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Visual detection of melamine in milk products by label-free gold nanoparticles

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ABSTRACT

A simple, rapid, field-portable colorimetric method for the detection of melamine based on melamine-induced color change of label-free gold nanoparticles (Au NPs) was developed in this study. Melamine can induced the aggregation of Au NPs and results in the color change from wine-red to purple, which provided a platform for rapid and field-portable colorimetric detection of melamine. The proposed method can be used to detect melamine in liquid milk and infant formula with a detection limit of 1.0 and 4.2 ppm, respectively, within 30 min by naked eyes observation without the aid of any advanced instrument and the need of any complex pretreatment, and detect as low as 0.15 ppm of melamine in liquid milk and 2.5 ppm of melamine in infant formula with UV–vis-spectroscopy. The proposed method is promising for on-site screening of melamine adulterant in milk products.

1. Introduction

Melamine (2,4,6-triamino-1,3,5-triazine) is usually used to make melamine–formaldehyde resin, fertilizer, flame retardants and other products. It is not allowed to use as an additive in food or related ingredients. In the past few years, melamine was illegally adulterated in pet food and infant formula to increase apparent crude protein value in some developing countries since melamine contains 66% nitrogen by mass [1]. However, the excessive intake of melamine will result in the formation of insoluble melamine cyanurate crystal in kidney and finally cause renal failure [2,3]. It was reported that a large number of cats and dogs in the United States were ill or killed by consuming melamine contaminated pet food in 2007 and more than 50,000 infants and young children in China suffered from renal complication due to the consumption of melamine contaminated infant formula and dairy products in 2008 [4]. Consequently, a safety limit of melamine (2.5 mg kg^{-1}) in milk and milk based products was set by Food and Drug Administration (FDA) of USA and European Union [5,6]. The maximum residue levels of melamine in infant formula and other dairy products are legally regulated at 1 and 2.5 mg kg^{-1}, respectively, by Chinese government after the melamine accident. Therefore, there is an urgent need for establishing a rapid and reliable analytical method, which is capable of detecting melamine in milk-based products at level desired by regulatory authorities.

Currently, the most common methods for the analysis of melamine in milk and milk-based products are liquid chromatography–tandem mass spectrometry (LC–MS/MS) [7–9] and gas chromatography–mass spectrometry (GC–MS) [10–11]. Other separation techniques such as capillary zone electrophoresis (CZE) [12,13], micellar electrokinetic chromatography (MEKC) [14,15], capillary electrophoresis with diode array detection (CE-DAD) [16] and high performance liquid chromatography (HPLC) with UV detection have also been developed [17–19]. Additionally, chemiluminescence (CL) [20], infrared spectroscopy (IR) [21], Raman spectrometry [22], fluorescence [23] and spectrophotometric absorption have been proposed to detect and monitor melamine too [24]. Although these methods have high sensitivity, many of them are time-consuming and labor-intensive due to the complex pretreatment, require expensive instrumentation and high cost of personnel and are not readily adaptable to on-site detection. Therefore, the development of simple, rapid, low-cost and field-portable methods for detecting melamine in milk products has become increasingly attractive.

Gold nanoparticles (Au NPs) and silver nanoparticles (Ag NPs) have been widely used as colorimetric probes for chemical sensing and biosensing, relying on their unique size-dependent and/or

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interparticle-distance dependent absorption spectrum and solution color. When the nanoparticles approach each other and aggregate, the color of the nanoparticles changes from red to purple (or blue) for gold nanoparticles and from yellow to red (or dark green) for silver nanoparticles, respectively, due to the shift of the surface plasmon band to longer wavelength [25,26]. The major advantage of metalic nanoparticles-based assays is that molecular recognition event can be transformed into color change, which can be easily observed by the naked eyes, and therefore sophisticated instruments are not required. Recently, Lu group [27] and Li group [28] developed 1-(2-mercaptoethyl)-1,3,5-triazinane-2,4,6-trione (MTT) modified Au NPs and p-nitroaniline modified Ag NPs for visual detection of melamine in infant formula, respectively. These methods exhibited relatively high sensitivity for melamine, however, the complex modification of nanoparticles limits their potential application. More simple colorimetric methods for the detection of melamine in raw milk and infant formula by unmodified nanoparticles were proposed by Li et al. [29] and Zhang's group [30], respectively. Whereas, the tedious sample preparation by solid phase extraction is disadvantageous for on-site detection [30].

In this study, a simple, economical and field-portable visual method for the detection of melamine was developed. The method is based on a rapid color change from red to purple when label-free Au NPs was mixed with melamine. A fast and simple pretreatment was constructed to remove the protein and fat in milk products by trichloroacetic acid and chloroform without the need of solid phase extraction. The proposed method can be used to detect melamine in liquid milk and infant formula with the naked eyes or UV–vis-spectroscopy within 30 min.

2. Experimental

2.1. Chemical reagents

Chloroauric acid ($HAuCl_4$), sodium citrate, trichloroacetic acid and sodium carbonate were purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjian, China). Melamine and cyanuric acid were obtained from Fluka and Acros, respectively. Chloroform was acquired from Shanghai reagent factory. All solvents and reagents are of analytical grade and were used without further purification. Millipore Milli-Q (18 MΩ cm) water was used in all experiments. A stock solution of 1.0 mM melamine was made by dissolving 0.126 g of melamine in 1 L of water. Liquid milk and infant formula were purchased from local supermarket.

2.2. Apparatus

Absorption spectra were measured by Lamda 750 UV–vis-spectrophotometer (PE, USA), Transmission electron microscopy (TEM) measurements were made on Tecnai G2 F20 S-TWIN transmission electron microscope (FEI) with an accelerating voltage of 200 kV. Samples used for TEM measurement were prepared by placing a drop of colloidal solution on carbon-coated copper grid and dried it at room temperature. The photographs were taken with IXUS105 digital camera. The pH measurements were carried out on model pHS-3C pH meter (Shanghai Dapu Instrument Factory).

2.3. Synthesis of Au NPs

All glassware used in the experiment was soaked in a aqua regia and rinsed thoroughly in water and dried in air prior to use. Au NPs were synthesized according to previous method [31]. Firstly, 5 mL of trisodium citrate (38.8 mM) was rapidly injected into 50 mL boiling solution of $HAuCl_4$ (1 mM), and the mixture was further refluxed for 15 min. The mixture was then cooled to room temperature under continuous stirring and the wine-red solution of Au NPs was obtained. The wine-red solution of Au NPs was stored at 4 °C before use. The surface plasma resonance peak of Au NPs solution was measured to be 520 nm and the size of Au NPs was deduced to be about 13 nm.

2.4. Detection of melamine in liquid milk and infant formula

For the detection of liquid milk samples, about 1.6 g sample was weighed for the determination. The sample was firstly mixed with 2.5 mL of water, 0.7 mL of 10% trichloroacetic acid and 1.0 mL of chloroform. Then, the mixture was ultrasonically treated for 15 min and centrifuged at 13,000 rmp for 6 min to separate the deposit. The solution was transferred into another centrifuge tube and adjusted to pH 8.0 with 1 M of Na_2CO_3 solution. The solution was centrifuged at 3000 rmp for 1 min to remove the deposit again and the final solution was used for detection.

In the case of infant formula, about 0.6 g sample was used for the determination. Firstly, sample was dissolved with 2.0 mL water in a centrifuge tube, and then 2.0 mL of 10% trichloroacetic acid and 1.2 mL chloroform were added. The whole was plenty mixed and ultrasonically treated for 15 min. Then, the mixture was centrifuged at 13,000 rmp for 6 min to separate the deposit. The solution was then transferred into another centrifuge tube and adjusted to pH 7.0 with 1 M of Na_2CO_3 solution. The solution was centrifuged at 3000 rmp for 1 min to remove the deposit again and the final solution was used for detection.

For the detection of melamine, 0.2 mL of sample solution (or standard solution) was taken and added into 0.1 mL Au NPs solution, then, the mixture was allowed to react for 3 min at room temperature. Finally, the absorption spectra of the reacted solution were determined with 1 mm pathlength cell and the concentration of melamine was quantified based on the absorption ratio (A_{650}/A_{520}) or naked eyes observation. The color change of the mixture solution was also recorded by digital camera.

3. Results and discussion

3.1. Detection principle

It was reported that the Au NPs in aqueous solution can be stabilized by coating it with negative-charged citrate ions [31]. As shown in Fig. 1, the stable Au NPs (13 nm in diameter) solution has a surface plasma resonance absorption peak at 520 nm (Fig. 1A, solid line) and shows wine-red color (Fig. 1A, inset: left). After adding melamine into Au NPs solution, it was observed that the Au NPs quickly aggregate in solution. This aggregation was verified by the SEM images (see Fig. 1B and C). As a result of aggregation, the Au NPs solution became blue-gray (see Fig. 1A, inset: right) and the absorbance at 520 nm decreased and a new absorption band around 660 nm appeared (Fig. 1A, dashed line). The resulting aggregation-based change in color can be developed into a simple, rapid and field-portable colorimetric method for the detection of melamine by naked eyes or UV–vis-spectroscopy.

The reasons for the aggregation of Au NPs were also investigated in this study. It has been reported that the amino group and ring nitrogen of hybrid aromatic may strongly bind to the surface of Au NPs by the ligand exchange with citrate ions, and the ligand exchange decreases the electrostatic repulsion between individual Au NPs and finally results in the aggregation of Au NPs [32–34]. Melamine molecule contains three exocyclic amino groups and a three-nitrogen hybrid ring. Chi et al. considered that three exocyclic amino groups and three-nitrogen hybrid ring of melamine

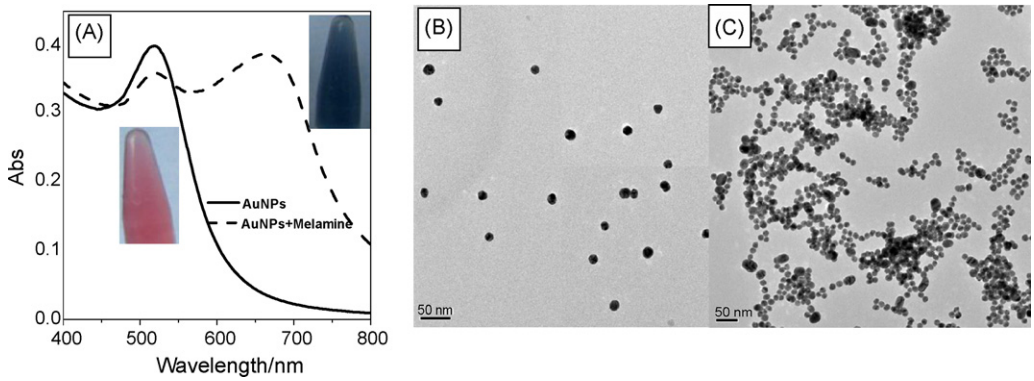

Fig. 1. (A) Absorption spectra of Au NPs in the absence of melamine (solid line) and in presence of melamine (dashed line). The insert are photographs of 100 μL Au NPs + 200 μL H_2O solution (left), 100 μL Au NPs + 200 μL melamine (2.0 μM) solution (right). (B) The TEM image of Au NPs in the absence of melamine. (C) The TEM image of Au NPs in presence of melamine. Experimental condition: incubation time, 3 min; reaction temperature, room temperature (~20 °C).

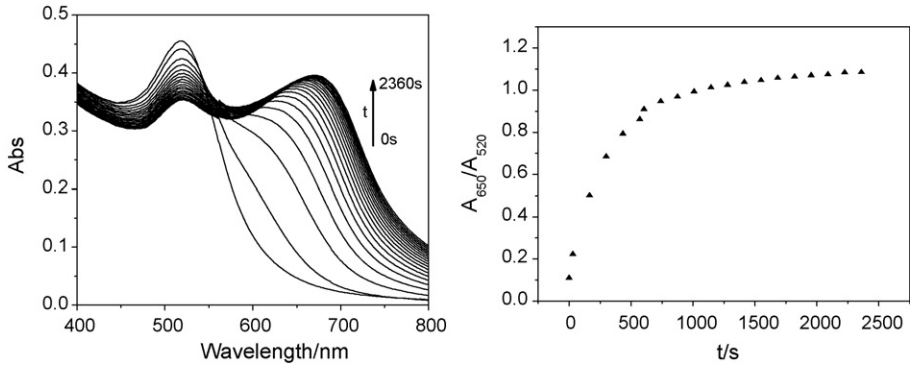

Fig. 2. Time-dependent absorption spectra (A) and time-absorbance ratio A_{650}/A_{520} (B). Data was obtained by adding 0.2 mL of melaminle solution (2.0 μM) to 0.1 mL Au NPs solution.

molecule are responsible for the aggregation of Au NPs [30]. However, Li et al. considered that only three amino groups of melamine molecule contribute to the aggregation of Au NPs [29]. In this study, a contrast experiment was carried out by using cyanuric acid, which three amino groups (–NH_2) of melamine were substituted by three hydroxy groups (–OH), as a substitute for melamine. The experimental result showed that cyanuric acid could not induce the aggregation of Au NPs (see Supplementary data), indicating that only three amino groups of melamine are responsible for the interaction between melamine and Au NPs. Our results are consistent with the phenomenon reported by Li et al. [29].

As a rapid and field-portable colorimetric method, the rate of interaction between melamine and Au NPs is another key point. The relationship between reaction time and absorption spectra was investigated by adding 0.2 mL of 2.0 μM melamine solution into 0.1 mL of Au NPs solution. Our result showed that the aggregation of Au NPs completed within 3 min (see Fig. 2).

3.2. Sensitivity of melamine detection

The aggregation of Au NPs induced by melamine was monitored by UV–vis-spectroscopy (Fig. 3A). On the addition of melamine from 0 to 2.6 μM, the absorbance of Au NPs solution at 520 nm decreased gradually and the absorbance around 660 nm increased obviously. At the same time, the color of the mixture solution changed from wine-red to purple and finally to blue progressively.

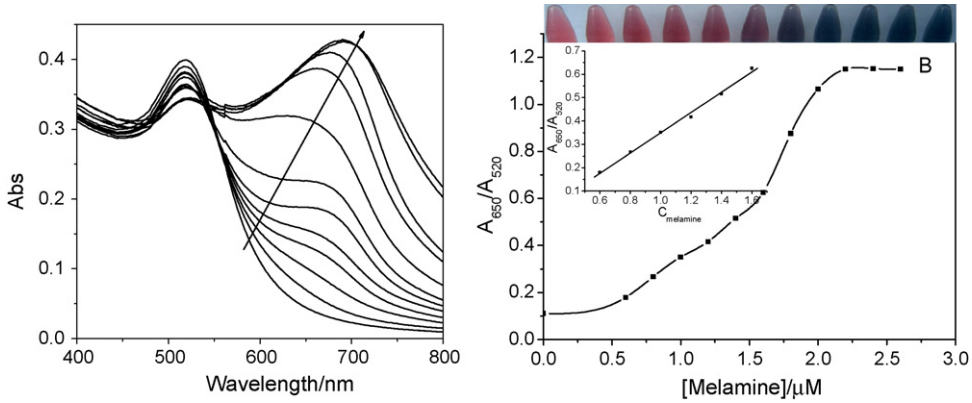

Fig. 3. (A) Absorption spectra of Au NPs in the present of melamine and (B) effect of melamine on the absorbance ratio of A_{650}/A_{520}. Insert in (B) are photographs of 100 μL Au NPs solution mixed with 200 μL melamine solution. The concentrations of melamine (from left to right) are 0, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6 (μM), respectively.

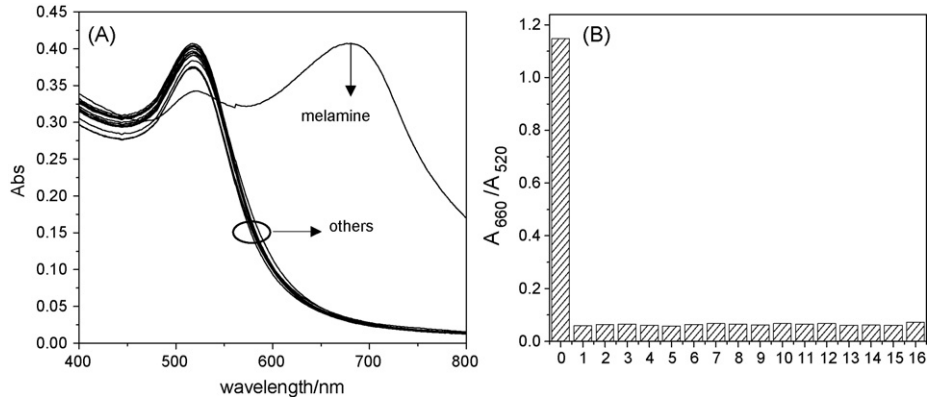

Fig. 4. (A) UV–vis spectra of Au NPs solution in the presence of different analytes. (B) The absorbance ratio (A_{650}/A_{520}) of Au NPs solution in the presence of different analytes. Analytes: 0, melamine; 1, Ca^{2+}; 2, K^+; 3, Na^+; 4, NH_4^+; 5, Cl^-; 6, SO_4^{2-}; 7, PO_4^{3-}; 8, nicotinic acid; 9, vitamin C; 10, lysine; 11, tryptophan; 12, threonine; 13, valine; 14, histidine; 15, glucose; 16, lactose. The concentration of melamine is 2.0 μM, the others are all 200.0 μM.

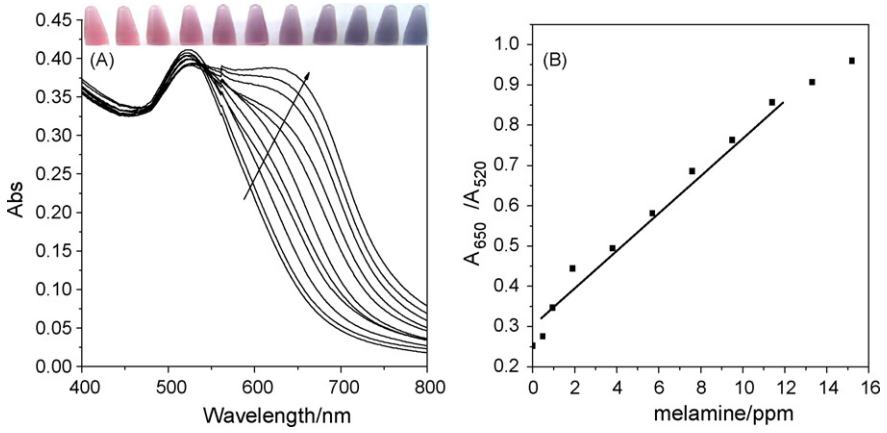

Fig. 5. Concentration-dependent absorption spectra of the label-free Au NPs (A) and the corresponding plot of A_{650}/A_{520} versus melamine concentration spiked in liquid milk (B). Insert in (A) are photographs of 100 μL Au NPs solution mixed with 200 μL pretreated-solution of liquid milk. The concentrations of melamine spiked in liquid milk (from left to right) are 0, 0.48, 0.95, 1.90, 3.80, 5.70, 7.60, 9.50, 11.4, 13.3, 15.2 (ppm), respectively.

The color change and the absorbance of the mixture solution correlate with the concentration of melamine. As showed in Fig. 3B, a clear color change from wine-red to deep-red could be easily differentiated by naked eyes when the concentration of melamine is 0.8 μM (0.1 ppm), indicating that the proposed method can be used to detect as low as 0.8 μM (0.1 ppm) of melamine by naked eyes observation. The absorbance ratios (A_{650}/A_{520}) were calculated based on the data shown in Fig. 3A, and a good linear relationship (correlation coefficient $R = 0.99$) was observed between A_{650}/A_{520} and concentration of melamine in the range of 0.6–1.6 μM. The detection limit ($3\sigma/S$, the concentration necessary to yield a net signal equal to three times the standard deviation of the background) was calculated to be 0.2 μM (0.025 ppm) by using UV–vis-spectrometer, much lower than that of 0.1 ppm obtained with naked eyes observation.

3.3. Selectivity

In order to detection melamine in milk products, the interference of the common ions and excipients in milk products were

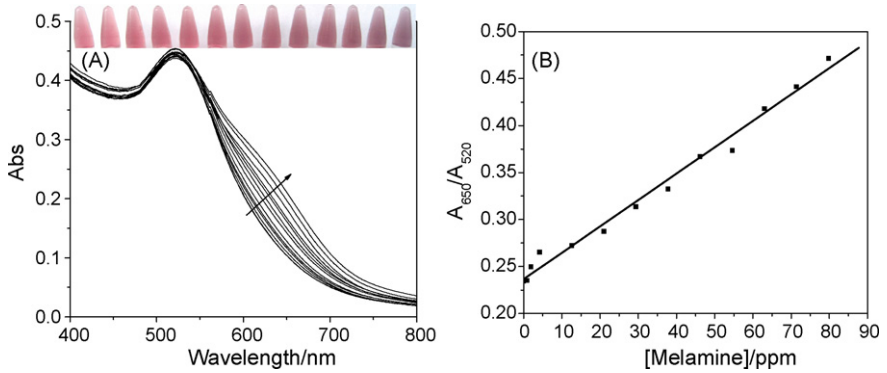

Fig. 6. Concentration-dependent absorption spectra of the label-free Au NPs (A) and the corresponding plot of A_{650}/A_{520} versus melamine concentration spiked in infant formula powder (B). Insert in (A) are photographs of 100 μL Au NPs solution mixed with 200 μL pretreated-solution of infant formula. The concentration of melamine spiked in liquid milk (from left to right) are 0, 0.8, 1.9, 4.2, 12.6, 21.0, 29.4, 37.8, 46.2, 54.6, 63.0, 71.4, 79.8 (ppm), respectively.

investigated. UV–vis spectra of Au NPs solution after added 100-folds of different analytes (200.0 μM) were shown in Fig. 4A and their absorbance ratios (A_{650}/A_{520}) were shown in Fig. 4B. It was clearly observed that melamine exhibited the highest absorbance ratio (A_{650}/A_{520}) value (1.15) and the others have a negligible value (0.07), indicating that 100-folds of common ions (Ca^{2+}, K^+, Na^+, NH_4^+, Cl^-, SO_4^{2-} and PO_4^{3-}), nicotinic acid, vitamin C, amino acids and sugar do not induce the Au NPs aggregation and interfere the detection of melamine. Above results indicate that label-free Au NPs can be applied to detect trace melamine in milk products.

3.4. Detection of melamine in real samples

In order to validate the reliability of the proposed method, real liquid milk and infant formula samples, which spiked with different concentration of melamine, were detected according to the procedure described in Section 2.4 and their results were shown in Figs. 5 and 6, respectively. In the case of liquid milk, the color change from wine-red to deep red can be clearly differentiated at a melamine concentration of 1.0 ppm (see Fig. 5A), indicating that as low as 1.0 ppm of melamine in liquid milk can be detected with naked eye observation. The absorbance ratio (A_{650}/A_{520}) exhibited a good linear correlation (correlation coefficient $R = 0.99$) with melamine concentration in the range from 0.5 to 11.0 ppm (see Fig. 5B), and the detection limit ($3\sigma/S$) was calculated to be 0.15 ppm. For the detection of infant formula, the color change from wine-red to deep red could be observed when the concentration of melamine is 4.2 ppm (see Fig. 6A), suggesting that our method can be used to detect as low as 4.2 ppm of melamine in infant formula by naked eye observation. The absorbance ratio (A_{650}/A_{520}) showed a good linear correlation (correlation coefficient $R = 0.99$) with melamine concentration in the range of 0–80.0 ppm (see Fig. 6B), and the detection limit ($3\sigma/S$) was calculated to be 2.5 ppm. Although the sensitivity of our method was lower than that of LC–MS/MS [7–9] or GC–MS [10,11], our method still reveals obvious advantage such as without advanced instrument and solid phase extraction, short analysis time and low cost etc. Compared to standard solution (see Fig. 3), the detection limits for the detection of liquid milk and infant formula were found to be relatively higher, this is probably due to the effect of complex matrix in milk products and the dilution effect during the pretreatment. In addition, the infant formula, which has a higher content of protein, fat, mineral salts and carbohydrate than liquid milk [9], exhibited the stronger matrix effect than liquid milk and resulting in lower detection sensitivity.

As we mentioned above, the maximum residue levels of melamine in infant formula and liquid milk are legally regulated at 1 and 2.5 mg kg^{-1}, respectively, by Chinese government. Therefore, our method can be used to detect melamine in real liquid milk with naked eyes observation and determine melamine in real infant formula with UV–vis-spectrometer within 30 min.

4. Conclusion

A simple, rapid and field-portable colorimetric method for the detection of melamine in liquid milk and infant formula based on melamine-induced color change of label-free Au NPs was developed here. The three amine groups of melamine molecule are demonstrated to be the key factor to induce Au NPs aggregation. The proposed method can be used to detect melamine in liquid milk and infant formula with a detection limit of 1.0 and 4.2 ppm, respectively, within 30 min by naked eyes observation without the aid of any advanced instrument and the need of any complex pretreatment. With the help of UV–vis-spectrometer, the proposed method can be used to detect melamine in liquid milk and infant formula with a detection limit of 0.15 and 2.5 ppm, respectively, which meets the safety limit of melamine (2.5 mg kg^{-1}) in USA and EU. The proposed method is promising for on-site screening melamine adulterant in milk products.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2010.07.035.

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