

Spectrophotometric determination of trace level arsenic in water by methyl orange as a chromogenic reagent

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ABSTRACT

A simple, rapid and sensitive Spectrophotometric method has been developed for the determination of arsenic using Methyl Orange as a chromogenic reagent. The method is based on the bleaching effect of liberated I_2 from the reaction of Arsenic(III) with Potassium Iodide/Iodate in presence of acidic media. The liberated I_2 oxidizes the methyl orange to form pale yellow colored specie having maximum absorption at 538nm. Detection limit of the proposed method is measured upto 0.2 ppb ($\mu\text{g/l}$).

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KEYWORDS

Arsenic Detection;
Chrmogenic Reagent;
Methyl Orange with liberated
Iodine;
Bleaching effect of Iodine.

INTRODUCTION

Arsenic (As) occurs in earth's crust at an average level of 2-5 ppm. The primary anthropogenic source is fossil fuel combustion. Mining provides a secondary source, especially as a by-product of copper, gold and lead refining. Dissolved arsenic can occur in natural waters in both inorganic and organic forms. Arsenic is a toxic element. Its biochemical effects include protein coagulation, enzyme inhibition, and uncoupling of phosphorylation. Acute poisoning results from the ingestion of ca. 100 mg of the element, and much lower levels cause chronic poisoning. There is some evidence that arsenic is also carcinogenic^[1]. For potable water, the US public health service recommended 10 $\mu\text{g/l}$ ^[2]. Therefore, simple, rapid, highly sensitive and accurate methods are required for the determination of the trace amounts of arsenic in samples.

Arsenic compounds are widely used and have long been recognized as toxicants^[3-5]. Trace con-

centrations of arsenic can also affect the physical and mechanical properties of metals and alloys^[6]. Arsenic may accumulate in soils of sediments due to use of arsenical pesticides, fertilizers, irrigation and oxidation of volatile arsine in air, dust from the burning of fossils fuels as well as disposal of industrial, municipal and animal wastes^[7]. Arsenic is a constituent of many foods such as meat, fish, poultry grains and cereals^[8]. It is used in medicine, glass manufacture, pigment production, rodent poisons, insecticides, fungicides, printing, tanning etc. In excessive amounts, arsenic causes gastrointestinal damage and cardiac damage. Chronic diseases can cause vascular disorders such as black foot disease^[8]. Arsenic and its compounds are reported to be carcinogenic, mutagenic and tetratogenic in nature. The toxicity, availability and environmental mobility of arsenic are very much independent on their chemical forms^[9].

Arsenic can exist in a variety of oxidation states

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and in organic and inorganic forms in many environmental matrices such as natural water and soil^[10]. The predominant oxidation states of arsenic are As(III) and As(V). Therefore, precise knowledge of the arsenic compounds present in a system required for an accurate assessment of the environmental and biological impact of arsenic, which have resulted in an increasing need of analytical methods for their determination at micro-trace and ultra-trace levels.

Many methods have been reported for the determination of arsenic such as flow injection analysis with hydride generation^[11], atomic absorption spectroscopy^[12], gas flourometry atomic absorption spectroscopy^[13], induced coupled plasma-atomic absorption spectroscopy^[14], neutron activation analysis^[15], fluorescence spectroscopy^[16]. Some of the chromogenic reagent used for Spectrophotometric determination of arsenic are ammonium pyrrolidine dithiocarbamate^[17], silver diethylcarbamate^[18], methylene blue^[19], diantipyrylmethane^[20], alizarine Red S^[21], chlopromazine^[22], methyl orange^[23], Bismuthol III^[24], dithiodiantipyrylmethane^[25], antipyrilazo-4-hydroxybenzenedithiocarboxylic acid^[26], malachite green^[27], and dithiopyryl-methane^[28]. However most of these methods suffer from certain limitation such as interference by a large number of ions,^[17,18] of low sensitivity^[21,23] and need of extraction into organic solvents or heating^[17,20].

Burgess & Ottaway reported a method for the determination of As(III) based on its effect on the redox reaction of bromate with bromide ion in sulfuric acid media^[29]. The bleaching of methyl orange with liberated bromine was used to measure the reaction time. They used different working conditions for the determination of different concentrations of As(III). In some condition, As(III) showed inhibitory effect at high concentrations and catalytic effect at low concentrations. Any calibration equation or other analytical parameters were not reported.

A.Afkhami, T. Madrakian & A.A. Assl described the development of a method for the determination of As(III) based on its inhibition effect on the reaction of iodate with hydrochloric acid. The method was very rapid, simple, sensitive and accurate. As(III) as low as 6 µg/l could be determined by this

method^[30].

In this paper a rapid and economic method is reported with ease to availability of the reagent. As mentioned above in literature a number of chromogenic reagents have been used for Spectrophotometric determination of Arsenic, but the availability of these reagents is a big challenge especially in remote areas. In this paper it is attempted to develop a method for the estimation of Arsenic with commonly available reagents i.e. methyl orange dye that is frequently used as an indicator in different titration methods. Analytical Laboratories situated in remote areas with limited chemical market access can easily adopt the method for the Arsenic estimation.

EXPERIMENTAL

Apparatus

Absorbance-Concentration graphs at fixed wavelength were recorded on a Shimadzu UV-Visible Spectrophotometer model UV-1800.

Reagents

All chemicals used were of AR Grade and distilled water was used for dilution of reagents and samples. Standard Arsenic (III) stock solution (1000 µg/ml) was prepared by dissolving 0.1732g of NaAsO₂ in 100 ml of distilled water. Working standard solution was prepared by dilution of stock solution. HCl 2.0 M, Potassium iodate 2%, Potassium iodide 2% solution are prepared. A 0.01% solution of Methyl Orange was prepared by dissolving 0.01g Methyl Orange in 100 ml of distilled water. The solution was stored in amber bottles. Figure-1 shows chemical reaction of Methyl Orange with Iodine. A.Afkhami et al determined the Tolerance limit of diversions on the mixture of 100 µg/l As(III) tested as shown in TABLE-1^[30].

METHOD

Preparation of calibration curve

A series of standard solutions containing 10 - 100 µg/L of Arsenic(III) were transferred into a series of 100ml calibrated flask, then 2ml of Methyl

TABLE 1 : Tolerance limit of diversions on the determination of a mixture of 100 µ g/l As(III) tested by A. Afkhami et al [30].

Ion	$W_{\text{ion}}/W_{\text{As(III)}}$
As(V), ClO ₄ ⁻ , Cl ₃ ⁻ , SO ₄ ⁻ , CH ₃ COO ⁻ , H ₂ PO ₄ ⁻ , tartrate, NO ₃ ⁻ , NH ₄ ⁺ , C ₂ O ₄ ⁻ , CO ₃ ²⁻ , Mo(VI), Cl ⁻ , CN ⁻ , citrate, Na ⁺ , Ba ²⁺ , Be ²⁺ , Hg ²⁺ , Ca ²⁺ , Cd ²⁺ , K ⁺ Mg ²⁺ , Ni ²⁺ , Pb ²⁺ , Zn ²⁺ , Al ³⁺ , F ⁻	100 ^a
Fe ³⁺ , Cu ²⁺	30
Sb(III), Br ⁻ , NO ₂ ⁻	1

^aMaximum limit tested**TABLE 2 : Standard solutions concentration vs. absorbance**

Sr. No	Sample ID	Type	Concentration (ppb)	Absorbance	Wgt. Factor
1	Std 10 ppb	Standard	10.000	0.001	1.000
2	Std 20 ppb	Standard	20.000	0.009	1.000
3	Std 40 ppb	Standard	40.000	0.024	1.000
4	Std 60 ppb	Standard	60.000	0.050	1.000
5	Std 80 ppb	Standard	80.000	0.075	1.000
6	Std 100 ppb	Standard	100.000	0.124	1.000

Orange and HCl (2.0M) 4ml, 4ml KI(2%), were added and mixture was gently shaken. This was followed by addition of 4 ml KIO₃ (2%). The solution volume was made up to the mark with distilled water immediately. The absorbance of colored species was measured at 538 nm against the corresponding reagent blank. Figure-2 shows the absorbance of different standard solution against the concentration (ppb), while TABLE-2 shows the values of Absorbance against known concentration.

Effect of iodide concentration and acidity

The oxidation of iodide to iodine is effective in the pH range 1.0 to 1.5, which could be maintained by adding 4ml of 2M HCl in a final volume of 100 ml.

The liberation of iodine from KI/KIO₃ in an acidic medium is quantitative. The appearance of yellow colour indicates the liberation of iodine. Although any excess of iodine in the solution will not interfere. It is found that 4ml of each 2% KI & 2M HCl and 2% KIO₃ are sufficient for the liberation of iodine from iodide/iodate. The variation of absorbance of known concentration of the iodate with pH of the medium is studied. The maximum absorbance

value is found at pH=1 ± 0.2.

RESULTS & DISCUSSION

Iodide/Iodate is reduced by chloride ion in acidic media to produce I₂ and Cl₂.

Equation-1



The produced I₂ and Cl₂ react with methyl orange decolorize it. Figure-1 shows chemical reaction of Methyl Orange with liberated Iodine.

Therefore, this reaction could be monitored spectrophotometrically by measuring the absorbance at 538 nm. Figure-3 shows the Analysis of unknown water samples, while TABLE-3 shows the values of Arsenic concentration detected in unknown samples.

The presence of As(III) in the medium slows the reaction, which is fairly fast in its absence or when the medium is very acidic. As(III) reacts with the liberated I₂ and Cl₂ according to the following reaction and causes an induction period [29,31].

Equation-2



TABLE 3 : Concentration vs. absorbance of unknown samples

Sr. No.	Sample ID	Type	Concentration (ppb)	Absorbance
1	NK1	Unknown	50.799	0.046
2	NK-2	Unknown	41.260	0.034
3	NK-3	Unknown	37.721	0.029
4	NK-4	Unknown	63.889	0.063
5	NK-5	Unknown	43.909	0.037
6	NK-6	Unknown	65.940	0.066

CONCLUSION

The proposed method is simple and sensitive with detection limit observed below to the WHO guideline value for Arsenic in drinking water of 0.2 µg/L (0.2 ppb). The method is very rapid, so the sequence of adding the reagents for standard solution and unknown samples are of great importance. KIO₃ (2%) must be added at the end of the preparation procedure and the absorbance at 538 nm is measured within after its addition for accurate detection.

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