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A Mathematical Model for Arsenic (V) Concentration Determination by an Image Processing Assisted Colorimetric Technique

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Abstract: Colorimetric method is one of the common methods used for the environmental monitoring of Arsenic on-site. However, the results that are mainly based on interpretation of the operator are less accurate and reliable. This study describes a more reliable approach to determine Arsenic (V) concentrations whereby an image processing technique is incorporated into a colorimetric method. In this approach, Arsenic (V) concentrations are quantitatively determined by digitized the color formed by the reaction of arsine gas generated from the ion with silver ion impregnated on the filter study. Multiple regression analysis is used to develop a mathematical model to analyze Arsenic (V) concentration by Minitab software. Validation of the developed mathematical model is performed by evaluating the model with the data from the Arsenic (V) standard solutions. The developed mathematical model to determine Arsenic (V) concentration is: Arsenic (V) concentration = 916-2.19 Red -2.30 Green -1.667 Blue. The correlation between the calculated Arsenic (V) and known Arsenic (V) concentration was high ($R^2 = 0.9997$). The results also revealed that relative bias (0.2 to 3.8%) and relative standard deviation (0.2 to 2.7%) of calculated Arsenic (V) concentrations are low. The accuracy of the Arsenic (V) concentration estimation by the model is between 96 to 99%. It can be concluded that the developed mathematical model is able to estimate the Arsenic (V) concentration accurately and precisely.

Key words: Arsenic (V), colorimetry, image processing, mathematical model, precisely

INTRODUCTION

Contamination of Arsenic in potable waters can be a major public health problem as it threats the lives of over 150 million people worldwide (Ravenscroft *et al*., 2009; Matschullat, 2000). The level of Arsenic in drinking water recommended by the World Health Organization (WHO) is 10 ppb (Ravenscroft *et al*., 2009; Bhattacharya *et al*., 2007; Mandal and Suzuki, 2002). Arsenic in the environment is normally found in the oxidation states of -3, 0, +3 and/or +5, in both inorganic and/or organic forms. In natural waters, Arsenic is most often found in inorganic forms and to a lesser extent in organic forms (Adriano, 2001; Smedley and Kinniburgh, 2002; Leermakers *et al*., 2006).

There are a number of Arsenic detection methods for analysis of As (III) and As (V) in water including various spectroscopic and electrochemical techniques (Hung *et al*., 2004). However the cost of these instruments, sample preparation and instrumentation handling often limit their application especially on site for Arsenic analysis. Consequently, Arsenic test kits were developed in which colorimetric method is widely used (Melamed, 2005). However, the measurement of the

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colored complex formed in these kits is based on the naked eye observation which leads to poor repeatability and a considerable determination error of 20-35%. As a result, efforts have been made to develop more a reproducible and precise technique by introducing image-processing technique to replace naked eye observation but the detection limit of this innovation is 60 mg L^{-1} which is not low enough for the monitoring of Arsenic in groundwater (Salman *et al*., 2012).

Mathematical models were developed by Firdaus *et al.* (2014) using simple linear regression of individual color red, green or blue (R, G or B) and multiple linear regression of all three colors R, G and B for determinations of chromium (VI) and iron (III) concentrations by digital image-based colorimetery.

Recently we have developed a very sensitive colorimetric method to detect Arsenic (V) by reducing the ion into arsine gas and reacting the gas produced with silver nitrate impregnated filter study to form a colored complex which is then detected by an image processing technique (Hung *et al*., 2004). In this study, we describe a mathematical model that was developed in the study to improve the accuracy and precision of the detection of the Arsenic (V) concentration by multiple regression analysis.

MATERIALS AND METHODS

The experimental stages consist of Arsenic (V) detection using colorimetric method followed by image processing and finally mathematical modelling by multiple linear regression analysis.

Arsenic (V) detection based on colorimetric method: The method used to detect Arsenic (V) in this study is described by Ong. Reduction of Arsenic (V) ion was carried in a 60 mL of polypropylene bottle. For each reaction, 50 mL of Arsenic (V) solution was mixed with sulfamic acid and zinc powder to produce arsine gas that reacted with a silver nitrate-impregnated filter study which was placed at the inner part of the reaction bottle cap. All experiments were conducted at room temperature and each experiment was duplicated. The reaction period between silver nitrate and arsine gas on the impregnated filter study were 5 and 10 min. The colored silver nitrate-impregnated filter study produced was then immediately removed from the cap and used for the image processing.

Image processing technique: Images of colored silver nitrate-impregnated filter study were recorded by a digital camera (Sony Cyber-shot, 14.1 Megapixels-model DSC-W610) at the distance of 15 cm with lighting in automatic mode. The central area of image was cropped and used for converting the color intensity into RGB color digital readings by Image J after importing the image to a computer.

Table 1: Images of colored complexes

Arsenic (V) concentration	Image (μgL^{-1})
	0
	10
	50
	100
	200
	300

Statistical analysis: Minitab Software release 17.1.0 (Minitab Inc., PA, USA) was used for data analysis and mathematical model development for Arsenic (V) concentration estimation. Linear regression model was used to determine the relationship of Arsenic concentration and the RGB values. The goodness-of-fit of the built model was used to evaluate the performance of the proposed model. Meanwhile, for validating the model, linear correlation was used.

RESULTS AND DISCUSSION

Development of a mathematical model to determine arsenic (V) concentration: A total of 30 experiments were performed using As (V) standard solutions of concentrations of between 0-300 ppb. The images of the color complex formed were recorded (Table 1) and analyzed for each test to obtain the corresponding RGB digital readings. The results showed that color intensity

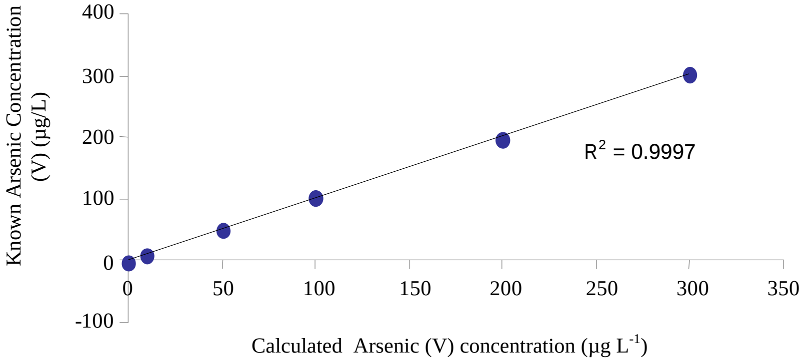

Fig. 2: Correlation between known Arsenic (V) concentrations and calculated (V) concentrations

of color complexes formed increased with the increased of the concentration. The mean RGB digital readings were used to develop a mathematical model that related to the mean As (V) concentrations using multiple regression analysis. The multiple regression model has the general form as presented in Eq. 1:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \ldots\ldots\ldots + \varepsilon \qquad (1)$$

Where:

X_1-X_3 = The independent variables
Y = The dependent variable
β_0-β_3 = The correlation coefficients and å designates the error term

The final fitted model based on the multiple regression analysis is expressed in Eq. 2:

$$\text{Arsenic } (\text{V}) \text{ concentration} = 916 - 2.19 \text{ Red} - 2.30 \text{ Green} - 1.667 \text{ Blue} \qquad (2)$$

The coefficient of determination as a measurement of the goodness-of-fit of the model of Arsenic (V) concentration and RGB digital readings is considerably high (R^2 = 0.9602), therefore it can be said that the developed model could fit Arsenic (V) concentration very well.

Validation of the developed mathematical model: Validation is one of the most important stages in the development of analytical procedures which conducted after the development of the analytical procedure. Hence, other sets of experiments were conducted in this study to validate the developed model by comparing the known Arsenic (V) concentrations (10-300 µg L^{-1}) with those calculated from the model.

Linear correlation analysis: Correlation between known Arsenic (V) concentration and calculated mean Arsenic (V) concentrations was evaluated to validate the model and the result is shown in Fig. 1. The results show that calculated (V) concentrations are highly correlated with known Arsenic (V) concentrations as indicated by high R^2 (0.9997) value. Therefore, the model can fit Arsenic (V) concentrations very well.

Accuracy and precision of the developed mathematical model: The accuracy of the measurements calculated by the developed model was evaluated by relative bias. The equation used to calculate the relative Bias (B) is expressed in Eq. 3:

$$B = \left|\frac{d}{C_R}\right| \times 100\% \qquad (3)$$

Where:

d = The difference between the calculated mean Arsenic concentration (V) in µg/L and the reference Arsenic (V) concentration
C_R = The reference Arsenic (V) concentration

In this study, the known Arsenic (V) concentrations were used as reference concentrations. Besides that, the precision of the measurement determined by the developed model was evaluated by Relative Standard Deviation (RSD) and it is expressed in Eq. 4:

$$RSD = \left|\frac{S}{C}\right| \times 100\% \qquad (4)$$

Where:

S = Standard deviation
C = Calculated mean Arsenic (V) concentration

The results of known Arsenic (V) concentrations, calculated mean Arsenic (V) concentrations, relative bias and relative standard deviations of calculated mean Arsenic (V) concentrations are presented in Table 2. In

Table 2: Comparison between known arsenic (V) concentrations and calculated mean arsenic (V) concentrations

Known arsenic (V) concentration (μg L^{-1})	Calculated mean arsenic (V) concentration (μg L^{-1})	S μg L^{-1}	RSD (μg L^{-1})	B (%)
10	9.820	0.263	2.7	1.8
50	51.144	1.146	2.2	2.3
100	103.830	0.884	0.9	3.8
200	198.360	3.262	1.2	0.8
300	300.520	0.557	0.2	0.2

general, there was good agreement between known Arsenic (V) concentrations and calculated mean Arsenic (V) concentrations. The relative bias and relative standard deviations of the calculated Arsenic (V) concentrations range from 0.2-3.8 and 0.2-2.7%, respectively, for detection of 10-300 ppb of Arsenic (V). The accuracy and precision of developed mathematical model is similar to that found by Firdaus *et al.* (2014).

The results also revealed that relative bias and relative standard deviation of calculated Arsenic (V) concentrations by the mathematical model were relative low. Therefore, it can be said that the mathematical model could give Arsenic (V) concentrations accurately and precisely.

CONCLUSION

In this study, a more reliable approach to determine Arsenic (V) by incorporation of image processing technique into colorimetric method was described. A mathematical model was developed by multiple regression analysis to detect Arsenic (V) concentration. The model was validated and the results showed that the correlation between the calculated Arsenic (V) and known Arsenic (V) concentration was high ($R^2 = 0.9997$). The results also revealed that relative bias (0.2-3.8%) and relative standard deviation (0.2-2.7%) of calculated Arsenic (V) concentrations were low. The accuracy of Arsenic (V) concentration estimation by the model is at least 96%. It can be concluded that the developed mathematical model can detect Arsenic (V) precisely and accurately.

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