Analytical Methods

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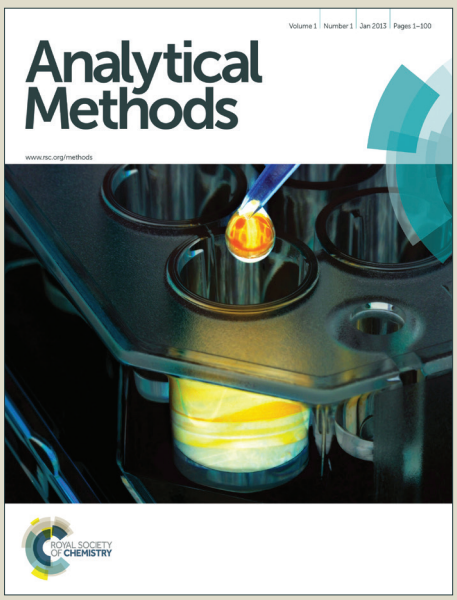

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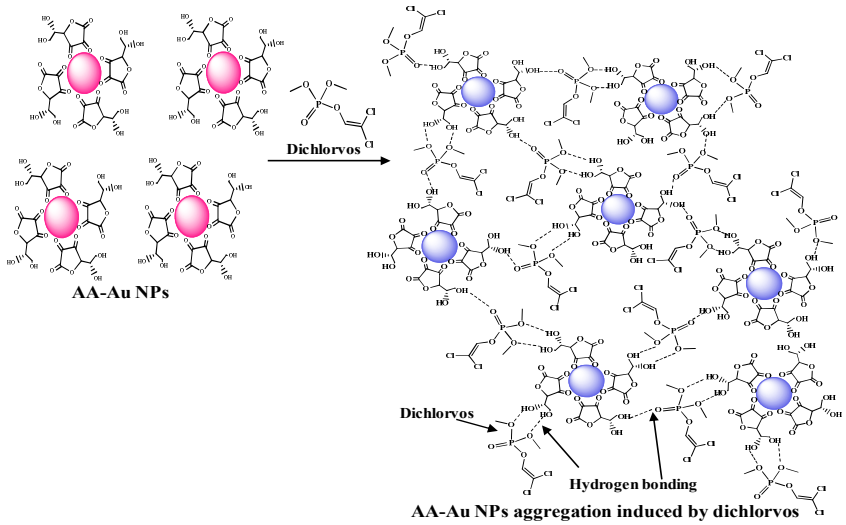
Graphical Abstract

We report the use of AA-Au NPs as a colorimetric probe for detection of dichlorvos in water and wheat samples. The aggregation of AA-Au NPs was induced by dichlorvos *via* hydrogen-bonding between AA-Au NPs and dichlorvos, which results a change in color from cherry red to purple that can be monitored by UV-visible spectrophotometer or the naked eye.



Schematic representation of the analytical process for detecting dichlorvos using AA-Au NPs as a colorimetric probe.

Ascorbic acid functionalized gold nanoparticles as a probe for colorimetric and visual read-out determination of dichlorvos in environmental samples

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Abstract

We report a facile, rapid, selective and sensitive colorimetric method for the detection of dichlorvos based on the aggregation of ascorbic acid (AA) capped gold nanoparticles (Au NPs) induced by dichlorvos. The influence of AA concentration on the UV-visible absorption spectra and color of AA-Au NPs was investigated. In the presence of dichlorvos, the UV-visible spectrum of AA-Au NPs was red-shifted from 525 nm to 620 nm, indicating that the aggregation of AA-Au NPs was induced by dichlorvos *via* hydrogen-bonding between AA-Au NPs and dichlorvos, which results a change in color from cherry red to purple that can be monitored by UV-visible spectrophotometer or the naked eye. The limit of detection was found to be 42.94 µM, and good recoveries in the range of 90.0 – 101.2 %, with relative standard deviation (RSD) <0.85%, respectively. The method was successfully applied to detect dichlorvos in water (tap, river and canal), apple and wheat samples.

***Keywords*:** AA-Au NPs, Dichlorvos, UV-visible Spectrometry, DLS and Environmental samples.

Introduction

Dichlorvos is an organophosphate insecticide and also known as DDVP (2,2-dichlorovinyl methyl phosphate or dichlorophos). It is used as an insecticide to control household, public health, and stored product from insects. It is widely used as an insecticide in agriculture and food products.[1] It acts against insects both as a contact and a stomach poison. Its presence in the environment has been attributed to several health effects such as inhibition of an enzyme (acetylcholinesterase) with neurotoxic effects including perspiration, vomiting, diarrhea, drowsiness, fatigue, headache, and at high concentrations, convulsions, and coma.[2-3] Due to its excessive application in agriculture and food products, the control of dichlorvos has been widely recognized as an important issue for public health.[4] In view of this, it has become increasingly important to detect and to monitor the level of dichlorvos in food and the environment. At present, the classical and standard assay for dichlorvos detection is based on pH-sensitive fluorescence probe[5], fluorometry[6], gas chromatography[7], high performance liquid chromatography,[8] and liquid-chromatography-mass spectrometry.[9] Similarly, Liu's group prepared a novel "fixed" or "flexible" three-dimensional plasmonic hotspot matrix by evaporating a droplet of citrate-Ag sols on a fluorosilylated silicon wafer and then integrated with a portable surface enhanced Raman spectroscopy for detection of various analytes with different natures, including pesticides and drugs.[10] The same group developed a new surface-enhanced resonance Raman scattering platform for the fast and sensitive detection of 2,4,6-trinitrotoluene using cetylpyridinium chloride capped Ag sols as a surface-seeking species.[11] Apart from this, few spectrophotometric methods have been described by using various reagents including resorcinol,[12] phloroglucinol,[13] and diphenyl semicarbazide[14] as coupling reagents to interact with dichloacetaldehyde, which is generated in the basic

hydrolysis of dichlorvos. Although some of the methods are sensitive and reliable, they are expensive and time-consuming.[9] Moreover, they require well-trained technicians and are not suited for on-site or in-field detection. In addition, on the one hand, spectrophotometric methods essentially require some organic reagents for the coupling of hydrolyzed product of dichlorvos. On the other hand, they are time consuming and poor sensitivity.

Recently, plasmonic-based gold nanoparticles have attracted great attention as colorimetric probes and found many applications in miniaturized analytical chemistry due to its excellent localized surface plasmon resonance properties exhibiting intense and well-defined colors, which is dependent on their dispersed and aggregation states.[15-16] Moreover, Au NPs exhibited unique optoelectronic properties that can easily be tuned by changing their size, shape or chemical environment.[17-18] The metallic NPs-based assays have recently become useful for the analysis of a wide variety chemical species without the need for advanced instrumentation because the molecular recognition events can be observed by their characteristic surface plasmon resonance (SPR) band red-shift towards longer wavelength and transformed into color changes.[19-20] As a result, Au NPs are functionalized with various organic ligands, including *p*-sulfonatocalix[6]arene,[21] cysteamine,[22] lipoic acid,[23] citrate,[24-25] azide-terminal alkyne[26] and ethylenediamine[27], and used as promising colorimetric probes for colorimetric detection of various pesticides including organophosphorus and carbamate pesticdies even at nanomolar concentrations. Jiang's and Wang's groups developed dual readouts (colorimetric and fluorometric) approaches for sensitive and selective detection of organophosphorus and carbamate pesticides by using rhodamine B-capped Au NPs.[28] Recently, our group also developed a simple and sensitive colorimetric assay for the detection of tricyclazole fungicide by using 5-sulfo

anthranilic acid dithiocarbamate capped Ag NPs as a colorimetric probe.[29] On the basis of the motivation described above as well as the achievement acquired by our group, a new Au NPs-based colorimetric strategy has been developed for detection of dichlorvos in environmental and food samples. In this work, we describe two, colorimetric and visual read-out procedures for the determination of dichlorvos using AA-Au NPs as probes. This method is based on the formation of a strong and stable molecular assembly between dichlorvos and AA which in turn coordinates on the surface of Au NPs, resulting their aggregation. Initially, AA-Au NPs are well dispersed in water and the color of solution is cherry red, because of the SPR of Au NPs, however, the color of the solution is changed from cherry red to purple, and their characteristic SPR band is red-shift from 525 nm to 620 nm, indicating that AA-Au NPs aggregation induced by dichlorvos *via* hydrogen bonding (Scheme 1). The color change of AA-Au NPs is investigated for the detection of dichlorvos in water, apple and wheat samples. To demonstrate the selectivity, pesticide mixtures were tested with the assay, and it was observed that the response of the colorimetric assay is highly selective towards dichlorvos.

Experimental

Chemicals and materials

Hydrogen tetrachloroaurate hydrate ($HAuCl_4 \cdot xH_2O$) and ascorbic acid were purchased from Sigma Aldrich, USA. Acephate, thiram and dichlorvos were received from Super Crop Safe Ltd, India. Monocrotophos, chlorpyrifos, quinalphos, indoxacarb, fenvalerate, triaxophos were received from Garda Chemicals, Ankleshwer, India. Glyphosate, matalaxyl and mancozeb was received from United Phosphate Ltd, Ankleshwer, India. NaCl, KCl, NaOH, Na_2HPO_4, K_2HPO_4, sodium

acetate and HCl were obtained from Finar Chemicals Ltd, India. All chemicals were of analytical grade and used without further purification. Milli-Q-purified water was used in entire practical work.

Instrumentation

UV-visible spectra were measured with a Maya Pro 2000 spectrophotometer (Ocean Optics, USA). Fourier transform infrared spectra (FT-IR) were measured by using FT-IR 8400S (Shimadzu, Japan). Transmission electron microscopy (TEM) images were obtained by using Tecnai 20 (Philips, Holland). DLS were measured by using Zetasizer Nano ZS90 (Malvern, UK).

Preparation of AA-Au NPs

The AA-capped Au NPs were prepared by the following procedure. Briefly, a aqueous solution of $HAuCl_4$ (4.5 mL,10^{-4} M) was taken into 50 mL reaction flask under constant stirring. To this, aqueous solution of AA (0.5 mL, 0.75 mM) was added under reflex condition at 100^{o}C and the mixture was stirred for 10 min during which its color changed from pale yellow to cherry red. The solution was cooled to room temperature and stored at 4°C. The AA-Au NPs SPR band is observed at 525 nm and their sizes were about 14.5 nm by DLS and TEM.

Analysis of dichlorvos by using AA-Au NPs as a colorimetric probe

The colorimetric detection of dichlorvos was performed at room temperature. To this, a volume of AA-Au NPs (1.0 mL) solution was added to 100 µL of various pesticides (acephate, monocrotophos, chlorpyrifos, quinalphos, triaxophos, glyphosate and dichlorvos, 1.0 mM) separately. Based on the colorimetric response of AA-Au NPs with dichlorvos, aliquots of dichlorvos (100 – 1000 µL) solutions were added to

1.0 mL of AA-Au NPs solution separately. The color changes were observed by digital camera and their spectral changes were monitored by UV-visible spectrometry. The relationships between the absorption ratio at A_{620}/A_{525} and the concentrations of dichlorvos was plotted as a calibration curve, which is used to calculate the limit of detection (LOD) of the present method.

Analysis of dichlorvos in environmental water and food samples

For water, three water samples (tap, canal, and river) were collected from different places of Surat and filtered by using micron (0.45 µm) filters syringe. The filtered samples were then spiked with different concentration of dichlorvos and then analyzed by the aforesaid procedure. For wheat and apple juice: The apples were chopped and edible parts of apples were crushed by a mixer grinder to obtain homogeneous liquid. 5 grams of apple juice and wheat were spiked with dichlorvos (5.0 mM) and kept for 24 h. Then, 25 mL of MeOH was used for the extraction of dichlorvos from each sample and the extract was concentrated to 2.0 mL. The AA-Au NPs solution was added to the above solutions and their color changes and UV-visible absorption spectra were measured.

Results and discussion

The Au NPs were synthesized by using AA as a reducing and capping agent. The prepared AA-Au NPs are cherry red in color and exhibited SPR band at 525 nm (Figure 1). In order to control the characteristic SPR band and color of AA-Au NPs, the influence of AA concentration was examined for preparation of Au NPs with SPR band at 525 nm. As shown in Figure 1, the absorbance of SPR peak at 525 nm is gradually increased with increasing concentration from 0.25 to 1.0 mM, after that the

color of AA-Au NPs solution is changed to purple color. To establish AA-Au NPs as a colorimetric probe, we selected 0.75 mM of AA as an optimum concentration for preparation of AA-Au NPs. The FT-IR spectra of pure AA and AA-Au NPs are shown in Supporting Information of Figure S1. It can be observed that α- and β-unsatured ketone group stretching vibration was observed at 1649 cm^{-1}. The peaks at ~1453 and 1522.3 cm^{-1} were attributed to the asymmetric and symmetric stretching of -C=C-, respectively. Besides, the characteristic peak of hydroxy groups is appeared at 3626 cm^{-1}. The peak at 1744 cm^{-1} corresponded to the absorption peak of keto group in AA. It can be observed that the above characteristic peaks were greatly reduced by the oxidation and reduction reactions between AA and Au^{3+} ion. These results indicated that AA was successfully acted as a reducing and capping agent for preparation and functionalization of Au NPs. The DLS data and TEM image of AA-Au NPs are presented in Figure 2. Their average diameter is approximately 14.5 nm. The DLS and TEM image revealed that the AA-Au NPs were spherical in shape and well dispersed in water.

For selectivity study, 100 µL of various pesticides (acephate, monocrotophos, chlorpyrifos, quinalphos, triaxophos, glyphosate and dichlorvos, 1.0 mM) were added to a solution containing 1.0 mL of AA-Au NPs solution. The sample vials were vortexed for 1 min and the UV-visible spectra of the resulting solutions were recorded. It can be observed that the characteristic SPR band absorbance at 525 nm (A_{525}) decreases and a new SPR band appears at 620 nm (Figure 3). As a result, the color of AA-Au NPs solution was changed to purple color, indicating that only dichlorvos induces the aggregation of AA-Au NPs *via* hydrogen-bonding. In order to investigate the effect of buffers and their pH on the dichlorvos-induced aggregation of AA-Au NPs, we studied the UV-visible absorption spectra of AA-Au NPs by the

addition of dichlorvos in the presence of sodium acetate (NaAc) and PBS pHs in the range of 2 – 12 (Figure 4 and Supporting Information of Figure S2). Supporting Information of Figure S3 shows the UV-visible absorption spectra of AA-Au NPs without addition of dichlorvos at PBS pH from 2 to 10. It can be noticed that the SPR peak exhibited a red-shift at PBS pH from 2 to 4. However, there are no obvious spectral changes in the UV-visible spectra of AA-Au NPs at buffer pH 6 - 10, indicating that AA-Au NPs are dispersed in solution, just as they are in AA-Au NPs solution. Figure 5 illustrates the DLS data of AA-Au NPs without addition of dichlorvos at different PBS pH from 2 to 6. At pH 2, the hydrodynamic diameter of AA-Au NPs was greatly increased to 154.6 nm, indicating that the self-aggregation of AA-Au NPs through the AA-Au NPs surface changes neutralization.[30] No further size enhancement was observed at pH 4 and 6, and the obtained DLS data is just like AA-Au NPs. Furthermore, we also studied the UV-visible absorption spectra of AA-Au NPs by the addition of dichlorvos with and without PBS pH 6 (Figure 6). These results illustrated that the effective dichlorvos-induced aggregation of AA-Au NPs was observed without buffer pH. This was probably due to the fact that the strong hydrogen-bonding may occur in aqueous solution. Furthermore, oxidized AA molecules contained two –OH groups, and dichlorvos also had four oxygen containing groups which meant that those units could easily form extended arrays of hydrogen bonding. As a result, the interparticle distance of AA-Au NPs is greatly decreased and resulted in obvious AA-Au NPs aggregation *via* strong hydrogen-bonding between AA-Au NPs and dichlorvos (Scheme 1). These results indicated that AA acted as a promising candidate for the reduction of Au^{3+} ions and for forming hydrogen-bonds with dichlorvos.

To check the effect of AA concentration on Au NPs, we measured UV-visible spectra of Au NPs with dichlorvos (1.0 mM) using different concentrations of AA from 0.25 to 1.0 mM (Supporting Information of Figure S4). It can be seen that the UV-visible spectra showed maximum absorption ratio A_{620}/A_{525} by using AA concentration at 0.75 mM, resulting a color change from cherry red to purple. The color and UV-visible spectra of Au NPs solution showed little change using AA concentrations at 0.25, 0.50 and 1.0 mM. Furthermore, oxidized AA molecules are predominately adsorbed on Au NPs surface since it contains keto groups and two hydrogen bonding sites; this has led to its ability to form hydrogen-bonding with dichlorvos. Based on these results, we can infer that 0.75 mM of AA is the best concentration for effective aggregation of Au NPs induced by dichlorvos via hydrogen-bonding. In order to study the effect of time on the absorption ratio A_{620}/A_{525}, we measured the UV-visible absorption spectra of AA-Au NPs with dichlorvos at different time intervals from 0 to 10 hours (Supporting Information of Figure S5). It can be observed that the maximum absorption ratio A_{620}/A_{525} was observed at zero time, indicating that this probe has ability to develop color with dichlorvos instantaneously. Meanwhile, the color was stable up to 10 h and the absorption ratio was slightly decreased.

With the addition of dichlorvos, AA-Au NPs solution exhibited a visible color change from cherry red to purple. Figure 7 shows the UV-visible absorption and the colors of AA-Au NPs solutions by the addition of different concentrations of dichlorvos. It was noticed that the absorption peak of AA-Au NPs at 525 nm is gradually redshifted with the appearance of new absorption peak at 625 nm. These results indicate that the aggregation of AA-Au NPs was gradually induced by the increasing concentration of dichlorvos, resulting a color change from cherry red to

purple. We can also observe the gradual color change from cherry red to purple when the concentration of dichlorvos increased from 100 to 1000 µM. UV-visible spectrometry was used to quantitatively determine the concentration of dichlorvos. As shown in Figure 7, the dichlorvos-induced AA-Au NPs aggregation was gradually increased with increasing concentration of dichlorvos, leading to a increased in the absorption ratio of A_{620}/A_{525}. As a result, a linear equation, ($A = 0.0004\ c + 0.4021$) ($R^2 = 0.994$) is obtained over the range of 100 – 1000 µM (Supporting Information of Figures S6). The detection limit of dichlorvos was 42.94 µM, and 400 µM with the naked eye. To confirm the aggregation of AA-Au NPs was induced by dichlorvos, we studied the DLS and TEM and the obtained data were shown in Figure 2. It can be observed that the average size of AA-Au NPs was increased to 278.1 nm, indicating that the aggregation of AA-Au NPs was greatly induced by dichlorvos.

To accomplish the direct colorimetric sensing of dichlorvos through the aggregation of AA-Au NPs that induced changes in their color and UV-visible spectrum, the influence of other pesticides (acephate, monocrotophos, chlorpyrifos, quinalphos, triaxophos, glyphosate, thiram, indoxacarb, fenvalerate, matalaxyl and mancozeb, from 0.25 to 1.25 µM) on dichlorvos (1.0 mM) induced aggregation state of AA-Au NPs is investigated. As shown in Supporting Information of Figures S7 and S8, the interfering pesticides even up to a concentration of 1.0 mM, cannot produce a color change from cherry red to purple; only dichlorvos induces the aggregation and color change of AA-Au NPs (inset of Supporting Information of Figure S8). These results indicated that the other pesticides have no effect on the determination of dichlorvos, indicating that AA-Au NPs is highly specific for colorimetric sensing of dichlorvos.

In order to test the applicability of the method, we used AA-Au NPs as a probe for the analysis of dichlorvos in environmental water (tap, river and canal), apple and wheat. The concentration of dichlorvos is determined by the standard addition method and the results are shown in Table 1. The obtained average recoveries of dichlorvos were in the range of 90.0 – 101.2 %, and with RSD <0.85%, indicating that there was no obvious system error of method. In order to estimate the accuracy of method, we studied intra- and inter-day precision and accuracy of the method for the analysis of dichlorvos in spiked water, wheat and apple samples. As shown in Table 2, this method shows good precision (RSD <0.62%) and accuracy (-1.2 to -4.3) for the analysis of dichlorvos in spiked samples. Supporting Information of Figure S9 shows the measured intra- and inter-day UV-visible spectra AA-Au NPs upon the addition of dichlorvos (750 μM). The above results demonstrated that the AA-Au NPs were successfully acted as a colorimetric probe for detection of dichlorvos in water, apple and wheat samples with reduced sample pre-treatment procedure.

Conclusions

In conclusion, we have successfully synthesized AA-Au NP in aqueous solution with average size 14.5 nm, where AA acted as a reducing and capping agent. The effect of AA concentration on the UV-visible spectra of Au NPs was demonstrated. Interestingly, we found that the dichlorvos induces the aggregation of AA-Au NPs *via* hydrogen-bonding, resulting a red-shift in their SPR peak from 525 nm to 620 nm, and a color change from cherry red to purple. This method was successfully applied to detect dichlorvos in environmental water, apple and wheat samples with good accuracy and precision. Based on these experimental results, AA-

Au NPs acted as a nanoplasmonic sensor for simple, selective, and sensitive detection of dichlorvos in environmental and food samples at minimal volume of samples.

Acknowledgements

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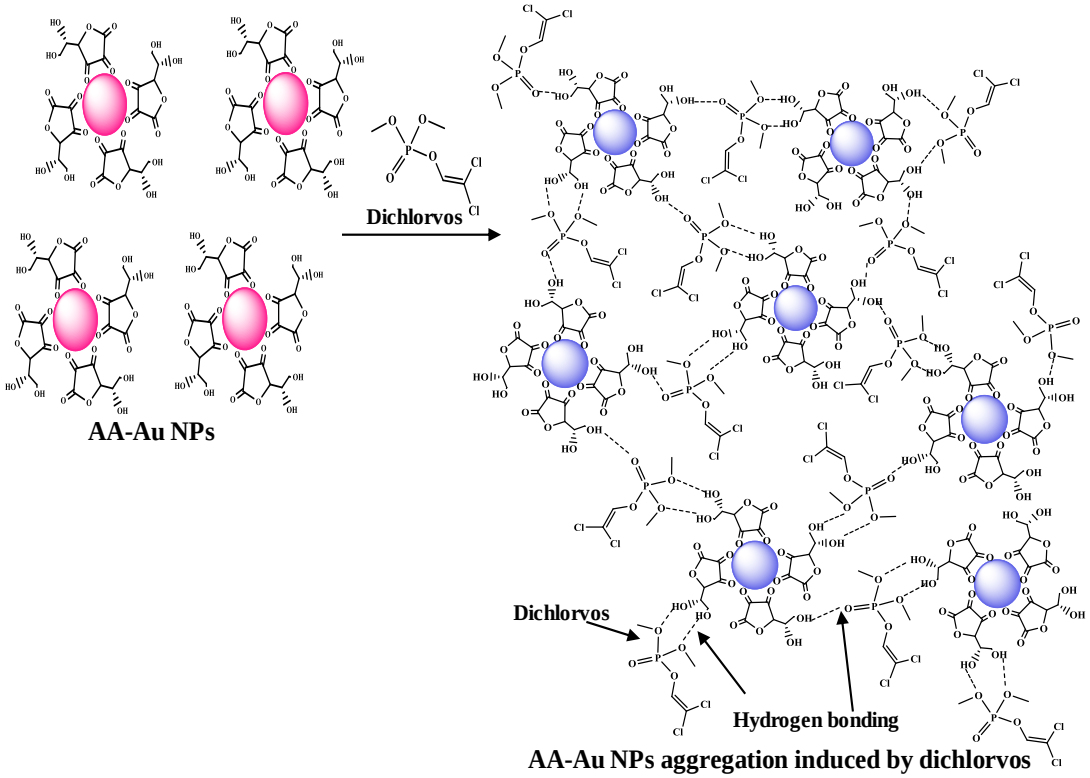

Scheme 1. Schematic representation of the analytical process for detecting dichlorvos using AA-Au NPs as a colorimetric probe.

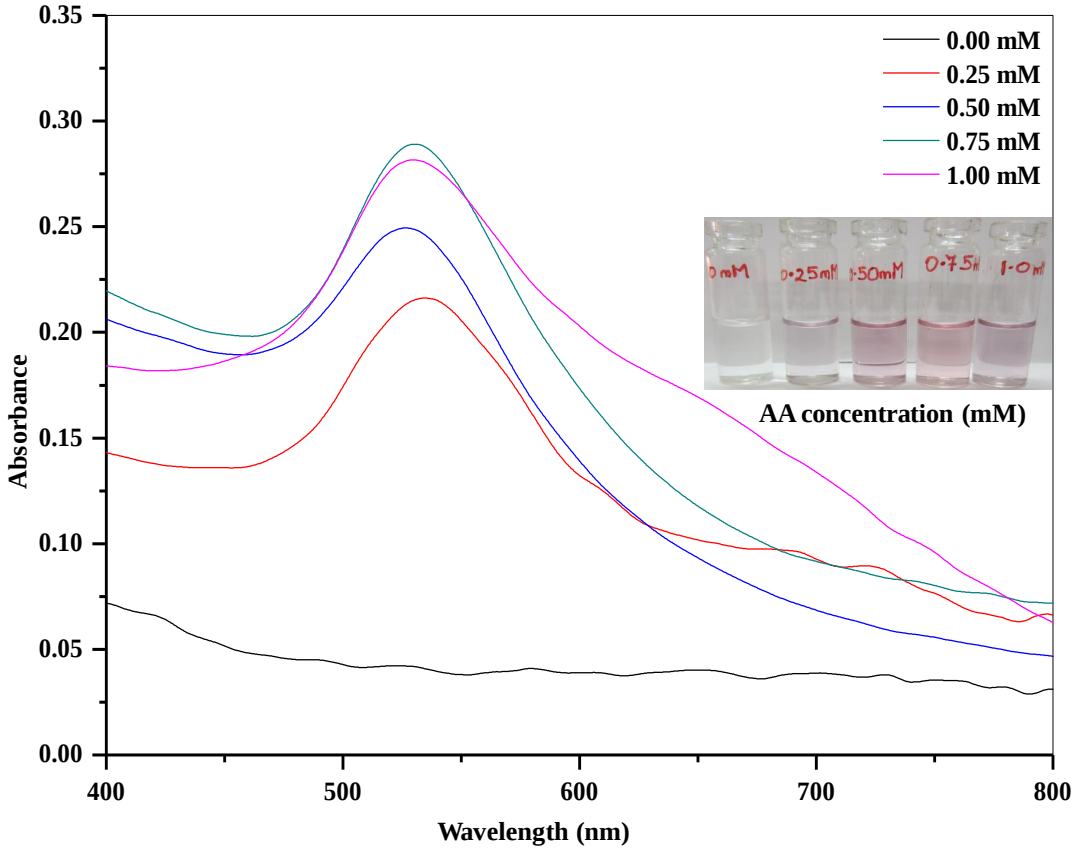

Figure 1. UV-visible spectra of Au NPs by using AA as a reducing and capping agent at different concentrations 0.25 to 1.0 mM. Inset picture shows AA-Au NPs at different concentrations of AA.

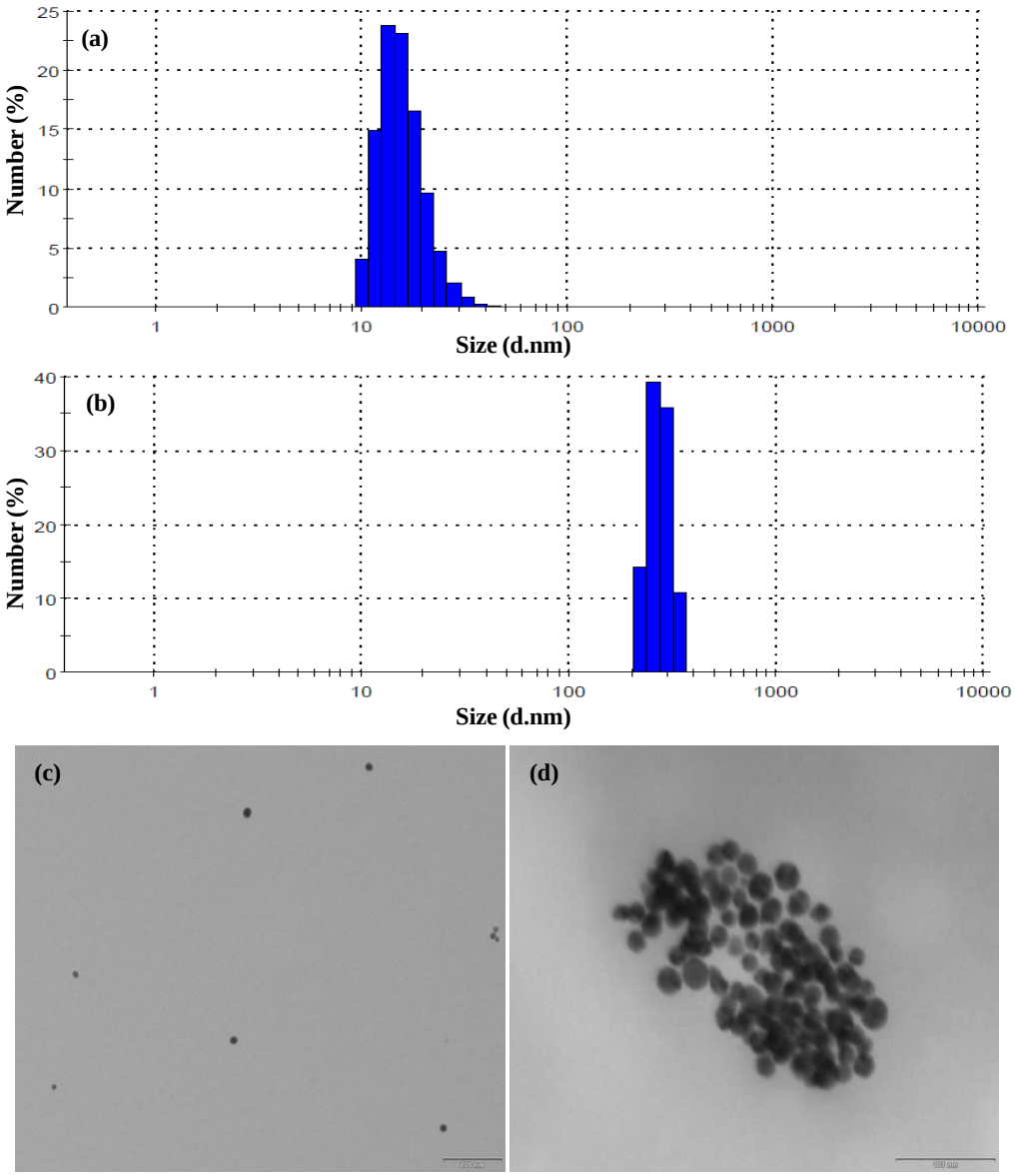

Figure 2. DLS of (a) AA-Au NPs and (b) aggregation of AA-Au NPs induced by dichlorvos. TEM images of (c) AA-Au NPs and (d) aggregation of AA-Au NPs induced by dichlorvos.

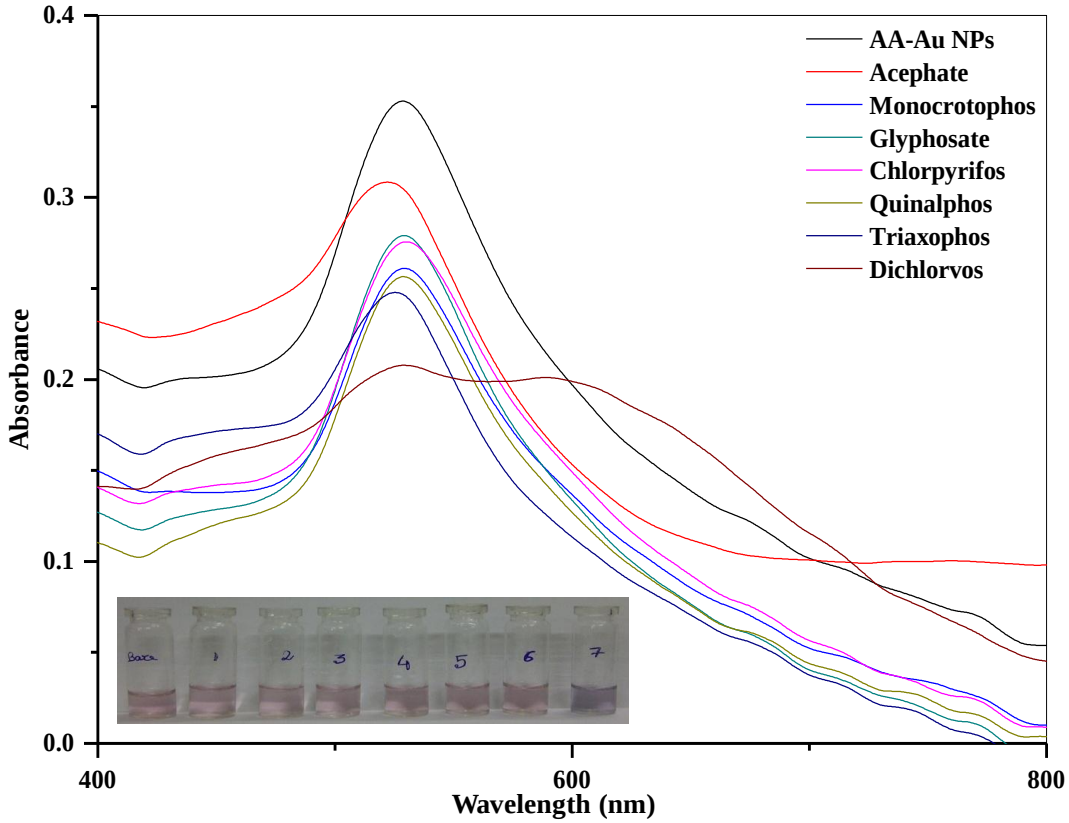

Figure 3. UV-visible spectra of AA-Au NPs in the presence pesticides (acephate, monocrotophos, chlorpyrifos, quinalphos, triaxophos and glyphosate). Inset picture shows AA-Au NPs in presence of different pesticides.

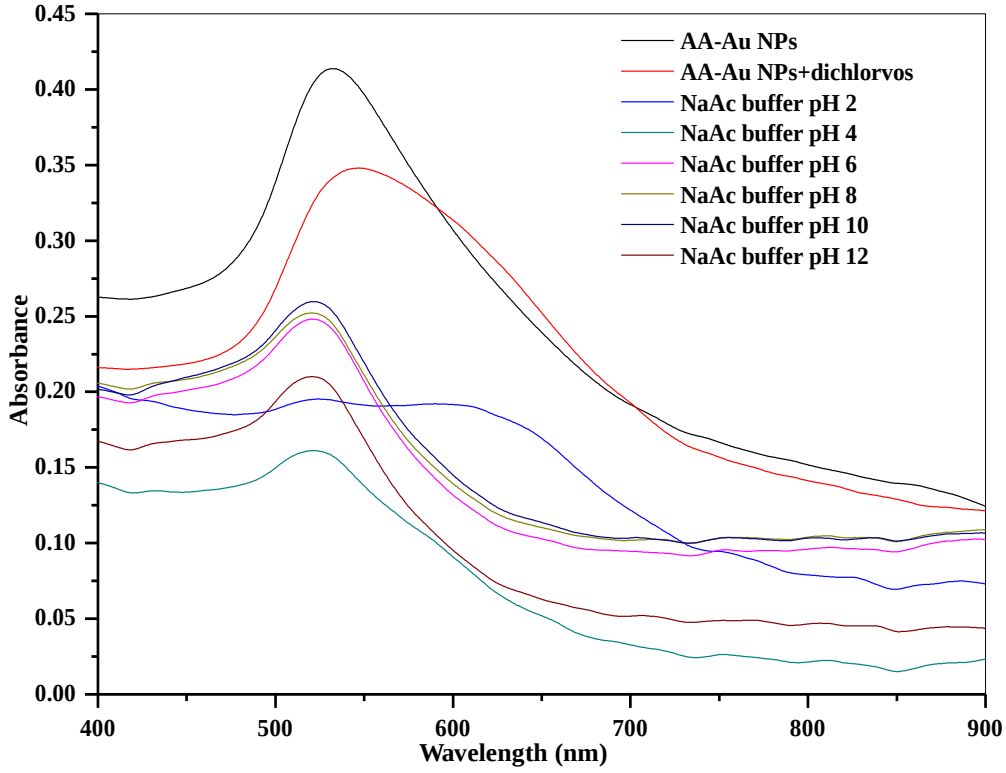

Figure 4. (a) UV-visible spectra of AA-Au NPs in presence of dichlorvos at NaAc buffer pH from 2 to 12. Inset image shows AA-Au NPs in presence of dichlorvos at NaAc buffer pH from 2 to 12.

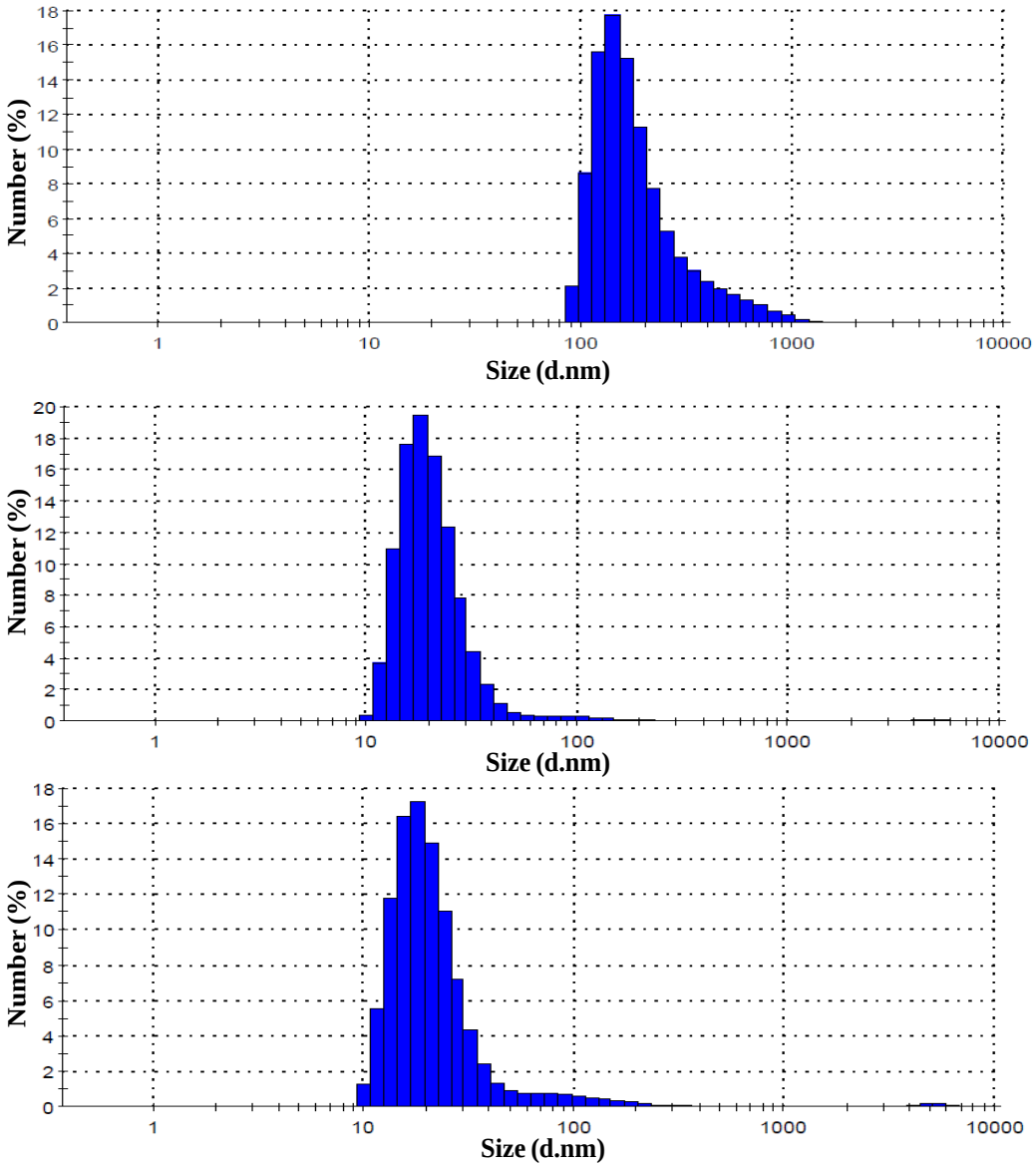

Figure 5. DLS of AA-Au NPs without addition of dichlorvos at (a) pH 2, (b) pH 4 and (c) pH 6.

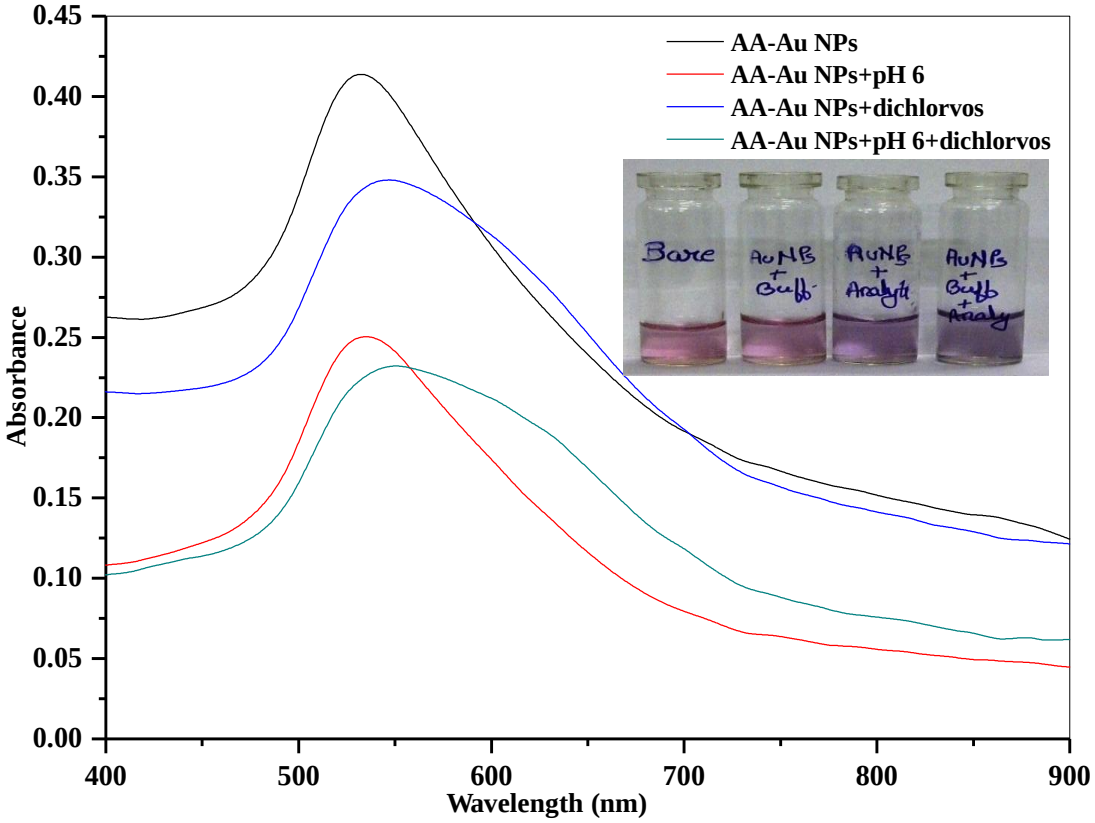

Figure 6. (a) The comparison of UV-visible spectra of AA-Au NPs after the addition of dichlorvos in the presence and absence of PBS pH 6. Inset image shows AA-Au NPs after the addition of dichlorvos in the presence and absence of PBS pH 6.

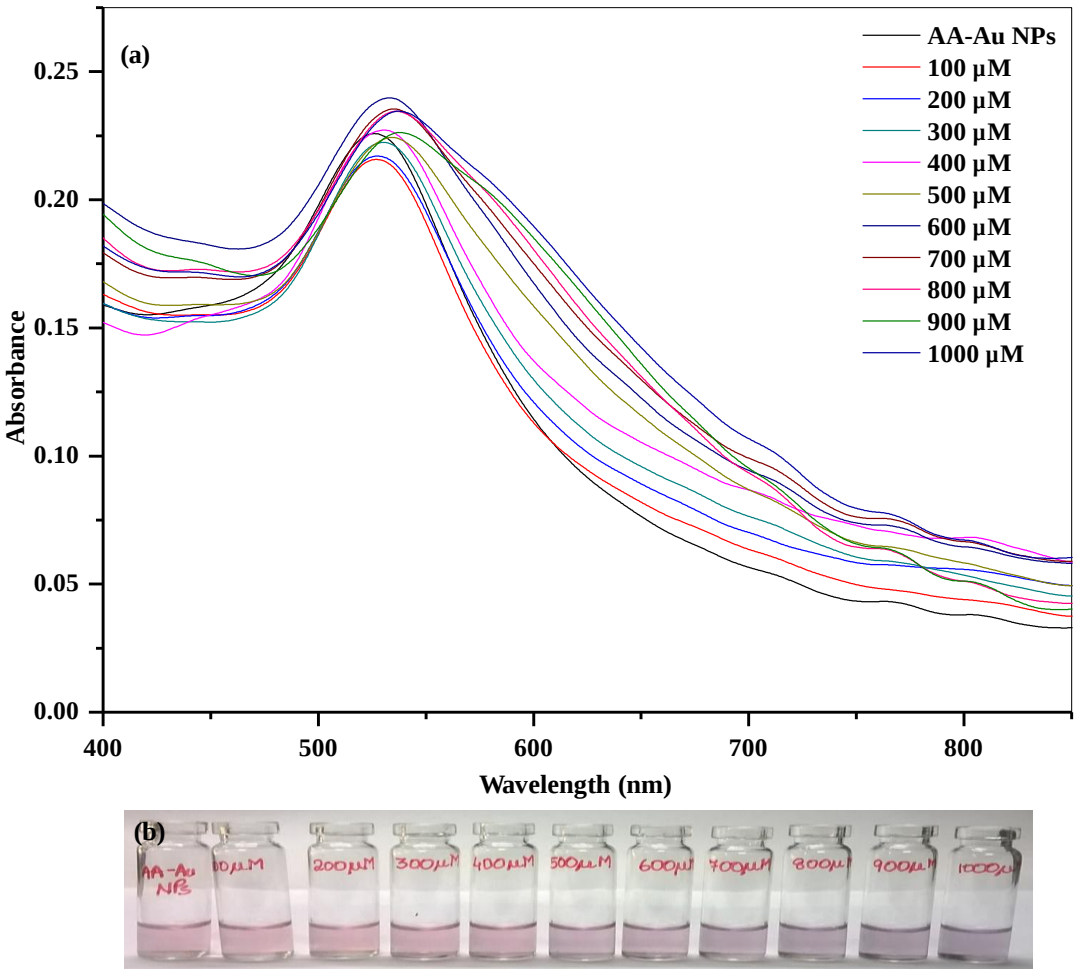

Figure 7. (a) UV–visible spectra of AA-Au NPs upon the addition of dichlorvos in the range of 100 to 1000 µM and (b) photographic image of Au-Au NPs with dichlorvos concentration in the range of 100 to 1000 µM.

Table 1. Analysis of dichlorvos in water, apple and wheat samples by using AA-Au NPs as a probe.

Sample	Added amount (μM)	Found amount (μM)	R.S.D (%, *n*=3)	Recovery (%, *n*=3)
Tap water	250	242	0.41	96.80
	500	480	0.17	96.00
	750	736	0.21	98.13
	1000	900	0.34	90.00
River water	250	241	0.65	96.40
	500	477	0.21	95.40
	750	713	0.21	95.06
	1000	900	0.25	90.00
Canal water	250	242	0.62	96.80
	500	450	0.33	90.00
	750	718	0.36	95.73
	1000	920	0.10	92.00
Wheat	250	237	0.42	94.80
	500	486	0.45	97.20
	750	759	0.34	101.20
	1000	970	0.13	97.00
Apple juice	250	234	0.85	93.60
	500	474	0.62	94.80
	750	721	0.24	96.13
	1000	962	0.15	96.20

Table 2. Precision and accuracy of method for the analysis of dichlorvos by using AA-Au NPs as a probe.

Sample	Known concentration (μM)	Intra-day			Inter-day		
		Found concentration (μM)[a]	RSD(%)[b]	Accuracy (%)[c]	Found concentration (μM)[a]	RSD(%)[b]	Accuracy (%)[c]
Tap water	500	480	0.17	-4.0	478	0.32	-4.3
	750	736	0.21	-1.9	733	0.31	-2.2
	1000	900	0.34	-9.9	901	0.27	-9.8
Wheat	500	486	0.45	-2.8	487	0.33	-2.6
	750	759	0.34	+1.2	758	0.28	+1.0
	1000	970	0.13	-2.9	969	0.21	-3.0
Apple juice	500	474	0.62	-5.2	476	0.35	-4.8
	750	721	0.24	-3.8	720	0.22	-3.9
	1000	962	0.15	-3.7	963	0.18	-3.6

[a]Mean (n = 5).
[b]Relative standard deviation.
[c]Accuracy (%) was calculated from (found concentration – known concentration)×100 / known concentration.