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Short communication

Determination of thiram using gold nanoparticles and Resonance Rayleigh scattering method

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ABSTRACT

A sensitive, simple and novel method was developed to determine thiram fungicide in water and plant samples. This method was based on the interaction between gold nanoparticles (AuNPs) and thiram fungicide followed by increasing of the Resonance Rayleigh scattering (RRS) intensity of nanoparticles. The change in RRS intensity (ΔI_{RRS}) was linearly correlated to the concentration of thiram over the range of 1.0–200.0 μg L^{-1}. Thiram can be measured in a short time (4 min) without any complicated or time-consuming sample pretreatment process. Parameters that affect the RRS intensities such as pH, concentration of AuNPs, standing time, electrolyte concentration, and coexisting substances were systematically investigated and optimized. Interference tests showed that the developed method has a very good selectivity and could be used conveniently for the determination of thiram. The limit of detection (LOD) and limit of quantification (LOQ) were 0.3 and 1.0 μg L^{-1}, respectively. Relative standard deviations (RSD) for 20.0 and 80.0 μg L^{-1} of thiram were 3.0 and 1.1, respectively. Possible mechanisms for the RRS changes of AuNPs in the presence of thiram were discussed and the method was successfully applied for the analysis of spiked real water samples and fresh plant samples such as tomato and cucumber.

1. Introduction

One of the major problems for public health is the application of pesticides and fungicides to crops in order to protect plants and increasing the yield of agricultural products. In recent years, pollution of surface waters by such toxic substances causes challenging environmental problems. Therefore, the aim of environmental scientists is to face the challenge of protecting clean water from pollution by these toxic substances and find new analytical methodologies for determination of trace amounts of these hazardous materials in water samples.

Thiram (THM) is a type of sulfur fungicides (Fig. 1) which belongs to the group of N,N-dialkyldithiocarbamate chemical pesticides [1]. THM is a non-systemic fungicide used to prevent crop damage in the field and to protect harvested crops from deterioration in storage or transport. It is also used as a seed protecting agent (e.g. tomato, cucumber, watermelon, cereal grains and other seeds) and to protect turf from fungal diseases. In addition, thiram is used as an animal repellent to protect crops from damage by rabbits, rodents, and deer. Thiram is applied to seeds prior to planting both by commercial seed treaters and on-farm applicators. Approximately 165,000 pounds of thiram are applied to 35,000 acres of strawberries, apples, and peaches annually. Approximately 631,000 pounds of thiram are used to treat approximately 1.3 billion pounds of seed annually [2]. Thiram has been used in the treatment of human scabies, as a sun screen and as a bactericide applied directly to the skin or incorporated into soap. Therefore, it is vital to develop sensitive and effective methods for the detection of THM in environmental samples.

Several analytical methods have been used for detection of THM. These methodologies include chromatography [3–8], mass spectrometry [9,10], UV–visible spectrophotometry [11–17], chemiluminescence analysis [18–20], polarography and voltammetry [2,21–23], and surface-enhanced Raman scattering spectroscopy [24]. From practical point of view, many of the above-mentioned approaches have limitations such as lack of instrument portability, limited selectivity, difficulties in real-time monitoring, operational complexity, and in some cases low sensitivity. Therefore, introducing fast, sensitive and convenient methods for the analysis of THM in environmental samples is necessary for the sake of human health and environmental pollution control.

In recent years, light scattering (LS) methods such as Resonance Rayleigh scattering (RRS) has drawn much more attention and made important contributions in many scientific areas. Resonance Rayleigh scattering occurs when the wavelength of Rayleigh scattering is located at or close to the molecular absorption band. When a particle is exposed to an electromagnetic radiation, the electrons in the particle oscillate at the same frequency as the incident wave.

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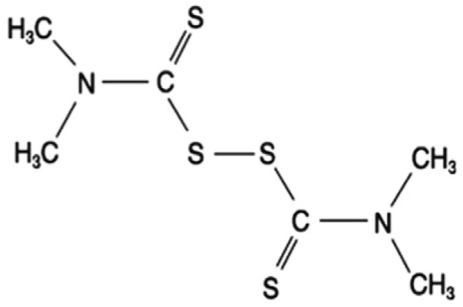
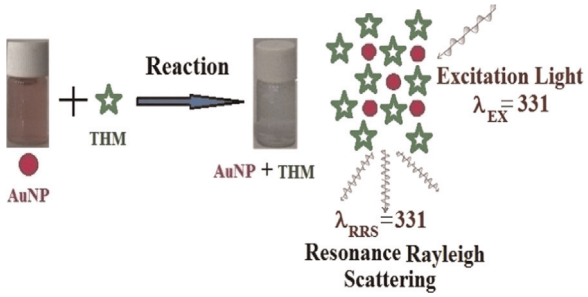


Fig.1. Chemical structure of thiram fungicide.



Scheme 1. Schematic of the reaction of AuNPs with THM fungicide which produces AuNP–THM complex at pH6.

The intensity of the Rayleigh scattered radiation increases rapidly as the ratio of particle size to wavelength increases. The properties of scattered light also depend on the composition, shape, homogeneity of the nanoparticles, and refractive index of the medium [25,26].

Different analytes have been determined by Resonance Rayleigh scattering (RRS) or resonance light-scattering (RLS) technique [27–30]. This methodology showed its high potential for the determination of metal ions [31], non-metallic inorganic substances [32,33], surfactants [34], biomacromolecules [35,36], and pharmaceuticals [37]. The method is characterized by high sensitivity, convenience in performance and simplicity in apparatus (usually common spectrofluorophotometer).

Some of nano-noble metals such as gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) possess novel physical and chemical properties, especially the surface Plasmon resonance (SPR) or Resonance Rayleigh scattering (RRS), which resulted as they are widely used in the fields of analytical chemistry and biomedical science as probes and sensors in recent years [38–40], exhibit their signals in the visible spectral region under appropriate conditions and give corresponding localized surface plasmon resonance light scattering (LSPR-LS) band of the NPs [41–43].

These noble metal nanoparticles show special optical properties such as strong resonance light scattering in the orders of magnitude higher than light emission from strongly fluorescent dye molecules [44]. Such a character makes them ideal optical probes for chemical, biological and clinical applications [45–47]. Gold nanoparticles (AuNPs) exhibit certain advantages such as higher extinction coefficients, sharper extinction bands and higher ratio of scattering to extinction. More recently, AuNPs are rapidly gaining popularity as a consequence, and some research groups have been developing several strategies for optical sensors and imaging techniques using AuNPs as building blocks and labeling probes [48–51].

Herein, a simple and sensitive method was established for the determination of THM using AuNPs. The method is based on the formation of THM–AuNPs aggregates (Scheme 1) and intensifying the RRS intensity of aggregated particles. The detection sensitivity can be significantly improved to $\mu g\,L^{-1}$ level by monitoring of signal changes of high sensitivity RRS by AuNPs. The proposed method (using RRS of AuNPs) shows lower LOD and better sensitivity toward sulfur fungicides with respect to our previous work (using RRS of AgNPs) [43].

2. Experimental

2.1. Materials and reagents

All chemicals used in the experiments were of analytical grade or higher without further purification. Thiram was purchased from Sigma-Aldrich (America) and a working solution of 10.0 $mg\,L^{-1}$ was prepared for use in the experiment. Sodium citrate and sodium borhydrate were purchased from Merck (Darmstadt, Germany). Buffer solutions were prepared by adjusting the pH of 0.1 $mol\,L^{-1}$ citric acid and phosphoric acid solutions to 6 using NaOH solution (0.1 $mol\,L^{-1}$). All solutions were prepared in high-purity water.

2.2. Apparatus

A Shimadzu RF-5301PC spectrofluorophotometer (Japan) was used for recording and measuring the RRS spectra. A pH-meter (827 pH lab, Metrohm1, Herisau, Switzerland) was used for pH adjustment. Transmission electron microscopy (906E, LEO, Germany) and scanning electron microscopy (SEM) (XL-30 electron microscope, Philips, Eindhoven, The Netherlands) were used to study the morphology of AuNPs and THM–AuNPs.

2.3. Preparation of AuNPs

The stock solution of Au (III) (1000 $\mu g\,mL^{-1}$) was prepared by dissolving 0.100 g of pure gold (24-carat) metal in concentrated $HCl:HNO_3$ (3:1) solution. Gold working solutions (10 $\mu g\,mL^{-1}$) were prepared by appropriate diluting of stock solution. AuNPs were synthesized by slow addition (drop wise) of 0.25 mL of citrate–borohydride mixture solution (10:0.75 w/v) into a beaker containing 10 mL of Au (III) (10 $\mu g\,mL^{-1}$) and 10 mL of sodium citrate (1% w/v) solution at room temperature. The color of this solution changed gradually from colorless to purple. The final concentration of AuNPs was 5 $\mu g\,mL^{-1}$ (2.53×10^{-5} $mol\,L^{-1}$). Above solution was stored at 4 °C.

2.4. Measurement of the RRS intensity of AuNPs–THM system

Appropriate amounts of the AuNPs solution (60 μL of 5 $\mu g\,mL^{-1}$), 1 mL of the citrate buffer (pH6), 1.0 mL of the 0.001 $mol\,L^{-1}$ of KCl electrolyte, and certain volumes of THM standard solutions were added into a 10.0-mL flask. The resulting solution was diluted to 10 mL and was vortex-shaken to mix thoroughly and stand for 4 min. The RRS spectra of the solutions were recorded with synchronous scanning at $\lambda_{ex}=\lambda_{sc}=331$ nm (i.e., $\Delta\lambda=0$ nm), slit widths were kept at 1.5 nm, and RRS intensity of AuNP solutions in the absence (I_0) and the presence of THM (I_{RRS}) was recorded. Fig. 2 shows the recorded RRS spectra of the blank solution (red) and the test solution (gray) and the difference in RRS intensity values ($\Delta I_{RRS}=I_0-I_{RRS}$) in the wavelength range of 230–430 nm. As it is seen in Fig. 2, at $\lambda_{ex}=\lambda_{sc}=331$ nm a large increase in the RRS intensity occurs after the addition of THM to AuNPs solution. So, 331 nm was selected as the optimum RRS wavelength for further works. Fig. 3 shows the absorption spectrum (red, wavelength range 200–700 nm) and also the RRS spectrum (green, $\lambda_{ex}=\lambda_{sc}=331$ nm, and $2\lambda_{ex}=\lambda_{sc}=662$ nm scattering wavelength range 200–700 nm) of AuNPs solution (blank). It must be mentioned that AgNPs were