Candidate method identification for heavy metal detection and quantification in water using optochemical strategies

Lace A.[1,*], Ryan D.[1], Bowkett M.[2] And Cleary J.[1]

[1]EnviroCore, Institute of Technology Carlow, Kilkenny Road, Carlow, Ireland.

[2]TE Laboratories, Loughmartin Business Park, Tullow, Ireland.

*corresponding author:

e-mail: annija.lace@itcarlow.ie

Abstract

The aim of this research is to identify and assess candidate colorimetric methods for arsenic detection in water. Preliminary assessment of a method's performance was carried out using UV-vis spectroscopy. The method is based on determination of arsenic (III) with potassium iodate in acid medium to liberate iodine, which oxidizes leucomalachite green to malachite green. The samples were analysed at 617 nm. A rapid colour change from colourless to green was observed after the addition of the dye. Beer's law was obeyed in the range of 0.02 – 4 µg mL^{-1}. The detection limit and quantitation limit were found to be 0.139 and 0.466 µg mL^{-1}, respectively.

The optimum reaction conditions and other analytical parameters were evaluated. The method's suitability for incorporation into microfluidic detection systems was assessed. Method's performance at low temperatures, small volume, and different reagent ratio effect was evaluated.

Keywords: arsenic, colorimetric detection, spectrometry

1. Introduction

Arsenic occurs naturally in Earth's crust in its organic form. It is ubiquitous in water, soil and sediment, but generally occurs at very low levels. Arsenic is very toxic in its inorganic form particularly in the form of arsenite which is one hundred times more toxic than arsenate (Tuzen 2010). The greatest threat to public health from arsenic arises from arsenic contaminated groundwater consumption and use for food preparation and crop irrigation (Gomez-Camireno, Becking 2001). Approximately 137 million people around the world consume arsenic-contaminated water, exceeding the World Health Organization (WHO) threshold of 10 µg/L (Unicef 2008). Inorganic arsenic is naturally present at high levels in the groundwater in several countries, including Bangladesh, India, Pakistan, China and Vietnam. In Bangladesh roughly three million tube wells over the last three decades have been shown to contain arsenic concentrations above the WHO guideline, with concentrations as high as 1660 µg/L (Kinniburgh, Smedley 2001). In Pakistan almost 75% of well water has arsenic concentration exceeding 50 µg/L and 93% over 10µ/L (Tameez 2004). Continuous consumption of water that contains high levels of arsenic results in arsenicosis. The symptoms of arsenicosis include skin lesions, different forms of cancer, birth defects and premature death (Pfeiffer, Hahn-Tomer 2015). Because of the serious implications of chronic arsenic exposure, development of cost effective, reliable and high quality water monitoring system is needed for management of water resources. A range of sensitive and selective methods for arsenic analysis has been reported in the literature. Analytical techniques used include atomic absorption spectroscopy (AAS), induced coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence and atomic fluorescence spectroscopy (Pillai, Gupta 2000). Although these are sensitive and reliable methods for arsenic detection in low concentrations, they are costly and require trained staff. Also, these techniques are not suitable for *in situ* measurements. Sample collection and transportation has significant manpower requirements and can be expensive depending on the location and the frequency of sampling. Autonomous analysers based on microfluidic detection systems, however, have a low operating and installation cost and can be used for continuous *in* situ measurements (Cleary, Diamond 2010). Optical chemical sensors have been developed for phosphate, nitrate, ammonia and pH detection using microfluidic analytical systems (Cogan, Diamond 2013). However, to date very few commercially available microfluidic detection systems have been developed for heavy metal monitoring in water. Among the challenges in developing a heavy metal quantification method is the low detection limit set by European Environmental Quality Standards Directive. This directive states that the maximum allowable concentration for arsenic in drinking water is 10 µg/L (Directive 2008/105/EC). Electrochemical sensors have been used for different heavy metal detection. However, these methods are difficult to implement for long term monitoring because of numerous limitations such as sensor drift, inability to analyze complex matrices, high cost of installation and operation, and biofouling (Chailapakul, Grudpan 2008). Analysis using optical detection systems minimizes fouling effects by avoiding the need for direct contact between sample and sensor.A wide variety of chromophoric dyes exist for heavy metal detection and quantification in aqueous solutions (Sareen 2004). In order to incorporate colorimetric methods into microfluidic detection system for arsenic detection in water

optimization and throughout assessment is required. Issues such as limited specificity, turbidity and poor sensitivity must be overcome. Also, the method should be rapid and yield reproducible results (Yogorajah, Tsai 2015). This present work aims at developing a rapid, selective and sensitive analytical method for arsenic detection in water. The method is adapted from Kumar *et al* 2007 and optimised to assess the method's potential for use in autonomous microfluidic detection systems. In this method leuco malachite green (LMG) dye is used. Arsenic is reacted with acidified potassium iodate to liberate iodine. The liberated iodine selectively oxidizes LMG to malachite green (MG) dye. Addition of sodium acetate buffer results in green color formation. The MG dye has absorption maximum at 617 nm (Kumar 2007).

2. Experimental

2.1Apparatus

Shimadzu 1800 UV- visible spectrometer was used with 1 cm and 0.1 cm quartz cuvettes for the absorbance measurements. Hanna pH 20 pH meter was used for pH measurements.

2.2 Reagents

All chemicals used were of analytical grade, and double deionized water was used for dilution of reagents and samples. As (III) stock solution (1000 mg L^{-1}) from Sigma-Aldrich was used. Working standards were prepared by appropriate dilution of stock solution. Potassium iodate: 1%, hydrochloric acid: 1M, leuco malachite green dye: 0.05%, sodium triacetate buffer: 13.6% were used.

2.3 Preparation of calibration curve

6 ml of arsenic-containing sample was transferred to a glass vial. Potassium iodate (1%, 1ml) then hydrochloric acid (1 M, 0.5 ml), and the mixture was gently shaken and left for 2 min. Leuco malachite green dye was added (0.05%, 0.5 ml), followed by sodium triacetate buffer (13.6%, 2 ml). The mixture was gently shaken and kept for 5 min. The absorbance was measured at 617 nm against reagent blank. Absorption spectra for sample and reagent blank are shown in Figure 1.

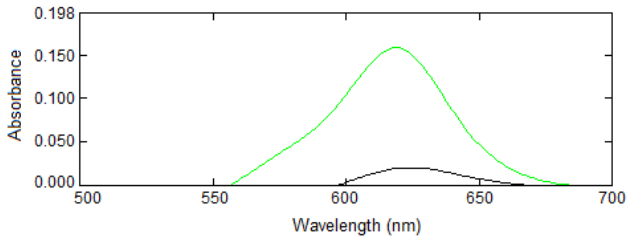

Figure 1. Absorption spectra of a sample containing 1µg ml^{-1} with reagents against reagent blank (above) and reagent blank against double deionized water (below).

3. Results and discussion

3.1 Analytical data

Beer's law was obeyed in the range of 0.02 – 4 µg mL^{-1}. The molar absorptivity coefficient was found to be 1.5 × 10^4 l mol^{-1} cm^{-1}. Sandell's sensitivity was found to be 0.2 × 10^{-2} µg cm^{-1}. The limit of detection (3se/S) and the limit of quantification (10se/S) (where se is the standard error of the calibration curve and S is the slope of the calibration curve) were found to be 0.139 and 0.466 µg mL^{-1}, respectively.

3.2 Accuracy and precision

The spectrometric measurements were carried out in triplicate. Standard deviation and relative standard deviation (RSD %) were calculated to assess the precision of the method. The results can be viewed in Table 1. To calculate the accuracy of the method arsenic working standard preparation technique Varian ICP-MS was used. The settings of the ICP-MS were the following: plasma flow: 15 L min^{-1}, auxiliary flow: 1.55 L min^{-1}, sheath gas flow: 0.2 L min^{-1}, nebulizer flow: 0.9 L min^{-1}, sampling depth: 6.5 mm, pump rate: 4rpm. The following internal standards were used: Li^6, Sc^{45}, Y^{89}, Tb^{159}, Ho^{165}, Th^{232}.

Table 1. (1) RSD% calculated from the spectrophotometric method. (2) RSD% calculated from the ICP- MS measurements.

Conc (µg ml^{-1})	RSD % (1)	RSD % (2)
0	115.470	14.32
0.02	18.182	3.99
0.04	21.724	4.11
0.06	8.449	4.30
0.08	17.886	7.97
0.10	13.846	5.79
0.20	16.952	6.16
0.40	4.693	3.73
0.60	6.472	4.51
0.80	6.033	5.37
1.00	1.438	4.81

Conc (µg mL^{-1})	Average absorbance	Absorbance from calibration curve	% Relative error
0.02	0.003	0.003	0.08
0.04	0.014	0.014	0.18
0.06	0.020	0.021	2.30
0.08	0.032	0.032	0.70
0.2	0.049	0.053	7.54
0.4	0.082	0.094	12.70
0.6	0.136	0.148	8.10
0.8	0.173	0.179	3.07
1	0.201	0.240	16.00

Table 2. Average absorbance and % relative error of spectrophotometric method.

3.3.1 Temperature

A range of different incubation temperatures (4 – 60 °C) were analysed. Low temperatures were used in order to

determine the viability of the method in low-temperature environments. The method performed best at 50 °C as shown in Figure 2. For practical applications carrying out the method at high temperatures would add to the cost and over all complexity of the method. The difference in absorbance between the different incubation temperatures was not significant, thus ambient room temperature would be sufficient for the analysis. The slope and linearity of 4 °C incubation temperature was low compared to the other temperatures. It can, however, be concluded that the method has the potential to be applied in low temperature environments, and further examination of the kinetics of the reaction at low temperatures will be carried out.

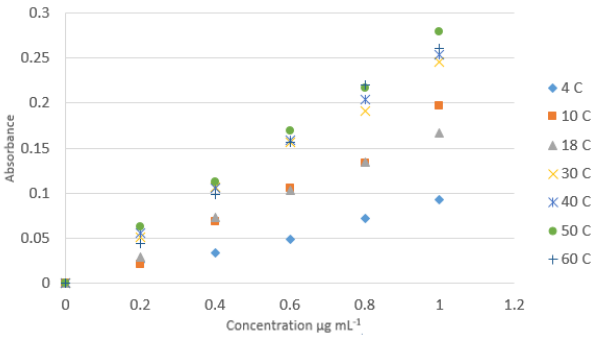

Figure 2. Absorbance differences between different incubation temperatures.

Temperature (°C)	Slope	Intercept	Coefficient of determination
4	0.089	0.0009	0.987
10	0.194	0.0092	0.982
18	0.169	0.0004	0.997
30	0.243	0.0039	0.996
40	0.134	0.0028	0.997
50	0.273	0.0035	0.999
60	0.270	0.0049	0.997

Table 3. Slope, intercept and coefficient of determination of different incubation temperatures.

3.3.2 pH

The effect of sodium triacetate buffer pH was studied using a range of different pH (3.7-7.3). Buffer pH of 5.5 was found to be the optimum pH for the procedure (Figure 3).

3.3.3 Materials

Different material cuvettes were compared against standard 10 mm light path quartz cuvettes. Quartz cuvettes with 1 mm path length were used in order to determine how the method would perform in microfluidic chips, where the volume is small and the light path is short. Polystyrene (PS) and poly methyl methacrylate (PMMA) cuvettes were used for absorbance measurements to see if these materials would have an effect on absorbance. PS and PMMA cuvettes were selected due to their potential use as microfluidic chip materials. As expected, the quartz cuvettes with 1mm path length gave lower absorbance readings compared to standard 10 mm path length quartz cuvettes. PS and PMMA materials did not have a significant effect on the absorbance readings in comparison to standard quartz cuvettes. The results can be viewed in Figure 4.

3.3.4 Reagent ratio

The effect of combining different reagents and changing the reagent ratio was studied. Small number of reagents are desirable for colorimetric method's incorporation into microfluidic chip, as this simplifies chip design and fabrication processes. The original ratio of the method was sample (6): 1% KIO_3 (1): 1M HCl (0.5): LMG dye (0.5): sodium triacetate buffer (2). Firstly the dye and the buffer were combined to give a reagent ratio: sample (6): KIO_3 (2.5): 0.2M HCl (2.5): dye and buffer (2.5). Secondly 1% KIO_3 and HCl were combined to give reagent ratio of sample (6): KIO_3 and 0.4M HCl (2.5): buffer and dye (2.5). This reagent ratio was found to be the optimum reagent ratio for the assay and was used in further studies.

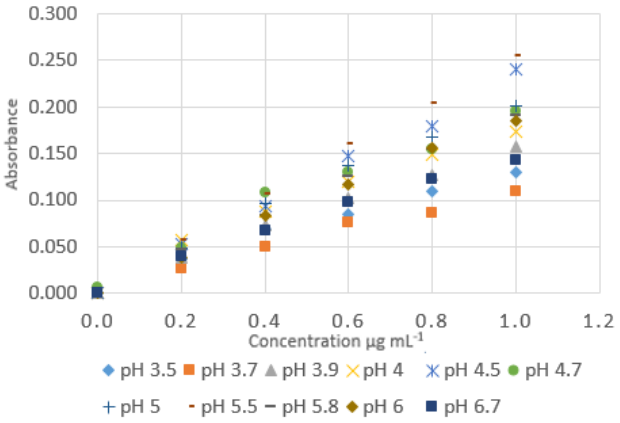

Figure 3. Absorbance difference at different buffer pH.

3.4 Time

The stability of the colour of the sample was tested over time. 0.1 µg ml^{-1} arsenic sample was tested for a time period of 600 minutes. The absorbance measurement was started after the addition of the dye. The results obtained are presented in Figure 5. The maximum absorbance was reached after 5 minutes after the addition of the dye. After 100 minutes 17.8 % decrease from the maximum absorbance was observed. After 600 minutes 39.2 % decrease in absorbance was observed.

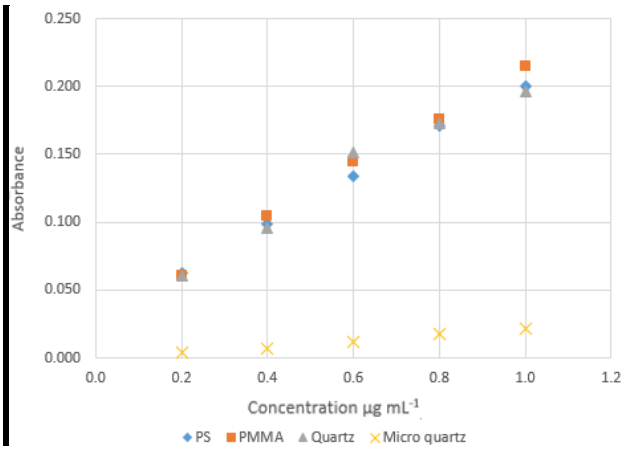

Figure 4. Absorbance difference between different material cuvettes.

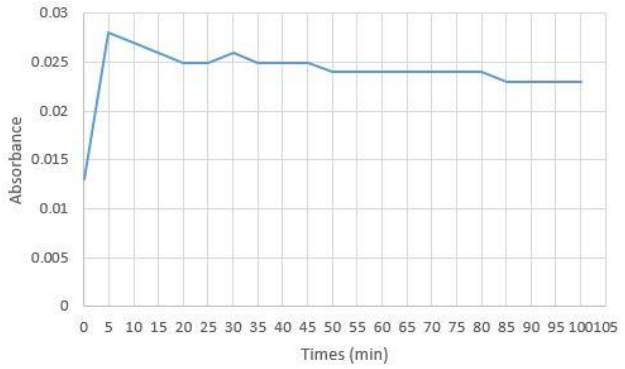

Figure 5. Absorbance versus time for 0.1 µg ml^{-1} arsenic sample. Data from first 100 min of a 600 min experiment are shown.

4. Conclusion

This paper reports the use of leuco malachite green for the spectrophotometric determination of arsenic and examines the method's potential incorporation and use in microfluidic chip. The method is simple, fast and cost effective and requires only small amount of chemicals, thus making it environmentally safe. The current sensitivity of the method does not meet the requirement of assessing compliance with relevant EU drinking water standards, nevertheless there are potential applications in the monitoring of wastewaters and in areas with particularly high arsenic levels.

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