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EFFECTS OF TEST PAPER DRYING AND REACTION PERIODS ON SILVER ION-ARSINE COMPLEX COLOUR DEVELOPMENT FOR A SIMPLE AND RAPID ARSENIC (V) DETERMINATION

(Kesan-kesan Tempoh Pengeringan Kertas Ujian dan Tempoh Tindakbalas terhadap Pembentukan Kompleks Ion Perak-Arsin untuk Penentuan Arsenik (V) dengan Ringkas dan Cepat)

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Abstract

Arsenic is a toxic element that exists in different forms in nature and can be accumulated by various biota and environmental media. Current techniques for the environmental monitoring of arsenic were usually sophisticated, time consuming and inappropriate for on-site analyses. We are developing a simple and rapid colourimetric quantitative method based on a colour complex formed by silver ion impregnated on a filter paper with arsine gas produced from arsenic ion reduction by hydrogen generated from zinc and sulfamic acid reaction in the sample. In this report we describe effects of drying of the silver ion impregnated filter paper and exposing period of this test paper to the arsine gas. The data obtained are digitized and used to develop a model for arsenic (V) ion estimation. The study reveals that when 4.0 g of sulfamic acid and 2.0 g of zinc powder are used to reduce 50 ml of arsenic solution sample, the drying and exposure periods needed are 20 seconds and 10 minutes, respectively. The best fitted model that relates arsenic (V) concentration (Ac) and the red colour intensity value (R) is Ac =120.1 – 1.071R. This model can accurately estimate the arsenic (V) concentration from 0 to 100 µg/l.

Keywords: arsenic (V) determination, colourimetric technique, drying period, reaction period, image processing

Abstrak

Arsenik adalah unsur beracun yang wujud dalam beberapa bentuk di persekitaran dan terkumpul di dalam pelbagai biota dan media persekitaran. Teknik analisis untuk pemantauan arsenik di dalam alam sekitar biasanya adalah kompleks, mengambil masa dan tidak sesuai untuk analisis in-situ. Kami sedang membangunkan satu kaedah kuantitatif kolorimetri yang ringkas dan cepat berdasarkan warna kompleks yang terbentuk daripada tindakbalas antara ion perak yang terjerap pada kertas turas dengan gas arsin yang terhasil daripada proses penurunan ion arsenik oleh hidrogen yang dihasilkan daripada tindakbalas antara zink dan sulfamik asid dalam sampel. Dalam laporan ini kami menerangkan kesan-kesan tempoh pengeringan kertas turas yang telah

dijerapkan dengan ion perak dan tempoh mendedahkan kertas ujian ini kepada gas arsin. Data yang diperolehi didigitalkan dan digunakan untuk membangunkan model untuk membuat anggaran kepekatan ion arsenik (V). Hasil kajian menunjukkan bahawa apabila 4.0 g asid sulfamik dan 2.0 g serbuk zink digunakan untuk menurunkan 50 ml larutan sampel arsenik, tempoh pengeringan kertas turas dan tempoh pendedahan gas arsin adalah masing-masing 20 saat dan 10 minit. Model yang paling sesuai untuk menghubungkait kepekatan arsenik (V) (Ac) dengan keamatan warna merah (R) adalah Ac = 120.1 – 1.071R, yang dapat menganggarkan kepekatan arsenik (V) di antara 0 hingga 100 µg/L.

Kata kunci: penentuan arsenik (V), teknik kolorimetri, tempoh pengeringan, tempoh tindak balas, pemprosesan imej

Introduction

Contamination of drinking waters by arsenic is a worldwide problem [1]. To date, over 100 million people are still exposed to untreated groundwater with arsenic concentrations far exceeding the World Health Organization (WHO) guideline of 0.13 µmol/L (10 µg/L) [2]. The current methods for detecting low arsenic concentrations are accurate and reproducible but require expensive laboratory instrumentations [3]. The most popular speciation approach combines an effective separation method (such as high-performance liquid chromatography) with an element-specific detection method (such as mass spectrometry or atomic fluorescence spectrometry). However, the methods are not designed for field applications. The spot test, a well-known Gutzeit method, has been used to detect arsenic at microlevels. The major drawback of this method is that the measurement of the coloured complex involves the naked eye, which leads to poor reproducibility that consequently causes a considerable determination error (20% – 35%) [4]. Therefore the development of a reliable, portable and affordable detection kit is imperative especially for routine arsenic environmental monitoring. We are developing a simple and rapid colourimetric quantitative method based on a colour complex formed by silver ion impregnated on a filter paper with arsine gas produced from arsenic ion reduction by hydrogen generated from zinc and sulfamic acid reaction in the sample. This paper describes effects of drying of the silver ion impregnated filter paper and exposing of this test paper to the arsine gas periods to detect arsenic (V) based on colourimetric quantitative method.

Materials and Methods

Arsenic (V) Stock and Working Standard Solutions

The arsenic (V) stock solution of 240 mg/L was prepared by dissolving analytical-grade sodium arsenate heptahydrate, (Sigma–Aldrich) in 1% (v/v) HCl solution. The arsenic (V) working standard solutions of 0 to 100 µg/l were freshly prepared by diluting the above stock solution using ultrapure water.

Silver Nitrate Solution of 5% (w/v)

The 5% (w/v) of silver nitrate solution was prepared by dissolving 5.0 g of silver nitrate in ultrapure water and made up to 100 ml with the ultrapure water.

Silver Nitrate-Impregnated Filter Paper

This paper was prepared from No. 3 Whatman filter paper. The paper was cut into a 2.5 cm diameter round-shaped piece, dipped into 5% (w/v) silver nitrate solution for 2 seconds and then dried by sandwiching it between two pieces of the dry Whatman filter papers pressed by 500 g load for 20, 40 or 60 seconds.

Arsenic (V) Detection by Colourimetric Method

Two reaction periods, 5 and 10 min, were used to study this parameter's effect on arsine gas and silver ion-arsine complex development. Arsenic (V) standard solutions with concentrations ranging from 0 to 100 µg/l were used. The reaction was carried out by using 50 mL of the arsenic (V) working standard solution in a 60 mL polypropylene bottle. After adding and dissolving by gently swirling the chosen amount i.e. 4.0 g of sulfamic acid, 2.0 g of zinc powder was added. The mass ratio of sulfamic acid to zinc powder was made 2 to 1. The bottle was then tightly closed with the bottle cap which its inner part was covered by the silver nitrate-impregnated filter paper that would react with the arsine gas generated from arsenic (V) reduction to produce the colour complex. The bottle was lightly shaken to facilitate the mixing and reaction was allowed to proceed until the chosen reaction period was over. The reactions were conducted at room temperature and each was repeated for five times. Immediately after the reaction period was completed, the coloured silver nitrate-impregnated filter paper placed in the bottle cap was taken out for image processing.

Image Processing Technique

Two images were taken for each coloured silver nitrate-impregnated filter paper by a digital camera (Sony Cyber-shot, 14.1 Megapixels – model DSC-W610). The distance between the digital camera and coloured silver nitrate-impregnated filter paper was 15 cm, and the lighting was in automatic mode for all experiments. The resolution of the image captured for each reaction period was 11 megapixels. The images were cropped to acquire only the coloured part. The cropped image was then converted into Red (R), Green (G) and Blue (B) intensity values by importing the images into a computer using the image processing software, Image J. For each image, a value from 0 to 255 was assigned for the R, G, and B intensity values.

Statistical Analysis

Correlations between the factors involved in the experiments were determined using analysis of variance (ANOVA) by Minitab release 16 (Minitab Inc., PA, USA). In evaluating the factors, an ANOVA table with a list of all possible terms corresponding to a linear model of a full factorial design with two factors was used. The two factors were drying (of 20, 40 and 60 seconds) for the silver nitrate-impregnated filter paper and reaction periods of arsenic (V) ions and hydrogen gas (of 5 and 10 min). The arsenic concentration served as the blocking variable because the experiment was conducted at different arsenic concentrations.

Models were formed for the R, B, and G intensity values subjected to Pearson correlation analysis and regression model analysis using the statistical software mentioned above. Important or significant terms were selected from the corresponding full model to explain the factors that contributed to colour formation on the silver nitrate-impregnated filter paper due to the reaction between arsine gas and silver nitrate.

Results and Discussion

Colourimetric determination of arsenic (III) ion based on reduction into arsine gas and complex formation with a metal ion was developed by Cherukuri and Anjaneyulu [5]. This method was later modified by Ong et al. [6] by using less toxic colour forming reagent in which mercuric bromide was replaced by silver nitrate. In this study we propose a quantitative analysis of arsenic (V) ion technique by combining reduction arsenic (V) to arsenic (III) and the above arsenic (III) analysis technique. Since both reductions of arsenic (V) ion to arsenic (III) ion and arsenic (III) ion to arsine can be carried out using the same chemicals, i.e. sulfamic acid and zinc powder, therefore using sufficient amount of these reagents, both reductions can be carried out in a one-step reaction.

To optimize the complex colour formation, effects of drying of the silver nitrate- impregnated filter paper and exposing periods of this test paper to the arsine gas were studied. Table 1 shows the results of ANOVA of the B intensity value based on the digital analysis on coloured spots. The results of ANOVA showed that only one of the two factors i.e. reaction period is a significant contributor to the B intensity value. Meanwhile, the interaction between the two factors is not statistically significant at $\alpha = 0.05$. Tables 2 and 3 show the same findings found for the R and G intensity values, respectively.

Table 1. Analysis of variance for blue intensity value

Source	DF (Degrees of Freedom)	Sum of Squares	Mean Squares	F value	p (probability value)
Drying period	2	26.8	13.41	0.29	0.747
Reaction period	1	1493.8	1493.82	32.78	0.000
Drying period*reaction period	2	211.4	105.72	2.32	0.116
Aresenic (V) concentration	6	36080.2	6013.36	131.94	0.000

Table 2. Analysis of variance for red intensity value

Source	DF (Degrees of Freedom)	Sum of Squares	Mean Squares	F value	p (probability value)
Drying period	2	15.3	7.64	0.24	0.789
Reaction period	1	2014.7	2014.72	62.81	0.000
Drying period*reaction period	2	147.5	73.77	2.30	0.118
Aresenic (V) concentration	6	59746.4	9957.73	310.43	0.000

Table 3. Analysis of variance for green intensity value

Source	DF (Degrees of Freedom)	Sum of Squares	Mean Squares	F value	p (probability value)
Drying period	2	3.0	1.5	0.02	0.976
Reaction period	1	917.6	917.6	14.87	0.001
Drying period*reaction period	2	229.5	114.8	1.86	0.173
Arsenic (V) concentration	6	12706.5	12706.5	205.86	0.000

Since reaction period is having significant contribution to all colour intensities, then multiple comparison tests were conducted using Tukey method to determine the mean difference of colour intensities between 5 and 10 minutes reaction periods. The results showed that red, blue and green colour intensities for both reaction periods were significantly different. As shown in the Table 4, the 10 min reaction period provides lower colour intensity value than that of the 5 min reaction period. Hence 10 minutes was considered as better reaction period in this study.

Table 4. Tukeys multiple comparison tests of each colour iintensity value for two reaction periods

Colour	(I) Group[1] (J) Group[2]	Mean Difference (I-J)	Standard Error	Sig.
RED	5 mins 10 mins	11.12	9.700	0.0000
BLUE	5 mins 10 mins	11.20	2.800	0.0000
GREEN	5 mins 10 mins	13.67	6.83	0.0000

[1]5 mins; [2]10 mins

Based on the ANOVA analysis and Tukeys multiple comparison tests, it can be said that when 4.0 g of sulfamic acid and 2.0 g of zinc powder are used to reduce 50 ml of arsenic solution sample, the drying of the silver nitrate-impregnated filter paper and its exposure to arsine gas periods are 20 seconds and 10 minutes respectively.

Linear correlations among the R, G, and B intensity values are illustrated in Table 5. The R, G, and B intensity values highly correlate with the value approaching to 1.

Table 5. Pearson correlation analysis matrix

Correlation	R	G	B
G	0.990[a]	1.000[a]	0.930[a]
	0.000[b]	-	0.000[b]
B	0.884[a]	0.954[a]	1.00[a]
	0.000[b]	0.000[b]	-

[a]*Pearson correlation;* [b]*P-value*

A strong correlation exists among the colour intensities. Thus, regression was adopted to establish a relationship between arsenic (V) concentration and each colour intensity value for the condition as mentioned earlier.

As illustrated in Figures 1 and 2, the relationship between arsenic (V) concentration and R intensity value is a linear model as shown in equation 1, whereas the G intensity value fits well in the linear model as expressed in equation 2 with coefficient of determinations of 88.3% and 85.0%, respectively.

Arsenic (V) Concentration, Ac = 120.1 – 1.071R (1)

Arsenic (V) Concentration, Ac = 113.9 – 0.9434G (2)

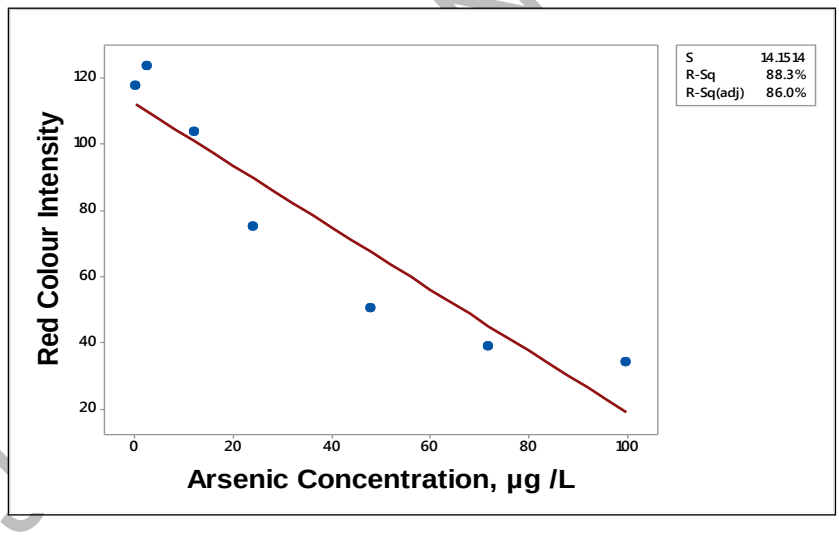

Figure 1. Relationship between arsenic (V) concentration and red (R) intensity value (drying period of silver nitrate impregnated filter paper = 20 seconds, reaction period between arsine and silver nitrate = 10 min)

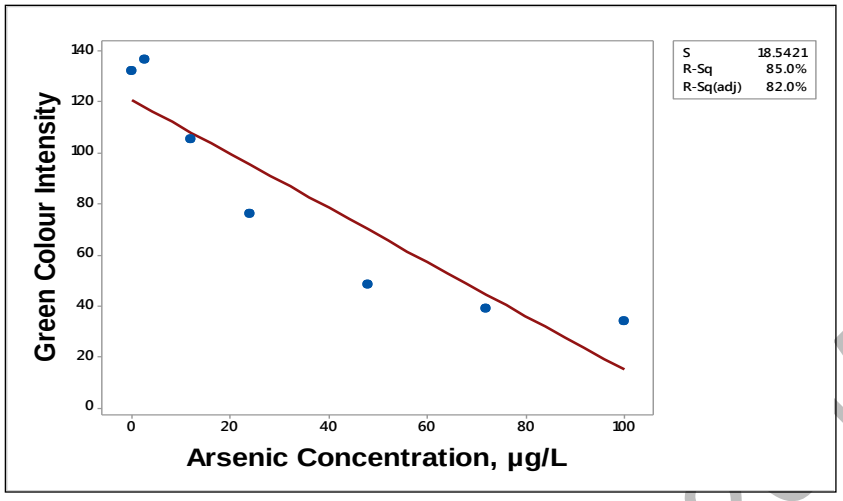

Figure 2. Relationship between arsenic (V) concentration and green (G) intensity value (drying period of silver nitrate impregnated filter paper = 20 seconds, reaction period between arsine and silver nitrate = 10 min)

Meanwhile, the relationship between arsenic (V) concentration and B intensity value in linear model as illustrated in Figure 3 with a coefficient of determination of 56.2%. The model can be expressed as equation 3 below

$$\text{Arsenic (V) Concentration, Ac} = 988.5 - 11.43B \quad (3)$$

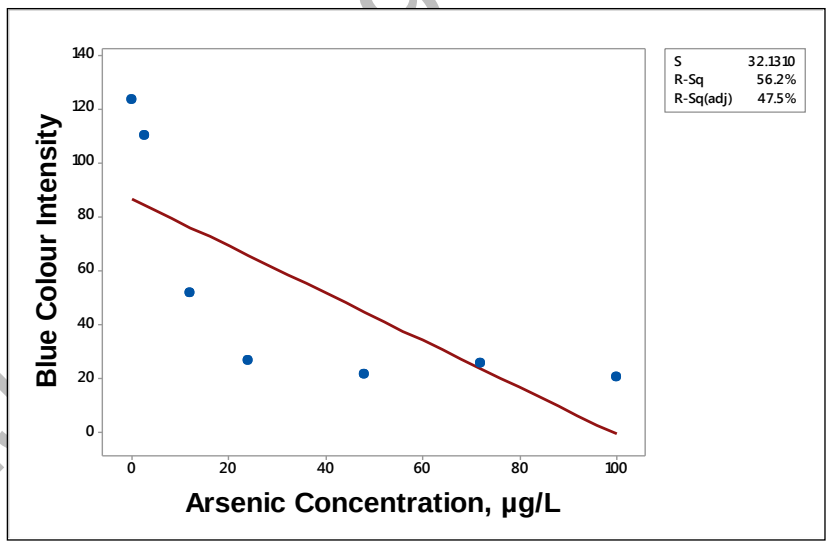

Figure 3. Relationship between arsenic (V) concentration and blue (B) intensity value (drying period of silver nitrate impregnated filter paper = 20 seconds, reaction period between arsine and silver nitrate = 10 min)

Among all the models above, it is ascertained that the relationship between arsenic (V) concentration and red intensity value is the best selected model with the highest coefficient of determination value as compared to green and blue intensities.

Table 6 shows a comparison of the detection period of the developed arsenic (V) detection paper with those of the commercial arsenic test kits. The detection periods for widely used field kits, i.e., EZ Hach and Merck, completed the detection after 20 min [7]. This comparison shows that the developed arsenic (III) detection paper has a faster response time than those of the commercialized kits.

Table 6. Comparison of the detection time with commercial test kits

Test Kit	**Detection period (min)**
EZ Hach	20
Merck	20
Quick Arsenic	20
Arsenic (V) detection paper (this study)	10

Conclusion

A simple, rapid and reliable arsenic (V) detection method based on reaction of arsine gas with silver ion impregnated filter paper was successfully developed. The study reveals that when 4.0 g of sulfamic acid and 2.0 g of zinc powder are used to reduce 50 ml of arsenic solution sample, the silver ion impregnated filter paper drying and its arsine exposure periods are 20 seconds and 10 minutes respectively. The best fitted model that relates arsenic (V) concentration (Ac) and the red colour intensity value (R) is Ac =120.1 – 1.071R. This model can be used to accurately estimate arsenic (V) concentration from 0 to 100 µg/L.

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