

Silver and gold nanocluster catalyzed reduction of methylene blue by arsine in micellar medium

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Abstract. Arsenic can be determined in parts-per-million (ppm) level by absorbance measurement. This method is based on the quantitative colour bleaching of the dye, methylene blue by arsine catalyzed by nanoparticles in micellar medium. The arsine has been generated *in situ* from sodium arsenate by NaBH_4 reduction. The absorbance measurement was carried out at the I_{max} of the dye at 660 nm. The calibration graph set-up for three linear dynamic ranges (LDR) are 0–8.63 ppm, 0–1.11 ppm and 0–0.11 ppm and limit of detections (LODs) are 1.3, 0.53 and 0.03 ppm, respectively. This method is simple, sensitive and easy to carry out. It is free from phosphate and silicate interference and applicable to real sample analysis.

Keywords. Arsenic; nanoparticle; micelle.

1. Introduction

Manifestation of higher levels of inorganic arsenic compounds in human body is well documented. Arsenic has taken its toll (WHO's guidelines, 1993, Geneva) all over the world. The situation is particularly alarming in India and Bangladesh where currently millions of people are suffering from arsenic related diseases by drinking arsenic contaminated underground water. It has been reported that in the Indian subcontinent, underground water reserves are utilized to procure drinking water and geological reasons are usually cited to account for contamination of such water reserves by arsenic. Other major factors reported for causing arsenic related diseases in other countries include excessive mining activity (e.g. copper and gold mining in Chili), and due to the uncontrolled use of arsenic containing pesticides, paints and pigments etc.

Keeping an eye on this grave situation of arsenic poisoning, we have developed a sensitive one-pot arsenic detection method at the sub-parts-per-million (ppm) levels using micelle catalyzed reaction (Pal *et al* 1998). The participation of silver or gold nanoparticle as catalyst (Jana *et al* 1999; Sau *et al* 2001) made the method more efficient. The reaction is simply fascinating (outlined in the scheme) and reported for the first time. A simple visible spectrophotometer serves the purpose of arsenic detection well below the WHO's permissible range (0.05 ppm) after concentrating water sample by boiling. The method is very selective i.e. free from common interfering substances.

2. Experimental

2.1 Apparatus

All UV-visible absorption spectra were recorded in a Shimadzu (Kyoto, Japan) UV-160 digital spectrophotometer equipped with 1 cm quartz cells. Gilson micropipette with disposable tips was used to add samples.

2.2 Procedure

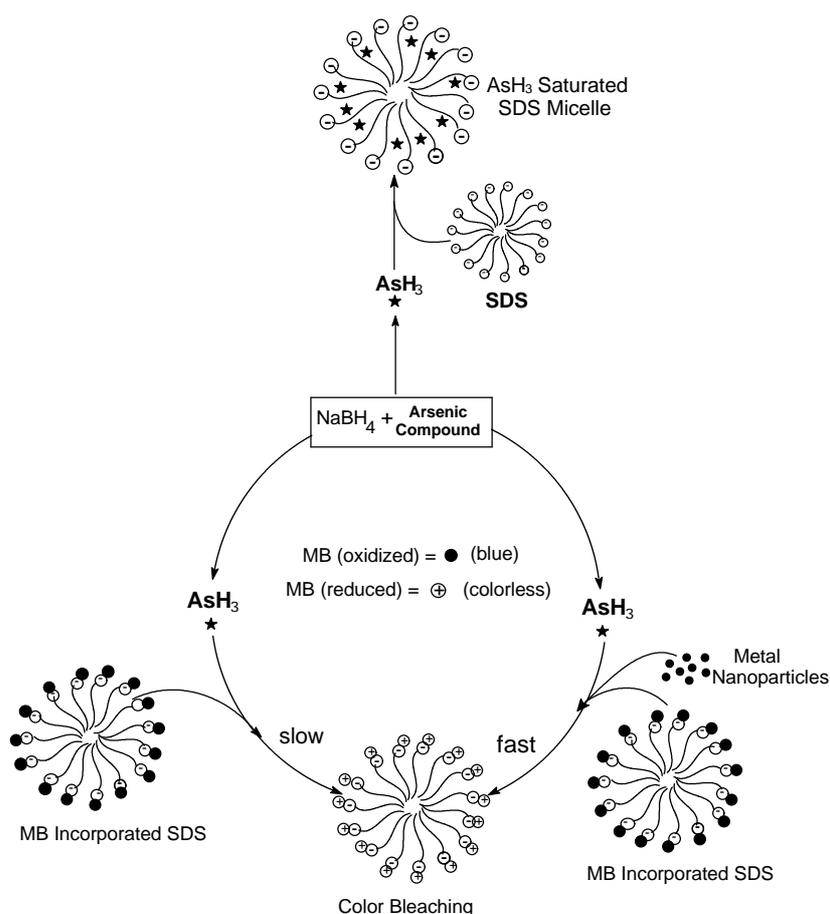
In a stoppered cuvette, 3 ml of SDS (10^{-2} M) and 50 μl of MB (0.5×10^{-3} M) were taken. To this was added 15–75 μg of arsenic (either in arsenate or arsenite state). Finally 100 μl of NaBH_4 (10^{-1} M) was added to it. After 3 min the decrease in the absorbance value of the micelle-stabilized MB was monitored at 660 nm. The colour bleaching of the dye gives a quantitative measure of the arsenic present in the system.

3. Results and discussion

3.1 Micellar catalysis and thermodynamic parameters

The quantitative colour bleaching of methylene blue (MB) (0.5×10^{-3} mol l^{-1}), a well known non-toxic cationic dye, by arsine (AsH_3) has been studied in aqueous micelle. The arsine is generated *in situ* (i.e. in the reaction medium) from arsenic containing samples with NaBH_4 (0.1 mol l^{-1}) while taken along with the reaction mixture containing the dye and micelle. In order to study the quantitative progress of the reaction, an anionic micelle (here it is aqueous SDS, sodium dodecyl sulfate, $\sim 10^{-2}$ mol l^{-1})

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Scheme 1. Schematic representation of the reduction of methylene blue by arsine in micelle.

has been found to be essential. The rates of MB reduction by AsH_3 carried out in different micelles are in the order of

$$\text{Rate}_{\text{SDS}} > \text{rate}_{\text{TX-100}} > \text{rate}_{\text{CTAB}} > \text{rate}_{\text{water}}$$

This is due to the fact that MB being a cationic dye is bound to SDS by both electrostatic and hydrophobic interactions (Pal and Jana 1996) and to TX-100 and CTAB by only hydrophobic forces. The progress of reduction of the dye was followed spectrophotometrically at the dye, I_{max} , at 660 nm. These one-pot and pseudo-first order reaction ($k = 0.12 \text{ min}^{-1}$) conditions provide good measure of the arsenic content of a sample even in the ppm level. The reaction could be followed even when MB is present in trace level ($\sim 10^{-7} \text{ mol l}^{-1}$). This is possible due to the high molar extinction coefficient ($\epsilon = 1 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$) of the dye at 660 nm. The calibration graph set-up for three linear dynamic ranges (LDR) are 0–8.63 ppm, 0–1.11 ppm and 0–0.11 ppm using 1.14×10^{-5} , 8.19×10^{-6} and $6.58 \times 10^{-6} \text{ mol l}^{-1}$ MB and the limit of detections (LODs) are 1.3, 0.53 and 0.03 ppm, respectively. Thermodynamically favourable reduction of the dye (E^0 for MB = -0.18 V ,

$\text{BH}_4^- = -1.33 \text{ V}$ and $\text{AsH}_3 = +0.60 \text{ V}$ vs NHE) was not observed in water, cationic and non-ionic micellar solutions i.e. no reduction of the dye was observed in the experimental reaction condition and time scale.

Gradual increase of arsine concentration (a direct measure of the amount of any arsenic compound present in the solution even if present in the sub ppm level) increases the extent of reduction of MB in the presence of anionic micelle. Dynamic light scattering (DLS) experiment revealed a 13-fold increase in size of the SDS micelle (schematically represented in scheme 1), while AsH_3 saturates SDS at 25°C . From kinetic data the activation energy of this reaction was found to be $13.36 \text{ kJ mol}^{-1}$ which indicates that the reaction rate is nearly diffusion controlled. In the absence of SDS micelle the reaction does not occur at all. Even in SDS solution the colour bleaching is relatively slow. Hence it has been thought that there is a kinetic barrier that prevents the dye reduction. In order to remove the kinetic barrier between the donor (AsH_3) and the acceptor (micelle bound methylene blue) the presence of metal nanoparticles was thought of and tested successfully.

3.2 Role of metal particles

Metal nanoparticle helps the electron relay (promotes the extent of reaction) from the donor to the acceptor. Interestingly, it has been observed that silver or gold nanoparticles (10^{-4} mol l^{-1} prepared (Pradhan *et al* 2000) and added, final concentration, 10^{-9} mol l^{-1}) served the purpose i.e. they could easily remove the kinetic barrier between the dye-micelle aggregate and arsine. The size of the silver nanoparticles (prepared by NaBH_4 reduction (Pradhan *et al* 2000) method) lies in the range of ~ 7 nm. The 'S' donor of the dye readily poisons gold nanoparticles, however, silver does not. Hence silver serves better than gold (Henglein 1993).

4. Application

The proposed method has been successfully applied for total arsenic determination in water samples. The method is free from phosphate interference. This method is applicable for the analysis of both surface and ground water and can be applied for real sample analysis. The standard deviations for all three curves lie within 0.0021 to 0.0083.

5. Interference

The method is free from phosphate and silicate interference. Most metal ions such as $\text{Fe}^{2+}/\text{Fe}^{3+}$, Ca^{2+} , Mg^{2+} , Na^+ , K^+ and common halides such as Cl^- , Br^- , I^- do not interfere in the determination.

6. Conclusions

This one-pot determination of arsenic is simple and easy to carry out. It does not require any costly reagents and sophisticated instruments. By using only an UV-visible spectrophotometer, arsenic can be quantified in the ppm range. It does not need any toxic chemicals and the method is also less time-consuming (an hour for the analysis of 10 samples). The method is free from interference due to phosphates and silicates and other common interferents.

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