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Resonance Rayleigh scattering method for determination of 2-mercaptobenzothiazole using gold nanoparticles probe

Hooshang Parham *, Nahid Pourreza, Farzaneh Marahel

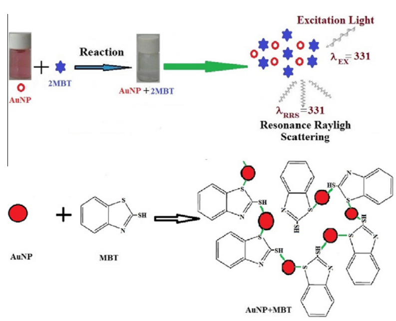
Chemistry Department, Faculty of Sciences, Shahid Chamran University, 6135714168 Ahvaz, Iran

HIGHLIGHTS

- A novel resonance Rayleigh scattering method was developed for trace 2MBT detection.
- AuNPs can be applied as sensor for 2MBT determination in real water samples.
- Resonance Rayleigh scattering of AuNPs was used for 2MBT detection in water samples.
- The method is fast and shows good accuracy and sensitivity for 2MBT detection.

GRAPHICAL ABSTRACT

Schematics of the reaction between AuNPs and 2MBT fungicide which produces AuNP–2MBT complex at pH 6.



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ABSTRACT

A sensitive, simple and novel method was developed to determine 2-mercaptobenzothiazole (2MBT) in water samples. This method was based on the interaction between gold nanoparticles (AuNPs) and 2MBT 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 2MBT over the ranges of 5.0–100.0 and 100.0–300.0 $\mu g\ L^{-1}$. 2MBT can be measured in a short time (5 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 determination of 2MBT. The limit of detection (LOD) and limit of quantification (LOQ) were 1.0 and 3.0 $\mu g\ L^{-1}$, respectively. Relative standard deviations (RSD) for 20.0 and 80.0 $\mu g\ L^{-1}$ of 2MBT were 1.1 and 2.3, respectively. Possible mechanisms for the RRS changes of AuNPs in the presence of 2MBT were discussed and the method was successfully applied for the analysis of real water samples.

1. Introduction

The quality of drinking water, pollution of surface water and water used in agricultural plants and removal of toxic substances from water samples are some critical environmental problems occurring in recent years. Therefore, this study aims to face the challenge of protecting clean water from pollution by these toxic substances and to suggest a removal mechanism for elimination of hazardous materials such as fungicides from water samples.

Mercaptans are a class of high production chemicals employed in various industrial processes. 2-Mercaptobenzothiazole (2MBT)

* Corresponding author. Tel.: +98 61 33331042; fax: +98 61 33331042.
E-mail address: hoparham@yahoo.com (H. Parham).

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(Fig. 1) is a member of mercaptans and is the most important members of the benzothiazole group, which are heterocyclic aromatic compounds. These chemicals are toxic and poorly biodegradable pollutants [1]. The production of 2MBT and its related salts was reportedly in excess of about 46 million pounds annually in the USA [2]. Estimates from the US EPA have reported that 1 million pounds of 2MBT are released annually into the environment. Its toxicity and allergenicity make its presence in the environment a challenge and a cause for concern [2–6]. The pollution effects of 2MBT on the environment are a major problem for environmental protection agencies (EPA) worldwide. The US EPA estimated that over 450 tons of mercaptobenzothiazole is deposited into the environment every year [7,8]. 2MBT is used as corrosion inhibitors to protect copper [9], it also has other applications such as in medicine as an antifungal drug [10]; a coating agent for metallic surfaces [11] and predominately, as a vulcanization accelerator in the rubber industry [12–14]. It is frequently found in effluent of wastewater treatment plants, in surface water and they are volatile organic compounds contributing to odor problems in wastewater treatment plants [15]. Environmental pollution by sulfur compounds is always of great concern for aquatic organisms and humans.

Several methods have been reported for detection and determination of 2MBT and thiols in environmental samples. Spectrophotometric and electrochemical methods have been mainly used for analysis of mercaptans [1,16–18]. Other methods for determination of aromatic thiols and aliphatic thiols are based on different chromatographic techniques [19–25]. However, to the best of our knowledge there has not been any report based on RRS for determination of trace amounts of 2MBT in water solution samples.

Resonance Rayleigh scattering (RRS) has drawn much more attention in recent years and made important contributions in many scientific areas. When a particle is exposed to an electromagnetic radiation, the electrons in the particle oscillate at the same frequency as the incident wave. Resonance Rayleigh scattering takes place when the wavelength of Rayleigh scattering is located at or close to the molecular absorption band. The properties of scattered light depend on the size, composition, shape, homogeneity of the nanoparticles, and refractive index of the medium [26,27].

Light scattering methods such as resonance Rayleigh scattering (RRS) or resonance light-scattering (RLS) has been widely applied to the determination of different analytes [28–30]. This method showed its high potential for the determination of metal ions [31], non-metallic inorganic substances [32,33], surfactants [34], biomacromolecules [35], and pharmaceuticals [36]. The method is characterized by high sensitivity, convenience in performance and simplicity in apparatus (usually common spectrofluorophotometer).

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 they are widely used in the fields of analytical chemistry and biomedical science as probes and sensors in recent years [37–39], 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 [40–42].

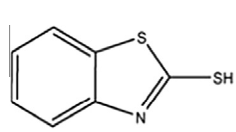
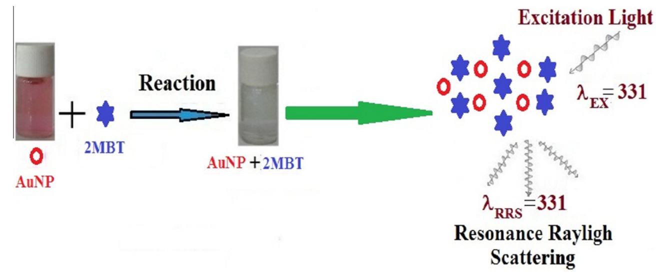


Fig. 1. Chemical structure of 2MBT fungicide.



Scheme 1. Schematic of reaction of AuNPs with 2MBT which produces AuNP–2MBT complex at pH 6.

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 [43]. Such a character makes them ideal optical probes for chemical, biological and clinical applications [44–46]. 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 [47–49].

Herein, a simple and sensitive method for determination of 2MBT using AuNPs as probes was established on the basis of the formation of 2MBT-AuNPs aggregates and intensifying the RRS intensity of aggregated particles. Scheme 1 shows the aggregation of nanoparticles occurs when AuNPs react with thiol groups of 2MBT. The reaction leads to an increase in the size of nanoparticles and also enhancement of the RRS intensity [28–32]. The detection sensitivity can be significantly improved to $\mu g\,L^{-1}$ level by monitoring of signal changes of high sensitivity RRS by AuNPs.

2. Experimental

2.1. Materials and reagents

All chemicals used in the experiments were of analytical grade or higher without further purification. 2MBT 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) was used to study the morphology of AuNPs and 2MBT-AuNPs.

2.3. Preparation of AuNPs

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. Working gold solution was prepared by appropriate diluting of stock solution. AuNPs were synthesized by slow addition (drop wise) of 0.25 mL of citrate–borohydride