



Modification of Molybdenum Blue Method for the Determination of total Arsenic Concentration with Oxone

Research Article

Abdus Samad^{1,*}, Mai Furukawa², Ikki Tateishi³, Hideyuki Katsumata², Satoshi Kaneco^{2,3}

¹Department of Chemistry, Jagannath University, Dhaka –1100, Bangladesh

²Department of Chemistry for Materials, Graduate School of Engineering, Mie University, Tsu 514-8507, Mie, Japan

³Mie Global Environment Center for Education & Research, Mie University, Tsu, Mie 514-8507, Japan

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Abstract: In this study, the use of oxone has been investigated for the first time as an oxidant for the oxidation of As(III) in order to determine the total arsenic concentration using molybdenum blue method. The various factors that may affect the arsenic oxidation and its determination including the effect of oxone on the rate of color development, oxidation time, oxone concentration, acidity of the solution and temperature were studied. The optimum time required for molybdenum blue complex formation was 40 min. Oxidation of As(III) by oxone was faster and only 20 min was needed for complete oxidation. High acid concentration ($\sim 0.4 \text{ mol L}^{-1}$) or low pH of reaction medium was suitable for color development. Although molybdenum blue complex formation rate was increased with the increasing temperature, room temperature was sufficient for arsenic determination. There was no effect of nitrate, chloride and bicarbonate ion on color development during investigation. Based on the required conditions, a calibration curve for the determination of total arsenic was plotted which showed good linearity with r^2 value 0.999. Since oxone is a metal free reagent, it can be used as a safe and nontoxic oxidizing agent for the oxidation of As(III) and the determination of total arsenic concentration using molybdenum blue method.

Keywords:

1. Introduction

Arsenic and arsenic compounds are recognized as the group 1 carcinogens by the International Agency for Research on Cancer (IARC) (Rahman *et al.*, 2021, Samad *et al.*, 2016). Previous literatures have reported that the increase in arsenic level in water is associated with cancer and other diseases like skin diseases, diseases of the blood vessels of the legs and feet, diabetes, high blood pressure and re-productive disorders (Timalsina *et al.*, 2021; Rahman *et al.*, 2008; WHO, 2011). The main

sources of arsenic are volcanoes, arsenic-containing minerals, and industrial processes (e.g., smelting, chromated copper arsenate for wood treatment, solid residues from mining extraction and agrochemicals) (Shaji *et al.*, 2021; Tsang *et al.*, 2007). Peoples in many parts of the world are exposed to arsenic primarily by drinking contaminated water. In many places arsenic concentration exceeds far more than the WHO guideline value ($10 \mu\text{g L}^{-1}$) which pose health vulnerability to millions of people (Hare *et al.*, 2019; Smedley and

*Corresponding author: Abdus Samad

E-mail: samad@chem.jnu.ac.bd

Kinniburgh, 2002). Bangladesh is one of the worst examples where chronic arsenic exposure is observed (Meng *et al.*, 2003). The toxicity and mobility of As depend on its oxidation state where arsenite (As(III)) is 25- 60 times more toxic than arsenate (As(V)) (Byeon *et al.* 2021, Korte and Fernando, 1997). Since the proportion of As(III) in most of the ground water is higher than As(V) and As(III) can partially be oxidized to As(V) by air oxidation during sample collection, storage and transportation could lead erroneous results (Meng *et al.*, 2003; Tabelin *et al.*, 2018). This problem can be overcome by using in-situ speciation analysis technique. However, the popular arsenic speciation methods for determining low concentrations are highly expensive due to sophisticated laboratory instruments (Reid *et al.*, 2020). For example, high performance liquid chromatography (HPLC) which needed adequate element-specific detector such as mass spectrometry and atomic fluorescence spectrometry can be used for separation and measurement of arsenic species concentration. However, these expensive facilities are not always available and it is often desirable to conduct measurements directly in the field. For routine environmental analysis, an easy to handle, fast, reasonably priced, portable and sensitive method for aqueous arsenic determination therefore is in high demand (Arora *et al.*, 2009; Liao and Deng, 2006; Rahman *et al.*, 2002). This problem can be overcome by employing colorimetric method based on molybdenum blue complex formation proposed by Osmond (1887) combined with Johnson and Pilson (1972) scheme which require a small photometer and inexpensive chemicals. This method can be considered as a viable alternative of expensive techniques due to its stability and high sensitivity.

The fundamental basis of the Molybdenum blue method for arsenic analysis is that only As(V) form molybdenum blue complexes (arseno-molybdate complex) with molybdate in reduced states while As(III) can't form similar complexes (Johnson, 1971). Many researchers have proposed the modification of molybdenum blue method in order to optimize various parameters and to increase the detection limit (AFNOR, 1997; Bogdanova 1984; Blomqvist *et al.*, 1993; Lenoble *et al.*, 2003). Since both As(III) and As(V) present in natural water, it is necessary to oxidize As(III) to As(V) in order to determine the total arsenic concentration. Different oxidant has been suggested by researchers. For example, Lenoble *et al.* (2003) investigated the suitability of a number of oxidant (H_2O_2 , NaOCl, FeCl, and $KMnO_4$) and found $KMnO_4$ and $FeCl_3$ are effective. However, the use of $FeCl_3$ causes the production of large quantity of contaminated sludge. The use of $KMnO_4$ may cause the formation of MnO_2 sludge that is responsible for the non

stoichiometric reaction between As(III) and $KMnO_4$ and may cause problem in recording absorbance value (Lenoble *et al.*, 2003). Dhar *et al.* (2004) proposed KIO_3 as oxidant for As(III), nonetheless, the usage of KIO_3 as oxidant could inhibit molybdate reduction (Hu *et al.*, 2012).

Recently, oxone is used in various reactions as oxidizing agent due to environmentally benign, inexpensive, simple handling, stability and the versatility of the reagent (Desai *et al.*, 2007; Lopa *et al.*, 2006; Hussain *et al.*, 2013; Xu *et al.*, 2019; Bringley *et al.*, 2021). In addition, oxone is a transition metal free oxidant and does not produce any sludge or toxic byproducts (Bai *et al.*, 2021). The active part of oxone is peroxy monosulphate (PMS) which is one of the most powerful oxidant. The standard two-electron reduction potential of PMS is 1.85 V vs NHE (Wang *et al.*, 2014) and the standard reduction potential of commonly used $KMnO_4$ is 1.51 vs NHE (Speight, 2005) while the two-electron oxidation potential of As(III) is 0.56 V vs NHE (Bard, 1985). Therefore, PMS is quite favourable for two electron oxidation of many chemicals including As(III) even compared to $KMnO_4$ on thermodynamic consideration (Wang *et al.*, 2014)

The present work focuses on the study of influencing parameters of the molybdenum blue method by using oxone as an oxidant for the oxidation of As(III) in order to determine the concentration of total arsenic. Molybdenum blue method for arsenic determination was modified by optimizing the rate of color development, effect of oxone on the oxidation time of As(III), effect of oxone concentration, effect of acidity and effect of temperature on color development. The effect of particular anions on color development was also investigated.

2. Experimental

2.1 Reagents

All reagents used in this research were of analytical grade purity and was used without further purification. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 99%) was procured from Fujifilm Wako pure chemical corporation. Potassium arsenite ($KAsO_2$, 90%), potassium arsenate (KH_2AsO_4 , extra pure), antimony potassium tartrate ($C_4H_4KO_7Sb \cdot 1/2H_2O$, 99.8%), ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 99%), sulfuric acid (H_2SO_4 , 98%), L-ascorbic acid ($C_6H_8O_6$, 99%), potassium permanganate ($KMnO_4$, 99.3%), sodium nitrate ($NaNO_3$, 98%), sodium hydrogen carbonate ($NaHCO_3$, 98%) and sodium chloride ($NaCl$, 98%) were purchased from Nakarai Tesque, Inc. Distilled water was further purified with an ultrapure water system (Advantec MFS, Inc., Tokyo, Japan) having resistivity >18 MV cm.

2.2 Preparation of working solutions

Stock solution of As(III) with concentration 1000 mg L^{-1} was prepared by dissolving calculated amount of KAsO_2 in 100 mL deionized water. Similarly, 1000 mg L^{-1} As(V) standard solution was prepared using KH_2AsO_4 . Dilute arsenic solutions were prepared using accurately measured aliquot of stock solution. All the solutions were prepared at room temperature ($\sim 25 \pm 3 \text{ }^\circ\text{C}$). Stock solution of oxone (0.1 mol L^{-1}) was prepared by adding estimated amount (6.15 g) in 100 mL volumetric flask and diluting to mark by deionized water. This solution is stable in both acidic and aqueous media.

2.3 Color development and analytical procedure

Arsenic solution for colour development was prepared according to the procedure described by Tsang *et al.* (2007) with some modifications. Tsang *et al.* used 45 mL arsenic solution where the final volume with all reagents was 50 mL. In this work, 20.0 mL arsenic solution was used for each experiment where the final volume was 25 mL. 2.5 mL sulphuric acid (1.84 mol L^{-1}) was used instead of concentrated H_2SO_4 (98%) so that the final concentration of acid in sample solution remains same as described by Tsang and his coworkers. Ascorbic acid solution (0.57 mol L^{-1}) of 0.5 mL was added followed by the addition of 1.0 mL ammonium molybdate solution of 0.87 mol L^{-1} (10.4 g ammonium molybdate and 0.0176 g potassium antimony tartrate were mixed in 30 mL H_2SO_4 (18.4 M) and diluted to the final volume (100 mL) using distilled deionized water very carefully as the reaction is highly exothermic). The solution was then allowed to keep for color development to a preselected time before absorbance measurement. A double beam UV-visible spectrophotometer (Model: ASV11D) was used for the absorbance measurement.

Time required for stable colour development was investigated by recording the absorbance of arsenomolybdate complex from 5 min to 2 hours with initially 5 min interval and later at higher time interval. The effect of oxidation time on colour development to study the complete oxidation of As(III) by oxone (0.02 mol L^{-1}) was evaluated by keeping arsenic and oxone mixture from 0 to 60 min on standing and then colour reagents were added. The role of oxone concentration on colour development was explored by varying oxone concentration so that the ratio of arsenic to oxone changes from 1:0 to 1:75 respectively. The effect of acid concentration on colour development and the stability of the arsenomolybdate complex was evaluated by changing the acid concentrations from 0.22 mol L^{-1} to 0.70 mol L^{-1} . A controlled digital heater was employed to explore the effect of temperature on color development and stability of complex. For the evaluation of the effect of anions like nitrate, chloride and hydrogen carbonate, estimated

amount of corresponding salts such as sodium nitrate, sodium chloride and sodium hydrogen carbonate were added in arsenic solution.

3. Results and Discussion

3.1 Colour development time

Oxone was used in this work as a new oxidant to modify molybdenum blue method in order to determine total arsenic concentration up-to $10 \text{ } \mu\text{g L}^{-1}$. Effect of various parameters such as color development time, As(III) oxidation time, acid concentration, oxone concentration, temperature and anion concentration were investigated to modify the molybdenum blue method for the determination of total arsenic. Two solutions such as ascorbic acid and ammonium molybdate and potassium antimony tartrate mixture solution were used for color development as described by Lenoble *et al.* (2003). The maximum absorbance peak (λ_{max}) of molybdenum blue complex solution was selected from the spectrum in the wavelength range of 400 - 1000 nm which showed λ_{max} at 843 nm. This value of λ_{max} is in close agreement with that reported by Tsung ($\lambda_{\text{max}} = 849 \text{ nm}$, Tsung *et al.*, 2007) and Lenoble ($\lambda_{\text{max}} = 870 \text{ nm}$, Lenoble *et al.*, 2003). Preliminary study was conducted to select color development time using 1.0 mg L^{-1} AS(III) solution and 0.5 mL 0.02 mol L^{-1} oxone solution keeping the concentration of other reagents unchanged as described before. The results are presented in Fig. 1 shows that highest absorbance value was reached at around 30 min. No significant change of absorbance was observed after 30 min, and until 120 min, absorbance remain unchanged. However, 40 min was selected for color development time to ensure the complete color development even in the cases when other conditions become changed.

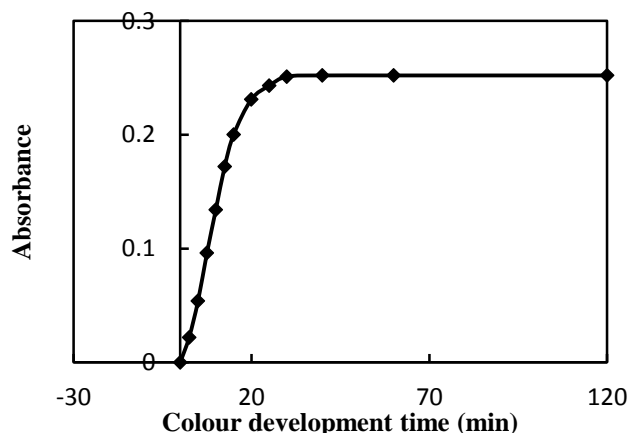


Figure 1. Arsenomolybdate complex formation as a function of time.

3.2 As(III) oxidation time

Reduced ammonium molybdate form blue colored arsenomolybdate complex with As(V) and As(III) is not

able to form such complex. Therefore, it is necessary to convert As(III) to As(V) prior to arsenic determination. The rate of As(III) oxidation and its effect on absorbance was evaluated by recording absorbance using 0.5 mL 0.02 mol L⁻¹ oxone in 1000 µg L⁻¹ As(III) solution and allow for a selected contact time prior to adding color developing solutions. The results are presented in Fig. 2. It can be concluded from the figure that the oxidation of As(III) occurred rapidly. More than 90% absorbance was achieved when oxone and color reagents were added simultaneously (0 oxidation time) indicating that oxidation of As(III) occurred very rapidly. Absorbance was virtually not increased after 10 min of oxone/As(III) contact time and remain unchanged upto one hour contact time. This oxidation time is comparable with that observed by Lenoble and coworkers (5 min) where KMnO₄ was used for As(III) oxidation. However, we used 20 min as oxidation time for further experiments to ensure sufficient time for oxidation even at different condition.

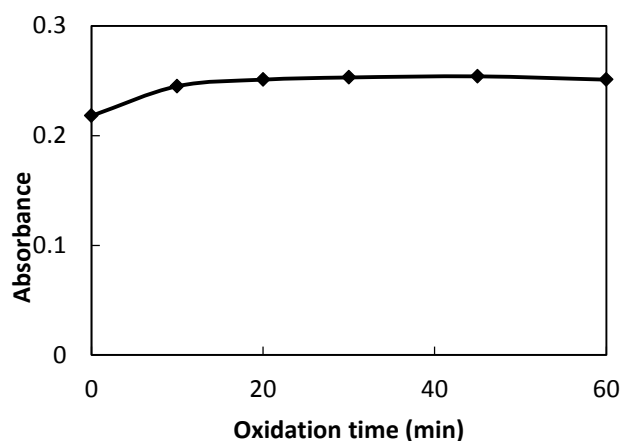


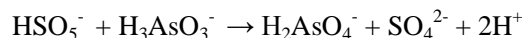
Figure 2. Effect of oxidation time on color development.

3.3 Oxone concentration

Different concentration of oxone was employed in arsenic solution before color development and optical responses were evaluated in order to explore the effect of oxone concentration on As(III) oxidation and color development. A 20 mL of 1000 µg L⁻¹ (1.3×10⁻⁵ mol L⁻¹) As(III) solution was used for this study. In each case, 0.5 mL oxone solution of different concentration was added in arsenic solution. The concentration of oxone in solution was selected to maintain various arsenic to oxone molar ratios. The oxone concentrations were 0, 5.34×10⁻⁴ mol L⁻¹, 1.07×10⁻³ mol L⁻¹, 2.67×10⁻³ mol L⁻¹, 8.0×10⁻³ mol L⁻¹, 1.07×10⁻² mol L⁻¹, 1.34×10⁻² mol L⁻¹, 2.0×10⁻² mol L⁻¹, 2.67×10⁻² mol L⁻¹, 4.0×10⁻² mol L⁻¹ corresponds to arsenic:oxone molar ratios 1:0, 1:1, 1:5, 1:10, 1:15, 1:20, 1:25, 1:50, 1:75, respectively. UV visible spectrophotometer responses were recorded 40 mins after adding color reagents. Experimental results are

shown in Fig. 3. It can be said that at low initial concentration, absorbance was quite low which is increasing with the increase of oxone concentration. Maximum absorbance were noted when oxone concentration were 1.07×10⁻² mol L⁻¹ (arsenic: oxone molar ratio 1:20) indicating complete oxidation of As(III). All the previous literature reported the requirement of higher oxidant/As(III) molar ratio in order to get complete oxidation. For example, Hu and coworkers (2012) showed that in the case of KMnO₄, the KMnO₄/As(III) molar ratio ~8 was needed for complete oxidation. Since one mole MnO₄⁻ can oxidize 2.5 mole As(III) and one mole oxone react with one mole As(III). Therefore, it can be concluded that oxone is equally efficient for As(III) oxidation as KMnO₄. Optical readings were not changed notably until oxone concentration 2.67×10⁻² mol L⁻¹ (arsenic: oxone molar ratio 1:50) demonstrating that plateau of absorbance has a large range over oxone concentration. This is significant because it indicates that unreacted oxone has less inhibitory effect on color development. However, oxone concentration higher than 2.67×10⁻² mol L⁻¹ showed inhibitory effect on color development as the absorbance is decreased with the increase of oxone concentration. Decreased optical response at higher oxidant concentration is also noted by Dhar *et al.* (2004).

Typically, oxone reacts with As(III) in 1:1 ratio with higher reaction kinetics (Wang *et al.*, 2014).



However, the oxidation of arsenic by oxone occurs through two distinct processes (Wang *et al.*, 2014). First process undergoes very rapidly where the second process is slower. Increasing oxone concentration enhanced the both processes. To ensure complete oxidation for higher concentration and for real water samples, higher oxidant concentration of oxidants was used by previous authors. Therefore, successive experiments were carried out using oxone concentration 0.020 mol L⁻¹.

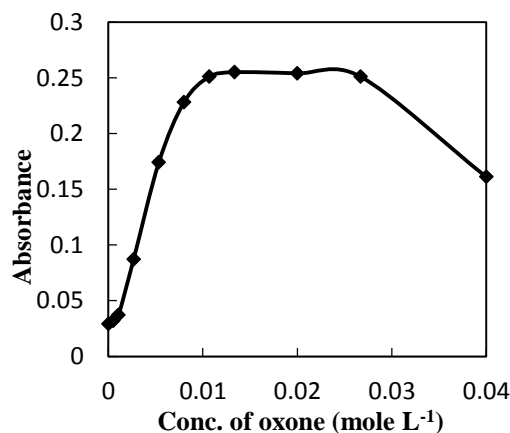


Figure 3. Effect of oxone concentration on color development.

3.4 Required acid concentration

Acidity of the solution affects the rate of color development and the stability of the arseno-molybdate complexes (Stauffer, 1983). The effect of acidity on color development was investigated in this study. The final concentration of acid in the arseno-molybdate solution was ranged from 0.22 mol L^{-1} to 0.70 mol L^{-1} . The minimum concentration of acid in solution was 0.22 mol L^{-1} because of the use of 1.0 mL molybdate solution having acid concentration 5.4 mol L^{-1} and no additional acid was added. Acid concentrations in final solution more than 0.22 mol L^{-1} were adjusted by adding calculated quantity of H_2SO_4 . Absorbance values were recorded at 1 h after adding color reagent. The results are presented in Fig. 4. It is revealed from the figure that color development occurs rapidly when acid concentration was 0.22 mol L^{-1} . However, the color intensity was not stable and was increased with time. This result is in agreement with the observation noted by Tsang *et al.* (2007). At low acid concentration (0.22 mol L^{-1}), arseno-molybdate complex undergo rapid polymerization and absorbance becomes abnormally high (Tsang *et al.*, 2007). The spectral responses increase with time and are not proportional to the analyte concentration. Color development is moderate with 0.3 mol L^{-1} sulphuric and color intensity is fairly stable although not constant and it was found that the absorbance value is slowly increasing with time. With the acid concentration of 0.4 mol L^{-1} , the absorbance value remains constant for almost 5 h and the rate of color formation is optimum. The complex formation and intensity of color started to suppress when the acid concentration becomes higher than 0.4 mol L^{-1} . Absorbance value turned to be pretty low when acid concentration was 0.6 mol L^{-1} and more. Previous literature suggested that although higher acid concentration is a suitable in order to avoid the polymerization of arsenomolybdate complex, it also decreases the rate of color development (Murphy, 1983) which is in close agreement with the results of this study. Therefore, acid conc. of 0.4 mol L^{-1} was selected for further study.

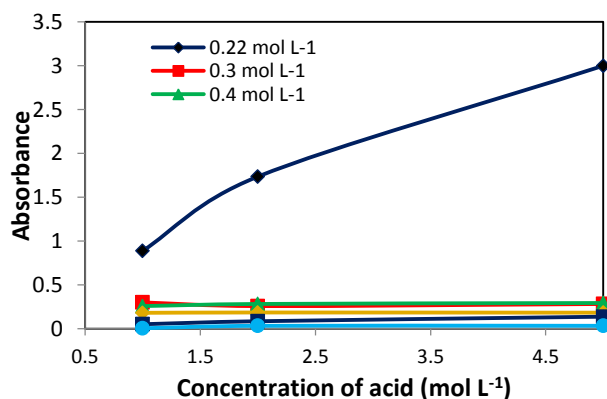


Figure 4. Effect of acid concentrations on color development

3.5 Required reaction temperature

Temperature of reaction medium significantly affects the rate of color development and the stability of arsenomolybdate complex (Lenoble *et al.*, 2003). The effect of temperature on color development was investigated in this study. Three temperatures such as room temperature (25°C), 40°C and 60°C were chosen for investigation. The results are presented in Figure 5. Increasing temperature is directly related to the rate of complex formation and consequently the optical responses as shown in Figure 5. Although complex formation rate increases at 40°C , the final responses remain same. These observations are in close agreement with Sjösten and Blomqvist's results on phosphate determination by the molybdenum blue method (Sjosten and Blomqvist, 1997) and Blomqvist *et al.* (1993) experiments. However, at 60°C , the complex is unstable after certain time (10 min in this case) tends to increase indicating the polymerization or thermal decomposition of complex at higher temperature.

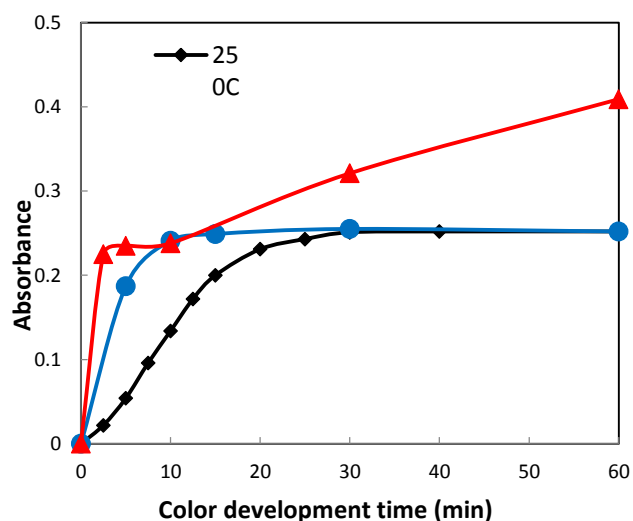


Figure 5. Effect of temperature on color development.

3.6 Interference by anions

Surface and ground water contain inorganic ions such as nitrate, sulphate, hydrogen carbonate, phosphate, silicate and chloride as well as dissolved organic matters. Although, phosphate ion can form phosphomolybdate complex of blue colour, however, the level of phosphate in ground and surface water is low ($<1.0 \text{ mg L}^{-1}$) (Fadiran *et al.*, 2008) which does not exert noteworthy interfering effect. The natural level of sulphate and silicate ion, and dissolved organic matter do not have considerable effect on colour development (Hu *et al.*, 2012). The role of nitrate, hydrogen carbonate and chloride on the determination of total arsenic concentration was

investigated in this work. Concentration of nitrate was used as 10 mg L^{-1} whereas the concentration of hydrogen carbonate and chloride was chosen as 1000 mg L^{-1} . These concentrations were chosen based on the natural abundance of these ions in surface and ground water. It has been found that optical responses for arseno-molybdate complex was not changed significantly due to the presence of these ions as shown in figure 6.

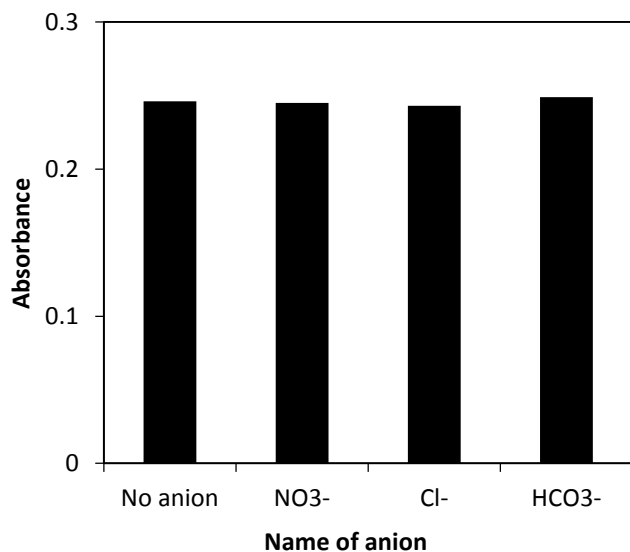


Figure 6. Effect of common anions on color development.

Calibration Curve

A calibration curve was plotted using arsenic solution in the range of $10 - 5000 \text{ } \mu\text{g L}^{-1}$. Optimized conditions were used to oxidize As(III) and to develop color. For example, the colour development time 40 min, As(III) oxidation time 20 min, conc. of oxone 0.02 mol L^{-1} , acid concentration of solution 0.4 mol L^{-1} and temperature 25°C . Standard solution of As(III) with concentration 10, 50, 100, 500, 1000, 2000 and $5000 \text{ } \mu\text{g L}^{-1}$ in aqueous solution was prepared. Colour developing agent and other chemicals were kept unchanged in all experiments. Results presented in Fig. 7 shows that the absorbance response was recorded even for the arsenic solution of $10 \text{ } \mu\text{g L}^{-1}$. This is significant because it will allow us to use this method to determine the concentration of arsenic solution at very low level. It is noteworthy that the linearity was maintained upto $5000 \text{ } \mu\text{g L}^{-1}$ indicating that this method can be applied to the wide range of arsenic concentration. The regression value was noted 0.999 signifying that the sample concentration and optical response maintain a good proportionality.

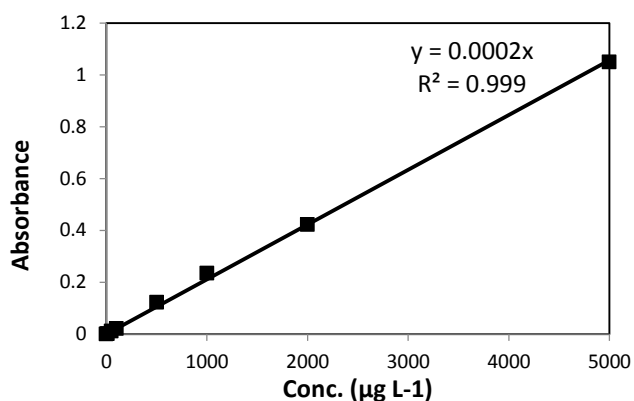


Figure 7. Calibration behaviour of As(III) oxidized by oxone to As(V).

4. Conclusion

Oxone was found to be suitable for As(III) oxidation and its concentration determination by molybdenum blue method. No inhibitory effect of residual oxone on colour development was observed since the absorbance value of arseno-molybdenum complex is comparable with contemporary available methods. The color development time needed was only 40 min which is faster compared to other methods. Oxidation of As(III) by oxone was fast since the optimum time was only 20 min. Virtually no interference was noted due to the major ions presented in surface water. Therefore, oxone can be conveniently used for the oxidation of As(III) and for the determination of total arsenic.

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