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Spectrophotometric Determination of Trace Arsenic (III) Ion Based on Complex Formation with Gallocyanine

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ABSTRACT

In this study, a simple, selective and sensitive method, for spectrophotometric determination of As(III) with gallocyanine as the sensitive reagent was developed. The wavelength of an analytical measurement, for the determination of As (III), using gallocyanine was at 630 nm with an optimum response at pH 2. The RSD for the reproducibility of 100 ppm As (III) was 2.3%. The LOD was 0.04 ppm with linear dynamic range in As(III) concentration of 0.2 - 1.5 ppm. The developed method has been validated against Atomic Absorption Spectrophotometry (AAS). The interference study of several metal ions was carried out and it revealed that that Mn (II) ion was interfered the most.

Keywords: Gallocyanine, arsenic determination, metal toxicity

INTRODUCTION

Arsenic occurs in the environment in organic and inorganic forms. In more specific, arsenic is generally found in the inorganic form of arsenite and arsenate. Arsenic usually contaminates ground and surface water. The concentration of arsenic in both surface and ground waters generally ranges from 0.001 to 0.01 ppm, but elevated levels (1-50 ppm) have also been reported in groundwaters in China, India and Bangladesh (The Arsenic Crisis, 1998).

A long-term exposure to low concentration of arsenic has been linked to increased risk of cancer and can lead to death if ingested in large dose. Arsenic is usually exposed to human being through food and water. The maximum contaminant level (MCL) of arsenic, which is recommended for the implementation in the USA for drinking water, is 0.01 ppm (Arsenic, 2000).

Numerous analytical techniques have been employed to detect arsenic including spectrophotometry (Hashemi *et al.*, 2007; Afkhami *et al.*, 2001; Kundu *et al.*, 2002), chromatography technique (Sun *et al.*, 2007), atomic absorption spectrometry (Dang *et al.*, 1999) and inductively coupled plasma mass spectrometry (Steely *et al.*, 2007). Among these techniques, spectrophotometry offers the simplest and cheapest way for the detection of arsenic and it is readily amenable to portable instrumentation.

In the trioxide As_2O_3, As has valence +3, while in the pentoxide As_2O_5, the valence is +5. When oxides such as these are dissolved in water, they attract H^+ and OH^- ions, and may rearrange their structures. In the case of As_2O_5, the equation involved is:

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$$As_2O_5 + 3H_2O \rightarrow 2H_3AsO_4 \quad (1.1)$$

The molecule formed is orthoarsenic acid, which dissociates to give H^+ ions, and an acidic solution. Here, arsenic behaves as a non-metal, like phosphorus, and can form salts with metals or positively charged compound.

Gallocyanine or 7-dimethylamino-4-hydroxy-3-oxo-phenoxazine-1-carboxylic is an oxazine derivative. It is also known as alizarin navy blue, mordant blue and anthracene blue. The dye is soluble in acid and alkaline solutions, and partially soluble in water. In acidic solution, this reagent is present in a cationic form. Solutions can also be prepared in dioxane, pyridine, acetic anhydride and concentrated sulfuric acid (Feigl *et al.*, 1972). *Fig. 1* shows the structure of the reagent in both neutral and ionic forms. Gallocynine has been used in a few analytical applications such as the determination of iodate and periodate (Ensafi *et al.,* 2000) and boron (Skaar, 1964).

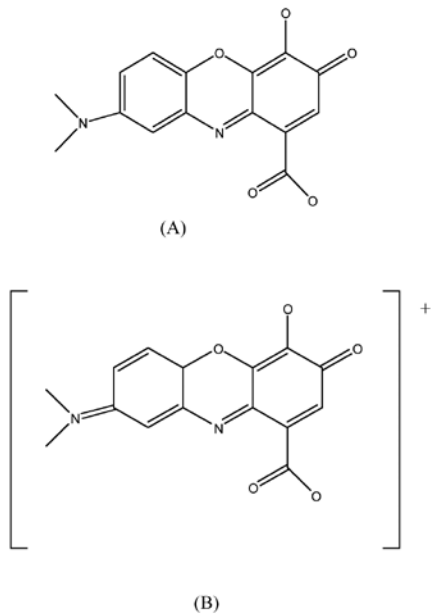

Fig. 1: Structure of gallocynine in neutral (A) and ionic form (B)

In this work, a simple way of detecting arsenic, based on the usage of gallocyanine in cationic form is proposed. The method proposed is indeed suitable for a particular need of fast and *in situ* analytical test.

The Experiment

(i) Reagent

All chemicals used were of analytical grade (BDH), and deionised water was also employed for solution preparation in the present study. Gallocyanine solution of 1.0×10^{-4} M was prepared by dissolving 0.006 g of gallocyanine in 200 ml of deionised water. Working standard solutions of As (III) were prepared by an appropriate dilution of stock solution

before use. Buffer solutions were prepared according to the method suggested in the *Handbook of Basis Tables for Chemical Analysis* (Svoronos and Svoronos, 1989).

(ii) Instrumentation

The measurements were made using the Ultraviolet-Visible Spectrophotometer (Varian-Cary Win UV 100). For this purpose, the Atomic Absorption Spectrophotometer was used for the validation study.

(iii) Procedure

The absorption spectra of gallocyanine were recorded before and after the reaction with 100 ppm As (III). The effects of pH on the complex formation was studied by mixing 2.5 ml of gallocyanine solution with 1.0 ml of 100ppm As(III) solution containing 0.5 ml of buffer at different pH values (pH 1.0 – 10.0).

The effect of gallocyanine concentration, on the As (III) complex formation, was studied by adding 1.0 ml of 100 ppm As (III) solution into a volumetric flask containing 5.0 ml of different concentrations (2.0×10^{-6} M to 3.8×10^{-5} M) of gallocyanine, and diluted to the mark with deionised water.

A dynamic range of As (III) concentration was studied by introducing different concentrations (0.1 – 10.0 ppm) of As (III) to a cuvette containing 3.0 ml of gallocyanine (3.0×10^{-5} M).

The interferences, from both anion and cation, were studied by introducing 0.5 ml of 100 ppm As (III) to a cuvette containing 3.0 ml of 3.0×10^{-5} M of gallocyanine and interfering ions [the ratio of As (III) : interfering ion is 1:1]. Another cuvette, containing the similar proportion except for the interfering ion displaced with deionised water, was prepared as a control.

RESULTS AND DISCUSSION

Fig. 2 shows the absorbance spectra of gallocyanine and gallocyanine-As(III) complex. It was observed that the formation of the complex caused a decrease in the absorbance, due to a sharp colour change, i.e. from dark blue to light violet. Gallocyanine showed its maximum absorbance at 630 nm, while gallocyanine-As (III) complex showed the maximum absorption at 525 nm and very low absorption at 630 nm. The difference in the absorbance between gallocyanine and gallocyanine-As (III) complex at 630 nm was used for further analytical measurement. The biggest difference between gallocyanine and complex was obtained at pH 2. Therefore, this pH was used throughout the study.

The reproducibility study was carried out by running 10 replicates of similar proportion of As (III), gallocyanine and buffer. This was done to estimate the discrepancies in its response. The RSD was calculated to be 2.3%, suggesting that the developed method is reproducible.

The effect of the reagent concentration was studied using different initial concentrations of the reagent (2.0×10^{-6} M to 3.8×10^{-5} M). From *Fig. 3*, it is observed that the absorbance increased with the increasing amount of reagent, until it reached a point where the absorbance became almost constant. The same observation was also reported by Satienperakul *et al.* (2005) who studied the chemiluminisence determination of As (III). They reported that with the increase of the volume of reagents involved, the signal increased rapidly to a plateau.

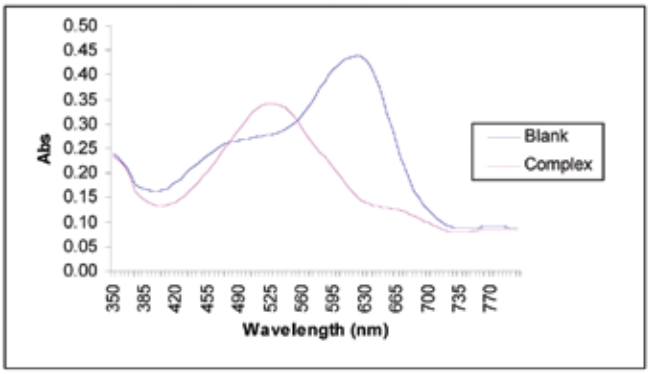

Fig. 2: Absorption spectra of gallocyanine (blank) and As (III)-gallocyanine complex

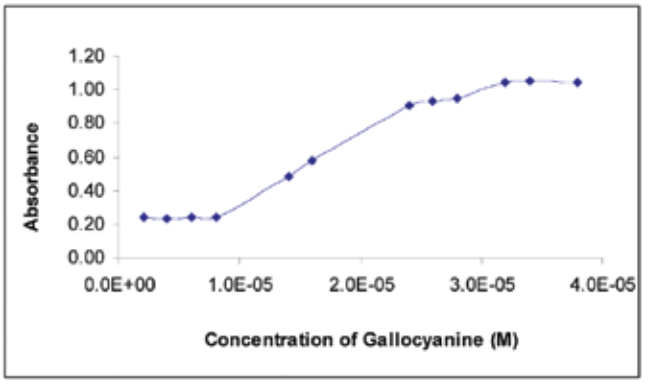

Fig. 3: The effect of the concentration of gallocyanine on the absorbance of As (III)-gallocyanine

Fig. 4 shows the response curve of the reagent towards different concentrations of As (III). It shows that the developed method produced a linear response when the As (III) concentration was within the range of 0.02 to 2.00 ppm. In the present study, the limit of detection (LOD) of As (III), defined as the concentration equivalent to a signal blank, plus three times the standard deviation of the blank, was calculated to be 0.04 ppm. Hashemi and Modasser (2007), who carried out a study on the detection of arsenic based on hydride generation and bleaching of permanganate, achieved LOD as low as 3.0 ppb; whereas, Afkhami *et al.* (2001) utilized the inhibitory effect of arsenic on the redox reaction, between bromate and hydrochloric acid, were able to detect arsenic at sub ppb level. Meanwhile, Kundu *et al.* (2002) proposed a simpler method for arsenic detection, based on the colour bleaching of methylene blue in micellar medium, with LOD of 0.03 ppm. Even though better LOD has been reported by these researchers, the use of multiple step reaction (hydride generation, inhibitory effect and arsine release for colour bleaching) usually imposes some effects on the response time. The use of the multiple reagents also limits the possibilities of miniaturization. When a comparison was carried out with the findings of these researches, the current research offered a single step detection with a short response time and fairly good LOD.

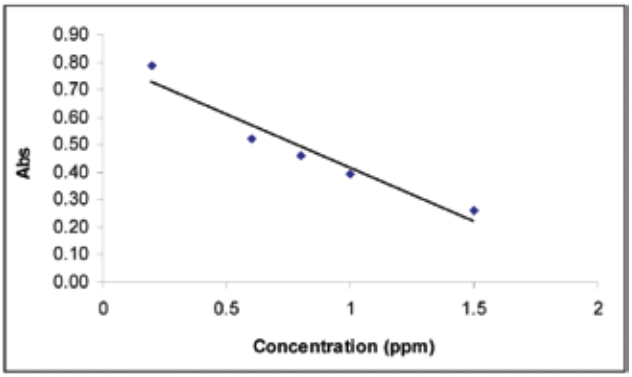

Fig. 4: The linear response towards different concentrations of As (III)

The degree of interference, measured from some foreign ions at 1:1 mole ratio of As (III):ion, is summarized in Table 1. The main cation interference was obtained from Mn(II). It was also found that NH_4^+ gave a high degree of interference since they are chemically reactive and capable of forming complex with lots of metal. Negative interference was observed for anions, whereas cation showed a positive interference. Musa and Narayanaswamy (1995) reported that the most common type of such interference was the complexing of the analyte by the interfering ion.

In this study, the developed method was validated against the AAS. The data for the developed method and AAS are shown in Table 2. Based on the data shown, the developed method was proven to be comparable with the conventional method (AAS).

TABLE 1
The percentage of interference from foreign ions

Anions/ cations	% Interference
Mn(II)	8.33
Cd(II)	6.79
Co(II)	1.84
Pb(II)	1.46
NH4+	7.84
Citrate	7.16
Phosphate	2.71

TABLE 2
Result of the comparative study of the developed method and AAS

Method	Concentration (mean), ppm
AAS	1.01 ppm
Developed sensor	0.97 ppm

CONCLUSIONS

The limit of detection of As (III), using the developed method, was found to be 0.04 ppm. The relative standard deviation (RSD), for the reproducibility of determination of As (III), was calculated to be 2.3%. In addition, it was also found that Mn(II) ion interfered most in the determination of As (III). An excellent agreement with the AAS method was achieved, when the proposed method was applied in the determination of As (III). The characteristic of the method, i.e. simplicity, selectivity and rapid calibration, has made it especially suitable for a routine analysis.

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