods/materials	Analytical ranges/LODs	Comments	References
HPLC	50–400 pmol/10 pmol	Detection time: 18 min, specific electrochemical detector	[3]
GC	0.1–30 mg L^{-1}/10 μg kg^{-1}	Detection time: 13 min, laborious and time consuming extraction	[4]
GC-MS	0.05–5.0 mg L^{-1}/10 μg L^{-1}	Detection time: 20 min, high cost, expensive instrument	[5]
LC-MS-MS	1–500 μg L^{-1}/0.1 μg kg^{-1}	Detection time: 25 min, lots of acetonitrile, expensive instrument	[6]
Colorimetry/Au NPs	50–250 μg kg^{-1}/40 μg kg^{-1}	Detection time: 3 min, simple, visible, low cost	This method

Result and discussion

Origin of the analytical signal

The citrate-stabilized Au NPs colloidal can be dispersed in aqueous solution, and the color of the uniform colloid is wine red due to its strong surface plasmon resonance (SPR) at 519 nm. While exposure to nereistoxin, Au NPs aggregated due to chemical interactions of the Au–S bonding and electrostatic attractive force of amine and carboxylic group. As well known, the peak position of SPR band of Au NPs is closely related to the distance between nanoparticles. When the state of nanoparticles changed from dispersion to aggregation in the presence of nereistoxin, an obvious red-shift of the SPR peak of gold nanoparticles could be observed. As shown in Fig. 1a, with the increase of nereistoxin concentration from 150 to 400 μg kg^{-1}, the original absorbance of Au NPs at 519 nm significantly decreased, and a new characteristic absorbance band centered at 660 nm was observed due to the aggregation of Au NPs. To further understand the spectra property of the aggregation of Au NPs, a typical plot of the extinction ratio (A_{660}/A_{519}) in the absence of nereistoxin and presence of different concentrations of nereistoxin was obtained. As shown in Fig. 1b, the calibration curve is linear in the range of 150–350 μg kg^{-1} with an R value of 0.9932.

Simultaneously, color changes of Au NPs in the absence of nereistoxin and presence of different amounts of nereistoxin were recorded by digital camera. When different concentrations of nereistoxin were added from 0 to 400 μg kg^{-1}, the color of Au NPs changed from wine red to purple and finally to blue progressively (Fig. 1c), which indicates the developed method could be used to detect nereistoxin by visual evaluation. The change of Au NPs color and spectra property caused by aggregation is further verified by TEM observations. The Au NPs present high monodispersity in the absence of nereistoxin (shown in Fig. 1d). Significant aggregations of Au NPs in the presence of nereistoxin at 150 and 350 μg kg^{-1} were observed in Fig. 1e and f, respectively. Results of TEM analysis confirm directly the experimental observation discussed above, which well agrees with results of visible absorption spectra. These experimental phenomena well accords with previous research findings on the aggregated Au NPs cross-linked by other molecules, such as melamine [31], and cationic thiocholine [27].

Analytical performance under optimized conditions

The optimum experimental conditions that maximize the net signal of pesticides were investigated mainly in terms of AuNPs-pesticides measurement time, pH and ionic strength. The results shown in Fig. S1 (Electronic Supplementary Material, ESM) revealed that the maximum signal was attained at 3 min of reaction time, pH 4.0 of media and 0.9 mmol L^{-1} of $NaHSO_4$ addition. Under optimized conditions, the VIS spectra and color change of Au NPs solution with different concentrations of nereistoxin were further investigated. As shown in Fig. 2a, a good linear relationship exists between the value of A_{660}/A_{519} and concentration of nereistoxin in the range between 50 and 250 μg kg^{-1}, with a detection limit of 40 μg kg^{-1} (3δ). The calibration equation is $y = 6.283x/10^3 - 0.1367$, with R value of 0.9953. Correspondingly, with the increase of nereistoxin

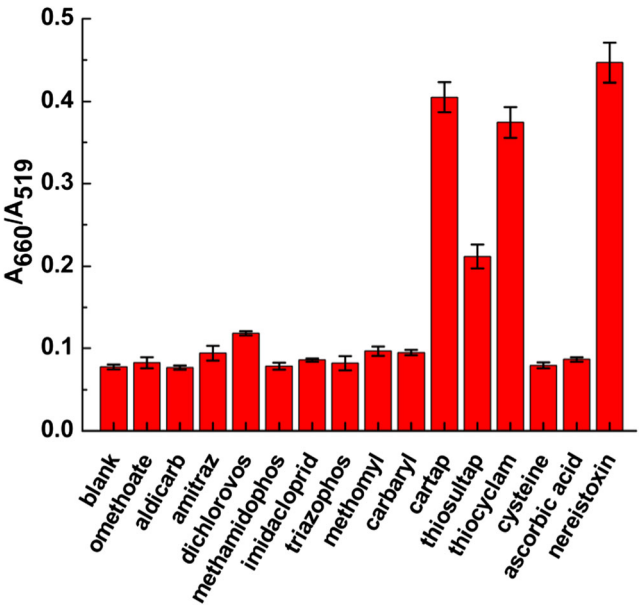


Fig. 3 A_{660}/A_{519} ratios of Au NPs with different analytes. Concentrations of cartap, thiosultap, thiocyclam and nereistoxin were all 200 μg kg^{-1}, while those of others were all 3 mg kg^{-1}

concentration, the color of mixture solutions changes from wine-red to purple and finally to blue (Fig. 2b). While, the color change of red at 50 μg kg^{-1}, could be distinguished by people of acute observation or purple red at 100 μg kg^{-1}, by common ones with the original wine red. Furthermore, the standard series of colors were given in Fig. 2c and corresponding RGB values of the color were also listed in Table 1, which allows us to printed extempore standard colorimetric card conveniently according to the color RGB values. Thus, the concentration of nereistoxin in the samples could be easily semi-quantify by the nearest chrominance of the standard series of colors.

Although there is still a gap between our method and other chromatographic methods (0.1–10 μg kg^{-1}) in terms of the detection limit [4–6], it should be noticed that the detection limit of the developed method is still below the strictest safety requirement. Actually, Japan sets the MRL of total nereistoxins at 100 μg kg^{-1}, while other countries and organizations set MRL of individual nereistoxin-related pesticide at the same level, so that we set 100 μg kg^{-1} as the alarming level. Importantly, as shown in Table 2, method developed in the present work provides many advantages, such as short detection time, low analysis cost, no requirement of professional techniques, and could facilitate future development of rapid detection for nereistoxin-related residues. Considering the color change of Au NPs solution occurred under the addition of 50–100 μg kg^{-1} nereistoxin, which is close to the permissible limits of MRL of nereistoxin-related pesticide, the developed method with vivid color for bare eye detection well meets all requirements of rapid detection and is also very simple in implementation. Thus, this analytical protocol offers an attractive platform for the possible practical applications in alarm system for prescreening and monitoring of nereistoxin-related pesticides.

An effective sample pretreatment for the Au NPs based colorimetric assay

One of the impediments for application of the current optical sensors is that their signals are possibly interfered by matrix and other analytes [32]. Indeed, it was suggested that colorimetric sensors with unmodified Au NPs should plunge into critical conditions owing to its less tolerance to interferences than ligand-stabilized Au NPs [27]. In most cases, the high specificity could be achieved by using recognition elements modified Au NPs [33, 34]. In this case, removing of interferences by a suitable purification process could improve the specificity. Similar with recent analytical methods for the detection of nereistoxin-related insecticides [4–6, 35], which are all converted into nereistoxin, the pretreatment procedure in this work was based on liquid–liquid extraction

Table 3 Results of total nereistoxin-related insecticides residue detection in agricultural products

Samples	Added concentration		GC measured concentration[a] (μg kg^{-1}, n=3)	Observed concentration[a] (n=3)		Recovery[d] (%)	CV (%)
	(μg kg^{-1})	(μmol L^{-1})		(μg kg^{-1})	(μmol L^{-1})		
Tea 1	200[b]	0.73	75	77	0.52	70.7	7.8
Tea 2	300[b]	1.10	131	127	0.85	77.8	10.9
Tea 3	400[b]	1.46	151	133	0.89	61.1	8.3
Kiwifruit 1	200[b]	0.73	97	105	0.70	96.5	8.6
Kiwifruit 2	300[b]	1.10	130	129	0.87	79.0	7.8
Kiwifruit 3	400[b]	1.46	185	174	1.17	79.9	6.9
Rice 1	200[b]	0.73	102	92	0.62	84.5	7.6
Rice 2	300[b]	1.10	136	132	0.89	80.9	6.1
Rice 3	400[b]	1.46	176	156	1.05	71.7	6.4
Rice 4	150[c]	0.55	85	87	0.58	105	6.9
Rice 5	300[c]	1.11	144	118	0.79	71.6	7.6
Rice 6	450[c]	1.66	181	153	1.03	61.9	6.5
Cabbage 1	150[c]	0.55	84	79	0.53	95.9	9.9
Cabbage 2	300[c]	1.11	137	126	0.85	76.5	8.7
Cabbage 3	450[c]	1.66	178	174	1.17	70.4	5.0

[a] The measured concentration of nereistoxins

[b] The spiked concentration of cartap

[c] The spiked concentration of thiocyclam

[d] Recovery % = Observed concentration (μmol L^{-1})/added concentration (μmol L^{-1}) × 100 %

and hydrolysis, with some modifications. On the whole, in order to convert nereistoxin-related insecticides to nereistoxin and remove the impurity, this developed pretreatment procedure involves ultrasonic extraction with diluted hydrochloric, hydrolyzing into nereistoxin under basic condition, and purifying with multistep liquid–liquid extraction, which is demonstrated here as an effective pretreatment method for the colorimetric determination of total amount of nereistoxin-related insecticides.

Selectivity and interference studies

To further investigate the application of the colorimetric method in more complex samples, nereistoxin or some potential interfering substances were added to nereistoxin detection system with different concentrations. After reaction for 3 min, the A_{660}/A_{519} value was detected to monitor the aggregation of Au NPs. As shown in Fig. 3, among these chemicals, nine kinds of non nereistoxin-related pesticides (omethoate, aldicarb, amitraz, dichlorovos, methamidophos, imidacloprid, triazophos, methomyl and carbaryl) and one kind of stabilizing ligand (ascorbic acid) at high concentration (15 times higher than that of nereistoxin) exhibit no obvious change of extinction ratio (<0.15). Interestingly, extinction ratio change is observed after addition of 3 mg kg^{-1} cysteine for 30 min, but not comparable to that of nereistoxin in detection time of 3 min. The results indicate that most of the non nereistoxin-related pesticides, sulfur containing molecules and stabilizing ligands could not disturb the selective detection of nereistoxin by this method. Although the typical nereistoxin-related pesticides (cartap, thiosultap and thiocyclam) at 200 μg kg^{-1} have serious interference, the effect is negligible in the real sample detection because they were converted to nereistoxins during the pretreatment process of real samples. These results suggest that the method enables highly specificity to total nereistoxin-related pesticides detection.

Analysis of total nereistoxin-related insecticides in spiked samples

To demonstrate the practicability in real samples analysis, different samples including tea, kiwifruit, rice and cabbage samples were spiked with different concentrations of cartap and thiocyclam, which are the most widely used nereistoxin-related insecticides, and pretreated according to the procedure described in Experimental section. Then the calibration curve in Fig. 2a was used for the quantitative determination. At the same time, the same samples were also examined by the standard method of GC (GB/T 5009.113, GB/T 5009.114). The results are listed in Table 3. Colorimetric results of these practical samples are gratified with recoveries between 61.1 and 105 % and variation coefficients between 5.0 and 10.9 %. Results show that there is a satisfactory agreement between the declared analyte content and the determined value both by the present method and GC. Therefore, the developed method could be reliably and practically used for the determination of nereistoxins in agricultural products.

Conclusion

In conclusion, we have developed a simple colorimetric and visible method for the sensitive and selective determination of total nereistoxin-related insecticides residues in agricultural products by using unmodified Au NPs as the colorimetric probe. This method is convenient and can be accomplished within 3 min. The concentration of analyte can be calculated based on the variation of UV–vis spectra or easily read out by bare eye according to the color change of Au NPs. Parameters, including ion concentration, pH and reaction time, were optimized to minimize the effect to assay sensitivity. Under optimized condition, the developed method can be used to detect nereistoxins with a detection limit of 40 μg kg^{-1} by UV–vis spectrometer, and 50–100 μg kg^{-1} by bare eye. Furthermore, possible interferential substances, including 12 kinds of most common insecticides, were tested to investigate the specificity of the assay. Results indicate that the developed method presents satisfactory linear range, low detection limit, good accuracy and specificity. Herein, the colorimetry, with a relatively simple test procedure and convenient experimental conditions, provides an alternative way for the detection of total nereistoxin-related insecticide residues and might have a great potential for on-site detection in agricultural products.

Acknowledgments This work was supported by National Science & Technology Pillar Program (2012BAK17B06), National Natural Science Foundation of China (No. 31101274, No. 31201357), the Shaanxi Provincial Research Fund (2014K13-10, 2012KJXX-17, 2014KJXX-42, 2014K02-13-03), Open Fund of State Key Laboratory of Electroanalytical Chemistry (SKLEAC201301), Program for New Century Excellent Talents in University (NCET-13-0483) and Fundamental Research Funds for the Northwest A&F University of China (2014YB093).

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