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Water Technology
ORIGINAL ARTICLE

Development of method for quantitative determination of water arsenic by field test kit

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ABSTRACT

Drinking of arsenic (As) contaminated ground water is threatening the health of millions of peoples of Bangladesh. The screening of tube wells (TWs) water for As in Bangladesh and elsewhere in the world is done by As testing kits. The results of water-As by these kits are semi-quantitative and personal error is high. An attempt has been undertaken for quantitative determination of water-As by MITech arsenic test kit by applying quantitative image analysis method from the digital picture of the colored test paper of the kit. In the quantitative image analysis method, the color of the test paper is numerically determined by color difference between the test water samples with the standard color chart which is calculated from Lab (lightness (L), color opponent green-red (a), and color opponent blue-yellow (b)) values. TWs water-As concentrations in Bashailbogh village, Munshiganj, Bangladesh were determined by using MITech arsenic field test kit by conventional method, quantitative image analysis method and inductively coupled plasma mass spectrometer (ICP-MS) method. The water-As by the quantitative image method gave quite close results (R^2 = 0.998) to those obtained with ICP-MS method at concentration up to 50 μg As L^{-1}. The water-As concentration more than 50 μg As L^{-1} by this method was underestimated. Hence, the developed method may be used for quantitative analysis of water-As in the range of 0-50 μg As L^{-1} for water-As screening program.

Keywords: Water arsenic, tube wells, field test kit, quantitative image analysis method, Bangladesh

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1 Introduction

Arsenic (As) contamination in groundwater of Bangladesh is geogenic in nature, originating from Holocene sediment aquifers of Ganges-Brahmaputra-Meghna (GBM) delta (Nickson et al., 2000; Smedley and Kinniburgh, 2002). Arsenic toxicity leads to adverse health outcomes such as skin cancer, dermatitis, black pigmentation, keratosis of the skin, lung cancer, hepatic dysfunction and diabetes (Chen and Ahsan, 2004; Wu et al., 2015). Most of the hand tube wells (TWs) installed at depths between 20-30 m in GMB delta are being contaminated with As (Chen and Ahsan, 2004; Rahman et al., 2006). Among 10 million TWs installed in Bangladesh, 30-40% of which have been estimated to contain As at levels exceeding the current Bangladesh drinking water standard value of 50 μg L^{-1} (BAMWSP, 2006). As a consequence, out of a total population of 160 million in the country, about 22 million are exposed to As concentration in drinking water above 50 μg L^{-1}, and about 5.6 million are exposed to As above 200 μg L^{-1} (UNICEF, 2009).

The concentration of As in TW water varies widely, both on a local and a regional scale possibly due to variation in the amount of burial organic matters in the Holocene sediments (Bhattacharya et al., 2006; Jakariya et al., 2007). Thus, As contamination cannot be accurately predicted by sporadic testing of water from a small number of TWs. Screening of water of all the TWs in the country is, therefore, needed to identify the extent and distribution of As in the groundwater of Bangladesh. Screening and regular monitoring of all the existing TW water is almost impossible using the laboratory method by atomic absorption spectroscopy (AAS) or inductively coupled plasma-mass spectrometry (ICP-MS) due to the limited availability of those facilities and poor economic situation of the country. Therefore, simple, low cost methods for As determination, such as the field test kits have proved to be most suitable for testing As in TWs water. Several investigations monitored As contamination in ground water by field test kits such as Hach EZ (van Geen et al., 2005; Steinmaus et al., 2006), Quick arsenic (Steinmaus et al., 2006), Merck (Jakariya et al., 2007), Wagtech Digital Arsenator and Chem-In Corp arsenic field test kit (Sankararamakrishnan et al., 2008), Arsenic Econo-Quick (EQ) kit (George et al., 2012) to evaluate their efficiency in field level. However, sometime only the results based on field test kits and reliability of test kits have often been questioned because of semi-quantitative results. In field testing As kits, the arsenate in the water samples are converted into arsine gas under acidic condition and the arsine gas is being trapped into filter paper impregnated with chemicals. The color of the filter paper is related to the particular concentration of As in water. In general, the As concentration is visually determined by the As field test kit based on the color of the test paper which is colored according to the As concentration. It is likely to cause the wide inter individual variability and the difficulty to apparently discriminate a small color difference, which results in error of measurement. The As concentrations in water measured by As testing kit are not continuous but can be measured only a few values (Table 1). Therefore, development of a quantitative determination of water-As method that can be used in the field has come to the fore.

In this study, an effort was undertaken to evaluate the performance of MITech arsenic test kit to determine As in TWs in Bashailbogh village, Munshiganj, Bangladesh and to apply quantitative image analysis from the digital picture of test paper and standard color chart of the As field test kit to get continuous quantitative results for As concentration in water samples.

2 Materials and Methods

2.1 Study area

Bashailbogh village is located about 30 km south of Dhaka city, and belongs to Munshiganj district of Dhaka division, Bangladesh. Groundwater of this village is heavily contaminated with As (Bhattacharya et al., 2002). Most of the TWs were screened for water-As during the national screening program of As in tube well water in Bangladesh (Johnston and Sarker, 2007). The TWs drilled between 25-40 m termed as shallow depth tube wells, were generally contaminated with As in water (>50 μg L^{-1}) and were painted red during screening program for water-As by As testing kit. Some household owners drilled the TWs between 80-200 m to get the safe water and termed as deep set tube wells. These TWs have the water-As below 50 μg L^{-1} and are regarded as safe for drinking in Bangladesh.

2.2 Sampling method

Water samples were collected from TWs installed both at shallow depth (30-40 m) and at deep set (90-120 m) during February 2014. The numbers of TWs selected for shallow depth and deep set were 7 and 10, respectively. Each TW was purged 25 strokes before collecting water sample for As analysis. From each TW, water sample was collected in a 100-mL polyethylene bottles for As analysis by ICP-MS. Water sample was filtered by 0.45 μm membrane filter (hydrophilic PTFE; ADVANTEC, Japan), marked with the tube well ID and its pH was adjusted to 2 with HNO_3 (69 wt%) to prevent co-precipitation of As with iron. The acidified water samples were transported to Yokohama National University, Japan and the samples were kept at 4 °C until analysis in the laboratory.

Table 1. Comparison of field test kits for arsenic determination

Arsenic determination field test kit	Volume of water sample (mL)	Arsenic detection range (μg L^{-1})	Reagents	Reaction time (min)
NIPSOM	15	10, 20, 50, 100, 200, 300, 400, 500 and 700	HCl (1:1), KI, Zn powder, $SnCl_2$, bromide paper (test strip)	5
GPL	15	10, 50, 100, 200, 400, 500, 600, 800, 900, 1000 and 1500	HCl (1:1), KI, $SnCl_2$, Zn powder, bromide paper (test strip), lead acetate cotton wool	20
ITS Econo Quick	50	0, 10, 25, 50, 100, 200, 300, 500 and 1000	Tartaric acid amended with small amounts of iron and nickel sulfate, Zn powder, mercuric bromide strip, potassium peroxymonosulfate (optional)	10
Hach EZ	50	0, 10, 25, 50, 100, 250 and 500	Sulfamic acid crystals, Zn powder, mercuric bromide strip	20
Merck	5 or 50	0, 100, 500, 1000, 1700 and 3000	Mixture of KI, $SnCl_2$, Zn and HCl	20
MITech (This study)	100	0, 5, 10, 20, 30, 40, 50, 60, 80, 100, 150, 200, 250, 300, 400, 500 and >500	Acidum tartaricum, Ferric sulfate(II).$7H_2O$, nickel sulfate(II) $6H_2O$, peroxymonosulfate potassium, potassium bisulfate, potassium sulfate, peroxydisulfate potassium, magnesium carbonate, zinc	12

Table 2. Arsenic concentration in TW water by ICP-MS, MITeck conventional method and color image method

Sample No.	ICP-MS (μg L^{-1})	MITeck kit Color image method (μg L^{-1})	MITeck kit (μg L^{-1})	Δ(Color image method-ICP-MS method)	Performance of color image method	Δ(Conventional method-ICP-MS method)	Performance of conventional method
Deep set tubewells (DSTW)							
DSTW-1	1.3	2.02	5	0.72	Overestimated	3.7	Overestimated
DSTW-2	1.76	3.33	5	1.57	Overestimated	3.24	Overestimated
DSTW-3	1.38	3.16	5	1.78	Overestimated	3.62	Overestimated
DSTW-4	1.77	2.64	5	0.87	Overestimated	3.23	Overestimated
DSTW-5	1.04	2.96	5	1.92	Overestimated	3.96	Overestimated
DSTW-6	1.69	4.23	10	2.54	Overestimated	8.31	Overestimated
DSTW-7	1.66	4.72	10	3.06	Overestimated	8.34	Overestimated
DSTW-8	2.31	3.1	5	0.79	Overestimated	2.69	Overestimated
DSTW-9	4.42	5.61	5	1.19	Overestimated	0.58	Overestimated
DSTW-10	1.1	2.78	5	1.68	Overestimated	3.9	Overestimated
Mean±SD	1.84±0.98	3.46±1.08	6.00±2.11	–	–	–	–
Shallow depth tube wells (SDTW)							
SDTW-1	476	119	500	−357	Underestimated	24	Overestimated
SDTW-2	104	105	200	1	Equal	96	Overestimated
SDTW-3	889	233	500	−656	Underestimated	−389	Underestimated
SDTW-4	308	202	500	−106	Underestimated	192	Overestimated
SDTW-5	58.4	156.2	200	97.8	Overestimated	141.6	Overestimated
SDTW-6	144	189	150	45	Overestimated	6	Overestimated
SDTW-7	88.9	152.2	250	63.3	Overestimated	161.1	Overestimated
Mean±SD	295±301	165±46	329±163	–	–	–	–

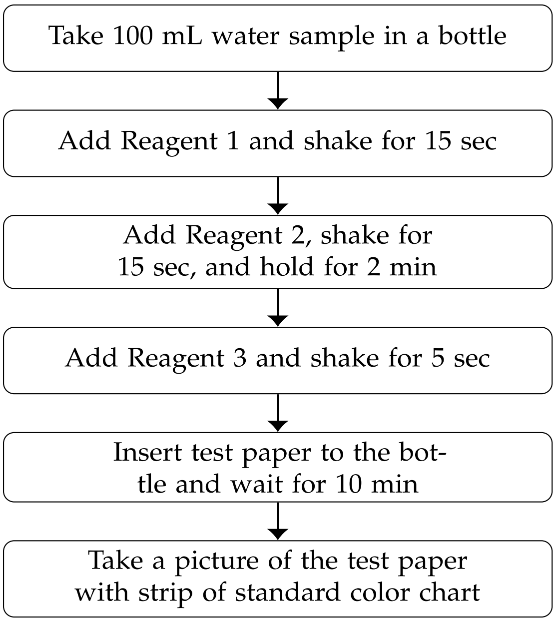

Figure 1. The determination procedure of MITech arsenic field kit

2.3 Arsenic determination by MITech kit (conventional method)

One hundred milliliter of TW water was collected in the sampling bottle and their As concentrations were determined by MITech kit (#481396, MITach Incorporated, Sendai, Japan). The test kit consists of three reagents. The determination procedure for water-As is presented in Fig. 1. The concentration of As was determined by the comparison of colors in test paper and standard color chart (Fig. 2). We call this a conventional method.

2.4 Arsenic determination by Quantitative Image Analysis Method

The picture of the colored test paper and strip of color chart of the MITech arsenic test kit was taken by a digital camera in the field (Cannon Inc., Tokyo, Japan). Color can be expressed by the addition of three primary colors; red, green, and blue (RGB). The intensity of the color on each test paper and standard colors on the strip of the color chart was quantified with the RGB values using the free software (Ryuhou, version 2.58, by Ryuhou (2017). The color for 0 μg As L^{-1} on the strip of the color chart was used as control. RGB values were converted to Lab color space (Hunter, 1984a,b) namely, lightness (L), color opponent green-red (a), and color opponent blue-yellow (b) values, by a free program on the internet (Color system conversion software (latest version 2015/1/19) by Inoue (2017). From Lab color space values, color difference, ΔE, was calculated by following equations.

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \qquad (1)$$

where ΔL, Δa, and Δb are the difference of L, a, and b values between the sample and the control, respectively. ΔE values were calculated for both test paper and standard colors on the strip of color chart for each site. Then, determination of As concentration for a site was carried out using the calibration curve constructed by that site. This procedure made it possible to disregard the difference of lighting conditions for each picture.

2.5 Arsenic determination by ICP-MS

Arsenic in water samples was determined by ICP-MS (Agilent 7700 series ICP-MS). Instrumental operating parameters were as follows. Radio frequency (RF) power; 1200 W, RF matching; 1.8 V, monitoring masses; 75 (As) and 77 (ArCl+), plasma flow rate; 1.2 L min^{-1}. Yttrium (Y; $m/z = 89$) was used as the internal standard. Multi-element standard solution (XSTC-13, SPEXCertiPrep, USA) was used to prepare calibration curves. The calibration curves with $R^2 > 0.999$ were accepted for concentration calculation. Before starting analysis sequence, relative standard deviation (RSD $< 5\%$) was checked by using a tuning solution (1 μg As L^{-1} each of Li, Y, Ce, Tl, Mg and Co in 2 wt% HNO_3) purchased from Agilent Technologies (Product No. 5188-6564, USA). Internal calibration standard solution containing 1.0 mg L^{-1} of Yttrium (Y) (ZSTC-538, SPEXCertiPrep, USA) was added to each sample. Working standards (0, 10, 20, 50, and 100 μg As L^{-1}) were prepared by diluting a multi-element stock solution, then the concentrations of As were determined by an internal standard method using Y. For each run, a blank and water samples were analyzed in duplicate to eliminate any batch-specific errors.

2.6 Statistical analysis

All statistical analyses were performed using Excel (Microsoft Office 2013). Non-parametric tests were used because of limited sample numbers. The Spearman rank order correlation coefficient was calculated to correlate the water As concentrations determined by MITech field test kit by our quantitative image analysis method and ICP-MS.

3 Results and Discussion

3.1 Standard curve using Quantitative Image Analysis Method for MITech Kit

In the quantitative image analysis method, the color of the test paper was numerically determined by color difference of Lab values between sample and color chart control. The standard As solutions (0, 5, 10, 50,

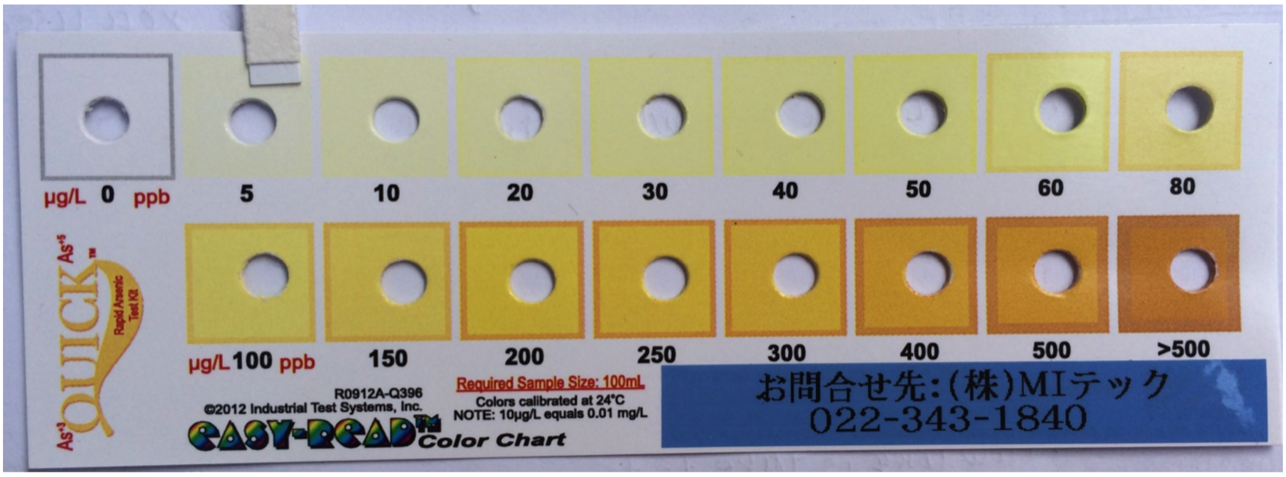

Figure 2. Picture of the color of the test paper with standard color chart of the MITech arsenic test kit

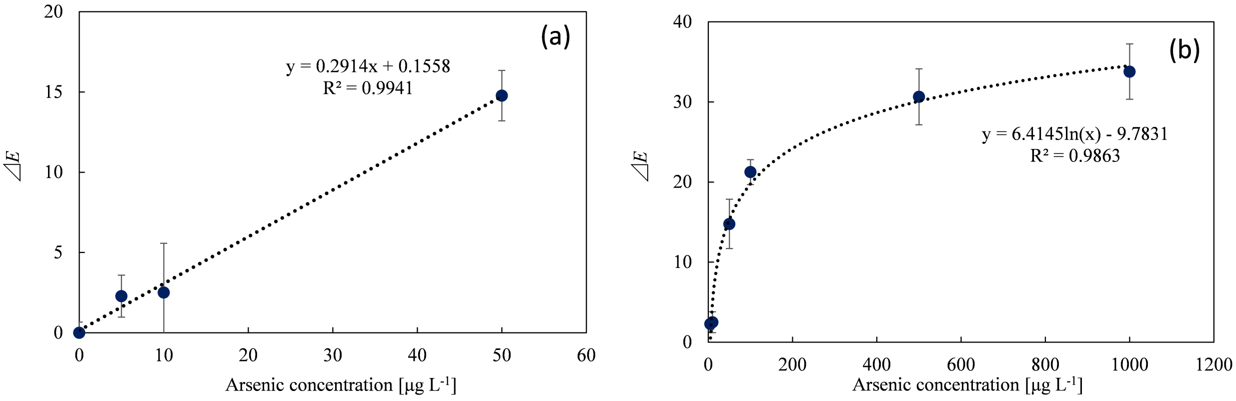

Figure 3. Standard curve for quantitative image analysis method. (a: up to 50 μg As L^{-1}; b: 0-1000 μg As L^{-1})

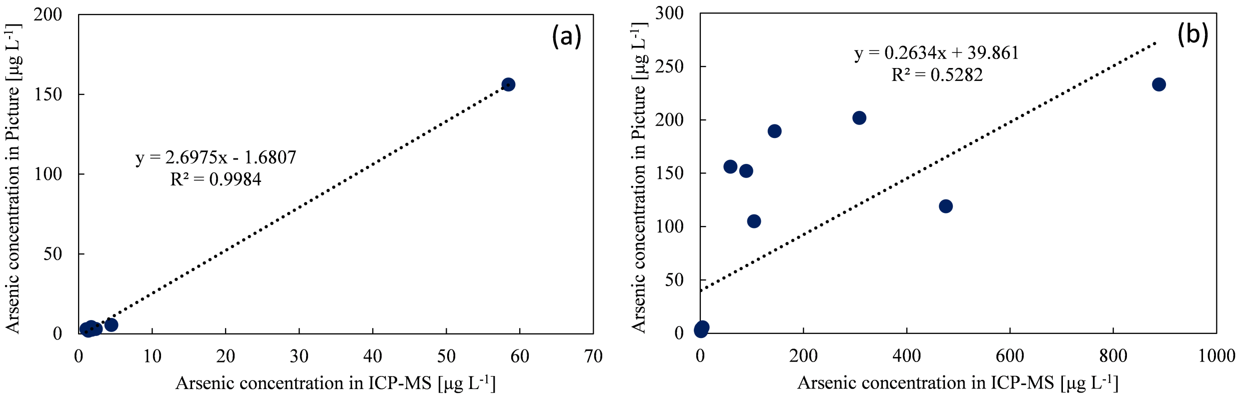

Figure 4. Correlations among arsenic concentrations of tube well waters determined by quantitative color image method and ICP-MS method. (a: up to 50 μg As L^{-1}; b: all the range)

100, 500, and 1000 μg L^{-1}) were prepared for making standard curve for MITech arsenic test kit coupled with the quantitative image analysis method. The calibration curve was linear (ΔE = 0.291 C + 0.156; R^2 = 0.994) up to the concentration of 50 μg As L^{-1} (Fig. 3a). The standard curve became curvilinear in the range of 0-1000 μg As L^{-1} and the regression equation was ; R^2 = 0.986 (Fig. 3b), where C is the As concentration (μg L^{-1}) and ΔE is color difference. It is expected that As in water can be measured accurately in the range of 0-50 μg As L^{-1} while it will be underestimated beyond that range.

3.2 Relationship among arsenic concentrations determined by different methods

Arsenic concentrations of tube well waters determined by using MITech arsenic test kit by conventional method, new quantitative image analysis method and ICP-MS method are presented in Table 2. The results show that the As determination of TW water samples by quantitative image analysis method using MITech Kit was quite close with the values obtained by ICP-MS method for the deep set TWs. The water-As concentrations were much higher when it was determined by MITech conventional method. On the other hand, at higher concentration of water-As (89-889 μg As L^{-1}), the quantitative image analysis method applied in MITech kit showed equal reading for one water sample, underestimated three samples, and overestimated three samples compared to the water-As determined by ICP-MS. Compared to ICP-MS, MITech conventional method showed one sample underestimated and six samples overestimated for TW water-As. The water-As concentration measured by MITech field test kit by quantitative image method and by ICP-MS method revealed a statistically significant correlation coefficient (R^2 = 0.998) in the As concentration lower than 50 μg L^{-1} while the corresponding correlation in whole range of the As concentration was insignificant (R^2 = 0.528) (Fig. 4). The acceptable levels of As concentrations in drinking water in Australia, WHO and Bangladesh are 7, 10 and 50 μg L^{-1}, respectively. Hence, quantitative image analysis method can be used confidently for screening of tube well water-As under field conditions.

Conclusion

The As concentrations measured by the quantitative image analysis method were in good agreement with those by ICP-MS method within 50 μg As L^{-1} that can be used for As screening program. This method can be applied for other As test kits.

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