Catalytic Diazotization Using Silver and Gold Nanoparticles and Spectrophotometric Determination of Parathion Residues in Fruit and Soil

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Abstract: The catalytic activity of silver and gold nanoparticles in the spectrophotometric determination of parathion using 1-naphthol as a new coupling reagent to form an azo dye is described. It is based on the reduction of nitro group in parathion with zinc/HCl to form an amino derivative, which is diazotized and subsequently coupled with 1-naphthol to form an orange colored azo dye in alkaline medium. The size and shape effect of silver and gold nanoparticles in the time for diazotization is thus studied. The important analytical parameters and optimum reaction conditions have been evaluated.

Keywords: Silver and Gold nanoparticles, Diazotization, Catalytic activity.

1. INTRODUCTION

Methyl parathion is one of the most hazardous insecticides that are used for the control of sucking and chewing insects in a very wide range of crops such as cereals, fruits, vegetables and cotton, and ornamentals [1]. It is also known as Alkron, Niram, Rhodiatox, Thiophos, E-605, 3422, and SNP. It is highly toxic to nearly all forms of life makes it extremely valuable as insecticide and acricide for controlling aphides, mites etc. [2-5].

Parathion residues are found in a variety of vegetable and foliage samples, which is causing great concern to national and international health authorities. The residual life of parathion on the plant surface was reported to be 5- 12 days. Parathion has a high mammalian toxicity with an acute oral LD_{50} to rats which varies from 5-15 mg/kg. A pesticide tolerance of 1 ppm (by weight) has been established by the Food and Drug Administration, USA [6].

It is reported to be mutagenic as well as teratogenic compound [7-8]. It is reported to be excreted in the urine as p-nitrophenol. There have been many epidemics of poisoning by parathion in foods.

The most common reaction mechanism evolved by microorganism to degrade parathion is the hydrolysis process through esterases [9]. The presence of reductive degradation systems among the micro-organisms is, however quiet apparent. For instance, the major degradation route for parathion is the formation of amino parathion by reducing agents. Parathion is highly toxic in human body because it inactivates an essential enzyme called acetyl cholinesterase (ACHE). This enzyme functions in the body by destroying the biochemical acetylcholine, a substance that is stored in small cavities within certain type of cells of the nervous system called neurons. Acetylcholine is responsible for the transmission of nerve impulses from one neuron to another.

The major medical problems by its misuses are respiratory failure, brain damage, gastric pain and salivation, etc.

Due to the well known toxicity and wide usage of parathion, it is very important to determine its concentration in ppm level in plant materials and other environmental samples. A number of analytical methods, including gas chromatography mass spectroscopy(GC-MS) [10], high-performance liquid chromatography(HPLC) [11], electrochemical [12] spectrophotometric [13] and Fourier transform (FT) Raman methods [14-15] have been reported for this use.

During the past few decades many results have been published in the area of spectrophotometric determination of parathion. The most common technique for the determination of parathion is spectrophotometry that is based on the reduction of nitro group present in parathion to amino group, which is subsequently diazotized and coupled with suitable reagent to give colored product or by colorimetric determination of p-nitrophenol after alkaline hydrolysis of parathion. Some of the spectrophotometric methods are also based on the enzymatic inhibitory efficiency of parathion.

In this paper we present an alternative method, reducing the diazotization time by using conventional spectrophotometric method using 1-naphthol as a coupling reagent in presence of silver and gold nanoparticles for the determination of parathion. The method is based on the reduction of the nitro group of parathion to amino group which is subsequently diazotized in presence of silver and gold nanoparticles and coupled with 1-naphthol to form an azo dye in alkaline medium. The dye shows absorbance maxima at 500 nm. The azo dye is found to be stable for more than 30 hours. The important analytical parameters like effect of reagents, time etc. The method has been successfully applied for the determination of parathion in fruit and soil sample.

2. EXPERIMENTAL

2.1. Instrumentation

- UV-visible spectra were recorded with Carl Zeiss Jena Spekol fitted with an EK-5 unit and matched glass cells of 1-cm optical path length.
- Variable volume (10-100 µl) micropipette, Glaxosmithline Pharmaceuticals Ltd., Finland was used for handling liquid volumes.
- Sartorius electronic balance, AG GÖTTINGEN Germany, Model CP225D (Precision 10 µg) was used for weighing measurements.

2.2. Chemicals

Parathion Solution (10 µg/25ml), Hydrochloric acid (5 M), Zinc dust, Sodium nitrite (0.25%), Sulphamic acid (3%), EDTA(0.1), 1-naphthol (0.2%), Sodium hydroxide (5M). All reagents used were of analytical grade (BDH/MERCK).

2.3. Procedure

An aliquot of standard solution containing 10-83 µg of parathion was taken in a test tube and to it ~ 1 g of zinc dust and 2 ml of 5 M hydrochloric acid were added. Then 1 ml of sodium nitrite and nanoparticles were added and the solution was kept for 10 minutes for complete diazotization. 1 ml of sulphamic acid was added to remove excess of sodium nitrite. Finally 2 ml of 1-naphthol was added and kept for 3 min for coupling. The solution was then made alkaline

with sodium hydroxide to produce an azo dye. The absorbance of this dye was measured at 500 nm against reagent blank.

3. RESULTS AND DISCUSSION

3.1. Spectral characteristics

The dye formed in the proposed reaction shows maximum absorbtion at 500 nm (Fig. **(1)**). All spectral measurements were carried out against demineralized water as the reagent blank showed negligible absorption at this wavelength. The color system obeys Beer's law in the range of 10.0-83 µg of parathion in 25 ml of final volume (Fig. **(2)**).

FIG. 1. Absorption spectra of the dye.

Concentration of Parathion: 10 µg/ 25 ml

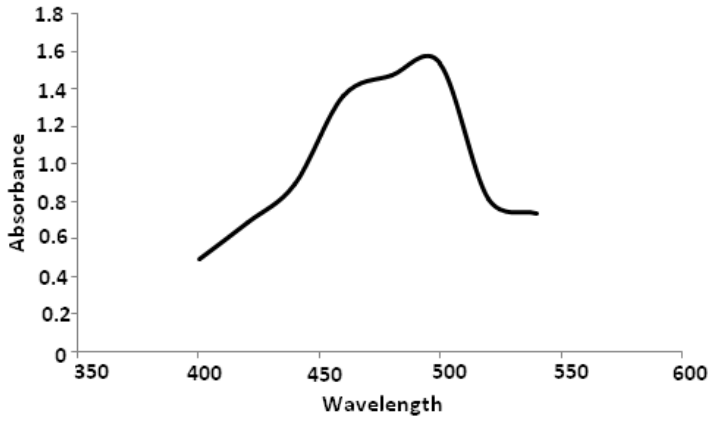
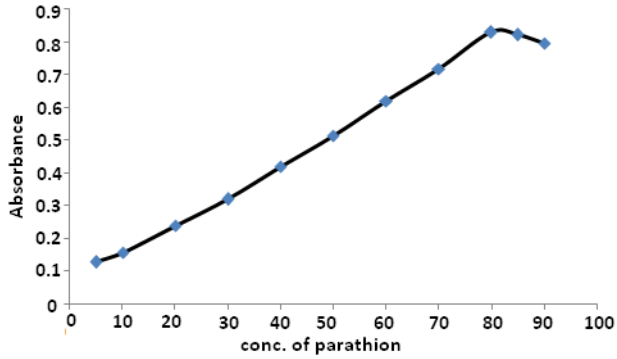


FIG. 2. Calibration data for the determination of parathion



3.2. Optimization of conditions

The reduction of the nitro group of parathion to amino group was studied at different acidity. It was observed that constant absorbance values were obtained over the acidity range 0.2-5.0 M hydrochloric acid (Fig. **(3a)**). At least 1 g of zinc dust and 2 ml of 5 M HCl were required for complete reduction. It was observed that 1 ml of sodium nitrite (Fig. **(3b**)) and 2 ml of 1-naphthol was needed for full color development (Fig. **(3c)**).

The effect of diazotization time was studied and it was found that minimum 10 min was required for complete diazotization (Fig. **(4a)**) but on adding silver (Fig. **(4b)**) and gold (Fig. **(4c)**) nanoparticles during diazotization it was found that the diazotization time was reduced to 5 min and 8 min respectively. Fig. **5a** and **5b** shows the TEM photographs of silver and gold nanoparticles respectively. It clearly shows that most of the silver nanoparticles are in triangular shape whereas gold nanoparticles are almost spherical.

FIG. 3a): Effect of acidity on the process of diazotization; Parathion concentration=10 µg/ 25ml

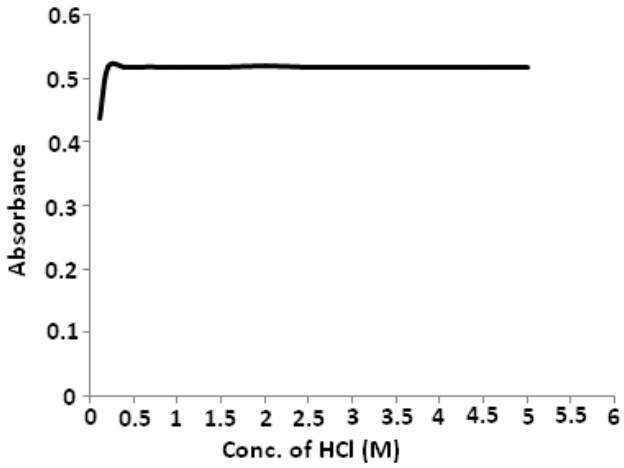


FIG. 3b): Effect of amount of sodium nitrite; Parathion concentration = 10 µg/ 25 ml

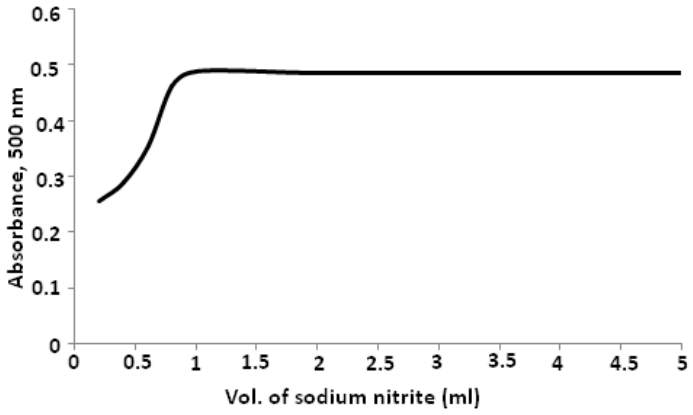


FIG.3c): Effect of amount of 1-naphthol; Parathion concentration = 10 µg/ 25 ml

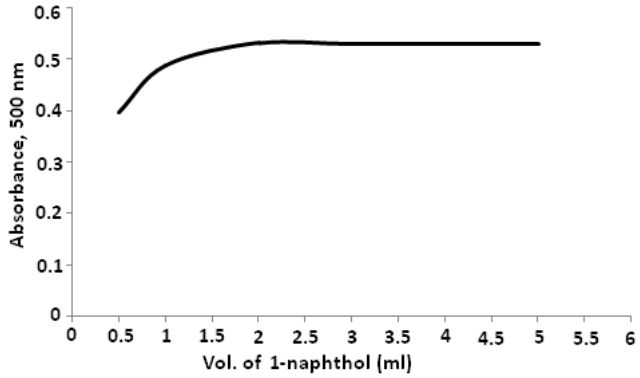


FIG.4a): Effect of time for diazotization; a = 5 mins; b = 10 mins.

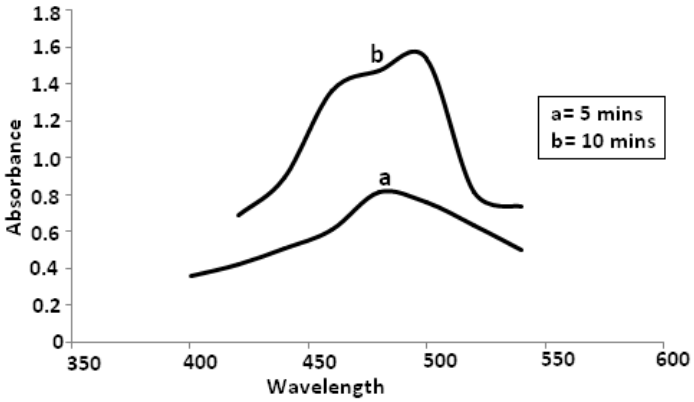


FIG.4b): Effect of time for diazotization using silver nanoparticles; a = 5 mins; b = 10 mins.

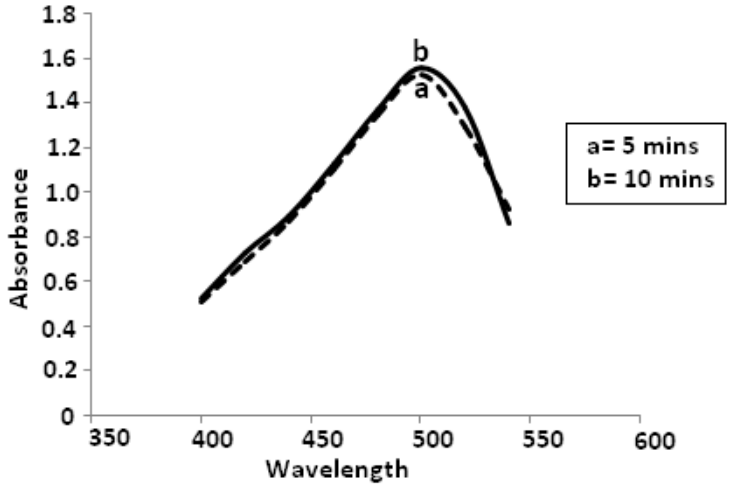


FIG.4c): Effect of time for diazotization using gold nanoparticles; a = 5 mins; b = 10 mins.

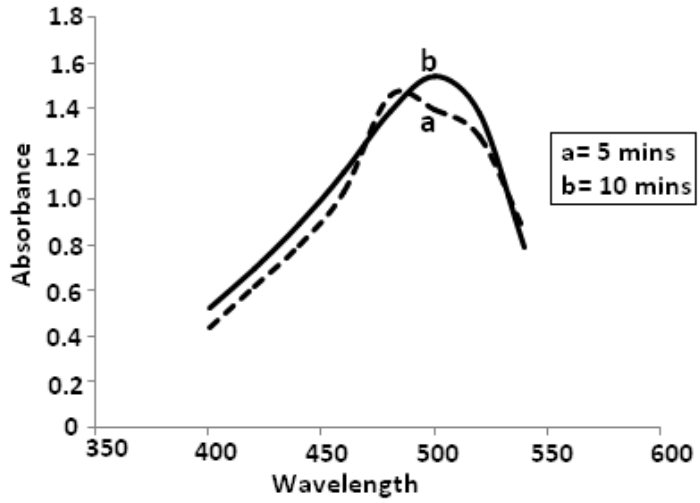
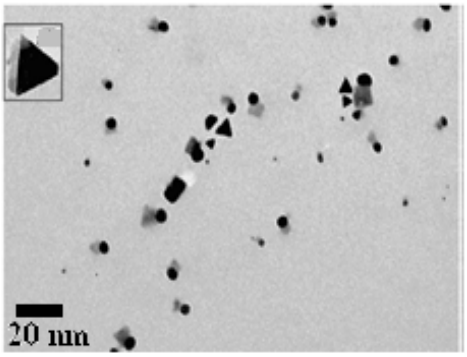


FIG.5a): TEM image of silver nanoparticle sample prepared in sodium citrate (microwave conditions: 300 W, irradiated for 3 min, inset showed a single silver nanoprism with spherical nanoparticles.



4. APPLICATIONS

4.1. Determination of parathion in fruit and vegetable samples

The samples were collected from an agricultural field, where parathion was sprayed as an insecticide. Samples were weighed, crushed into pulp and macerated with two 20 ml portions of ethanol-demineralized water (1+1), filtered through a thin cotton cloth and the filtrate was quantitatively transferred into a 25 ml volumetric flask and made up to the mark with 50 % ethanol and aliquots were used for the determination of parathion by the proposed method shown in (Table **1**).

4.2. Determination of parathion in soil sample

Known amount of soil sample was collected from an agricultural field. The sample was finely ground and washed with two portions of ethyl alcohol. The washings were collected in a 25 ml volumetric flask and made up to mark with ethanol. An aliquot of the extract was then analyzed by the proposed method shown in (Table **1**).

TABLE 1

Determination of parathion in various plant material and soil.

Samples	Parathion Added/(µg/25 ml)	Total Parathion Found//(µg/25 ml)	Difference/(µg/25 ml)	Recovery / (%)
Tomato[a]	10 20	19.5 40.5	9.5 20.5	95 103
Apple[a]	10 20	19.0 39.5	9.0 19.5	90 98
aSoil[a]	10 20	20.5 38.5	10.5 18.5	105 93

a = Amount of sample: 25 g

5. CONCLUSION

The proposed method is rapid, simple and sensitive and the reagent described here is sensitive and selective for parathion insecticides containing a nitro group. It can be precisely determined down to 0.2 ppm. The problem with low sensitivity and more time is resolved by the adsorption of parathion pesticides onto silver and gold nanoparticles during diazotization process. The catalytic activity of metal nanoparticles depends on their size and shape [16-17]. A change in electronic properties, a high surface to volume ratio, and an increase in numbers of edges, corners and faces contribute to the enhancement in activity and selectivity of nanoparticles, so it can be concluded that the relatively better result observed with silver nanoparticles in this work may be due to availability of triangular shape particles, as the shape variation, together with the

increased number of edges, corners and faces, is of critical importance in controlling the catalytic activity and selectivity of metal nanoparticles [18]. The present method shows the reduction of diazotization timing by using nanoparticles, fast process due to catalytic activity of nanoparticles and low detection limit. The application of this method in the determination of parathion in fruit and soil sample demonstrated the usefulness of the method for its determination at low levels.

6. ACKNOWLEDGEMENT

The authors are thankful to the Head, School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, India for providing laboratory facilities.

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