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Colorimetric determination of thiram based on formation of gold nanoparticles using ascorbic acid

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ABSTRACT

A novel optical method for the determination of thiram has been developed using surface plasmon resonance peak of gold nanoparticles (AuNPs). The stable and dispersed AuNPs were directly synthesized by reduction of $HAuCl_4$ with ascorbic acid in micellar media according to a simple approach. The presence of thiram during formation of AuNPs results in the decrease of the intensity of plasmon resonance peak. The variation in the plasmon absorbance allows the colorimetric determination of thiram. The effect of different variables such as pH, ascorbic acid and CTAB concentrations was studied and optimized. The proposed method is capable of determining thiram over a range of $2.0\times10^{-7}-1.0\times10^{-5}$ mol L^{-1} with a limit of detection 1.7×10^{-7} mol L^{-1}. The relative standard deviation of the method was $<3.7\%$. The method was successfully applied to the determination of thiram in water and plant seed samples.

1. Introduction

In recent years, nanoscience and nanotechnology have attracted worldwide research interests which have become a rapidly expanding area in different branches of science [1]. In this field, the marvelous advances of metals nanoparticles have established numerous fundamental studies and applications in a various scientific research. Many of these applications are inspired by the unique optical properties of metal nanostructures, which derive from the localized surface plasmon resonance (LSPR), a collective oscillation of the conduction electrons that (for spheres) typically occurs in the visible to near-UV region of the spectrum [2,3]. Therefore, the preparation and characterization of these particles with nanometer-sized dimensions have become an important aspect of materials research [4].

Due to the considerable chemical and physical properties, gold nanoparticles (AuNPs) have attracted much attention as an advantageous platform for highly sensitive colorimetric detection of target analyte. One of the most interesting properties of AuNPs is their strong surface plasmon resonance (SPR) absorption in the visible wavelength range which depends on their size, shape and surrounding medium [5–7].

Recently, colorimetric sensing in aqueous solution using plasmon resonance band of AuNPs has been developed for sensitive and selective detection of various species such as fluoride ion [8], amino acids [9], Ag^+ [10], dopamine [11] and Hg^{2+} [12]. In many reported methods, AuNPs were prepared before use and then utilized to detection systems, such as citrate reduction procedure.

The appropriate synthetic methods using different reducing agents have been reported for preparation of AuNPs [13–15]. Furthermore, the previous studies revealed that the AuNPs could be enlarged in a solution containing $HAuCl_4$ in the presence of some active molecules such as H_2O_2 [16], flavonoids [17], cholesterol along with cholesterol oxidase [18] nicotinamide adenine dinucleotide [19] and glucose together with glucose oxidase [20]. These researches have been extensively used in design of different kinds of biosensors for detection of such active molecules.

However, the application of ascorbic acid as a reducing reagent for formation of AuNPs has many advantageous including its water solubility, biodegradability and low toxicity. Up to our knowledge, there is no report of colorimetric detection methods using AuNPs formed by ascorbic acid in aqueous solutions. Thus according to capabilities of ascorbic acid, it can be applied as reducer for developing fast, eco-friendly and simple detection methods based on plasmon resonance band of AuNPs.

Thiram (tetramethylthiuram disulfide) is a dimethyl dithiocarbamate compound (Fig. 1) which belongs to the group of *N*,*N*-dialkyldithiocarbamate pesticides [21]. Thiram has long been known as a fungicide for preservation of fruits, vegetables, ornamentals and turf crops from deterioration in storage or transport and it has been widely applied for the seed treatment of small grains. Thiram is also used in rubber industry as a vulcanization accelerator, in the treatment of human scabies

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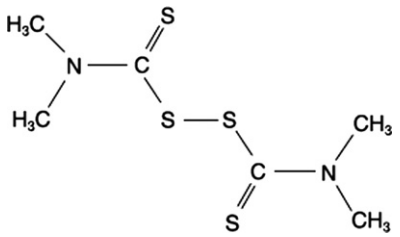

Fig. 1. Chemical structure of thiram (tetramethylthiuram disulfide).

and as a bactericide into soaps. Although the usability of this dithiocarbamate compound is undisputable, but its increasing use, results in being released into the environment leading to contamination of food and water which finally lead to hazardous effect in the living organisms through diverse pathways. The toxicity of thiram to the liver is well recognized due to the formation of carbon disulfide from the breakdown of thiram in the body [22,23].

Therefore, the use of thiram in different area requires the control of the concentration of this compound in underground and surface waters, soils and agricultural products.

In this study, a colorimetric assay method for the determination of thiram has been developed. The method is based on reduction of $HAuCl_4$ to AuNPs by ascorbic acid in the presence of thiram and CTAB. The quantitative analysis of thiram was achieved using plasmon resonance absorption peak of AuNPs.

2. Experimental

2.1. Apparatus

A GBC UV–vis spectrophotometer model Cintra 101 (Australia) was used for recording the spectra, and the absorbance measurements were made using a Perkin Elmer UV–vis spectrophotometer model 550S by 1 cm glass cells. Measurement of pH was performed using a Metrohm 632 (Switzerland) pH-meter with a combined glass electrode. Transmission electron microscopy (TEM) image of AuNPs was recorded by a Zeiss Em10C instrument (Germany) operated at 80 kV.

2.2. Reagents and solutions

All reagents were of analytical grade and double distilled water was used throughout the experiments.

A 1.0×10^{-2} mol L^{-1} of thiram stock solution was prepared by dissolving 0.121 g of thiram (Merck) in ethanol and diluting to 50 mL in a volumetric flask. Working solutions were prepared by adequate dilution of the stock solution. A hydrogen tetrachloroaurate(III) (chloroauric acid) stock solution, 1.8×10^{-2} mol L^{-1}, was prepared by dissolving 0.350 g $HAuCl_4\cdot3\,H_2O$ (Merck) in deionized water and diluting to 50 mL. An ascorbic acid solution, 1.0×10^{-2} mol L^{-1}, was prepared by dissolving 0.088 g of ascorbic acid (Merck) in water and diluting to 50 mL in a volumetric flask. This solution was kept in a dark cold place and working solutions were prepared daily. A 0.10 mol L^{-1} solution of CTAB (Cetyltrimethylammonium bromide) was prepared by dissolving 3.644 g of CTAB (Merck) in water and diluting to 100 mL. Britton–Robinson buffers [24] in the pH range of 2–13 were used for adjusting pH of solutions.

2.3. Analytical procedure

Under optimum condition, the appropriate amounts of Britton–Robinson buffer solution at pH 11.5, CTAB, $HAuCl_4$, thiram as analyte and ascorbic acid were added to a 10 mL volumetric flask, respectively. Then the solution was diluted to mark immediately and mixed slowly. After 6 min, the absorbance was measured at 527 nm which is λ_{max} of surface plasmon resonance peak of AuNPs. A blank solution was also run under the same procedure.

2.4. Preparation of plant seed samples

3.0 g of the plant seed sample (tomato, cucumber or watermelon) preserved by thiram, was weighed and placed into a 100 mL beaker, then 30 mL of ethanol was added, covered by a lid and stirred about 5 h. The solution was then filtered and diluted to 50 mL in a volumetric flask. An aliquot of the above solution was treated under the general procedure for determination of thiram.

3. Results and discussion

In this paper, AuNPs were formed by the direct reduction of $HAuCl_4$ using ascorbic acid in the presence of CTAB as stabilizer, at a certain pH and ambient temperature. The microscopic characterization of the prepared AuNPs showed that by the control of the experimental conditions, it was possible to synthesize highly dispersed AuNPs with an average size of 10 nm, as illustrated in the TEM image in Fig. 2. On the other hand, the plasmon absorption spectrum of AuNPs exhibits only a single peak at 527 nm. The presence of thiram during AuNPs formation has effective influence on the plasmon resonance absorbance which leads to decrease in its intensity. This effect can be due to interaction of sulfur atoms of thiram with gold.

The UV–vis spectra of the AuNPs plasmon in the absence and presence of different concentrations of thiram are shown in Fig. 3. As can be seen in the figure the absorbance at maximum wavelength, 527 nm, decreased with increasing of thiram concentration. Thus, the difference in plasmon absorbance of AuNPs in the absence and presence of thiram at 527 nm, ΔA, was used as analytical parameter for determination of this pesticide. The influence of different variables on ΔA was investigated and optimized.

3.1. Effect of pH

The formation and stability of AuNPs depends strongly on the pH of the solution. Therefore the effect of pH on the plasmon

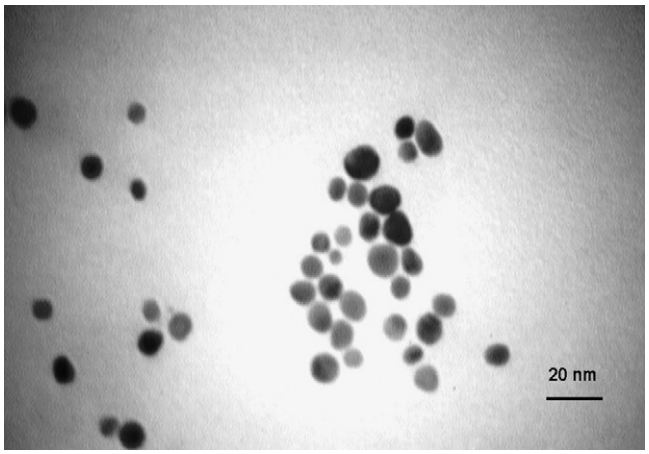

Fig. 2. TEM image of the obtained AuNPs. *Conditions:* $HAuCl_4$ concentration: 1.8×10^{-4} mol L^{-1}; CTAB concentration: 1.1×10^{-2} mol L^{-1}; Ascorbic acid concentration: 8.0×10^{-4} mol L^{-1}; pH=11.5.