Effectiveness of field methods for detecting Arsenic between 0 and 100 ppb in Bangladesh Groundwater

Field Report

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116

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Table of Contents

Executive Summary

The concentration of arsenic in Bangladesh groundwater is being widely measured using the field kit produced by Merck of Germany. This is a colourometric method relying on reduction of arsenic in a water sample to arsine gas which then reacts with mercuric bromide test paper to produce a colour change. This colour change is used to indicate the amount of arsenic present in the water sample. This method claims to be able to provide a measurement of arsenic at the level of 0 ppb or greater than 100 ppb. The Bangladesh standard for arsenic in drinking water is 50 ppb. For samples with arsenic concentrations of between 0 and 100 ppb it is not within the capabilities of the current Merck method to determine whether they lie above or below the standard. As there are a vast number of wells to be tested in Bangladesh, of which a substantial proportion are likely to have concentrations of arsenic between 0 and 100ppb, ideally a field kit with the capability to measure arsenic at these levels is required.

This study compared the results of the Merck 'doubling method' and the Asian Arsenic Network (AAN) method, both of which claim to be able to measure arsenic at these critical concentrations, with results obtained in a laboratory by Atomic Absorption Spectrometry. Only wells which were identified in the field with the Merck normal method as greater than 0 but less than 100 ppb were tested. This was done for a total of 241 wells out of 2581 in Panisara Union of Jhikorgachha Thana.

The results show that both methods correctly identify around 60% of these wells as having arsenic concentrations either greater than 50ppb or less than 50 ppb. The Merck 'doubling method' and the AAN method incorrectly identified 4% and 10% respectively as less than 50 ppb when they should have been greater than 50 ppb. These are 'false negatives' or a 'dangerous identification'; wells which would be painted green in the field indicating they are safe to drink from when in actual fact they should be red or unsafe. This level of error is unacceptable. Furthermore, the two methods would have incorrectly identified 36% and 26% respectively as greater than 50 ppb when they should have been less than 50 ppb. These are false positives or 'wasted' wells i.e. they would have been painted red in the field when they should have been green.

To accurately and consistently determine the arsenic concentration in water concentrations of >0 ppb and < 100ppb the only method currently available is laboratory testing by Atomic Absorption Spectrometry. The 'Arsenator' currently being developed by Walter Kosmos may have potential as a field instrument in future.

1. Introduction

At the present time the arsenic field test kit manufactured by Merck of Germany is being used by BRAC under the UNICEF/DPHE/BRAC project. This is a semi-quantitative colourometric method. Addition of chemicals to the water sample reduces arsenic present to arsine gas which then reacts with a mercury bromide impregnated test paper. The colour change is used to indicate the amount of arsenic present in the water sample.

Where the test paper shows no stain the wells are being marked green, where it shows a stain equal to or greater than 100ppb they are being marked red and where they show some stain (i.e. between 0 and 100ppb) they are being marked with a cross. It is still to be decided what will be the procedure with these 'cross-marked' wells.

In August 1999 it was agreed that it was necessary to determine whether either: the Merck kit 'doubling method' (described in Sen Gupta, S.K. et al, 1993); or the field test kit made by the Asian Arsenic Network (AAN) (described in AAN, 1999), is capable of reliably measuring arsenic in the critical range of >0 ppb and <100ppb.

To achieve this goal it was agreed that around 400 samples of groundwater collected from wells with arsenic concentrations between 0 and 0.1 ppm should be tested using the two field methods and subsequently in the laboratory. These samples came from Panisara Union, Jhikorgachha Thana. In actuality 400 samples were tested in the field, but it was only possible to test 241 of these in the laboratory. This was due to problems with sample storage and transportation to Dhaka as well as wastage of some samples by an initial laboratory chosen which proved to be unreliable.

This report details the results of testing of these 'cross-marked' tubewells.

2. Description of the field methods

Both of these methods rely on the reduction of arsenic in a water sample to arsine gas and subsequent reaction with mercuric bromide impregnated test paper. The colour change is used to indicate the original concentration of arsenic in the sample.

2.1 Merck 'doubling method'

The Merck 'doubling method' involves the same procedure as the Merck normal method, now well known in Bangladesh, only with an increase in the amount of chemicals added. The result obtained with this modified procedure is then halved. If this procedure is followed it is claimed by the manufacturers that it will be possible to determine whether there is greater than or less than 50ppb of arsenic in the sample. Thus it effectively becomes a 'Yes/No' kit. Below follows a description of the 'doubling method' -

1. The 'test strip' (Mercury (II) Bromide paper) is inserted in the slot in the test tube cap.
2. 10ml of sample (two syringe volumes) is transferred to the test tube.
3. Two spoonfuls of 'Reagent 1' (Zinc powder) is added to the sample water in the test tube.
4. Fifteen drops of 'Reagent 2' (Hydrochloric acid) are added.
5. The test tube is capped and then left for 30 minutes with occasional swirling.

6. The test strip is removed, washed with sample water and then the colour change is compared with the scale given.
7. The result given on the colour scale is halved to give the true value.

2.2 Asian Arsenic Network (AAN) Method

The Asian Arsenic Network (AAN) kit claims to be more accurate than the Merck kit and a colour comparator chart is given with 10 ppb intervals. The method is described below -

1. 10ml of sample is measured into test tube.
2. 0.1g of Tin Chloride is added.
3. A further 0.1g of Potassium Iodide is added.
4. The Mercuric Bromide paper is inserted into test tube stopper.
5. 0.3g of Zinc powder is added.
6. 2ml of Hydrochloric Acid is added.
7. The test tube is capped and left for 5-10 minutes.
8. Colour development on the test paper is compared with colour chart to find a result.

3. Field experience of advantages/disadvantages of methods
3.1 Merck 'doubling method'
3.1.1 Advantages

The main advantage of the Merck 'doubling method' is:

1. The Merck kit was found to be relatively simple to use. Even with the changes made to the standard procedure in order to detect arsenic at lower levels (the 'doubling method') it is our opinion that with a small amount of training any non-specialist can use it.

3.1.2 Disadvantages

The disadvantages of the Merck 'doubling method' are:

1. The 'doubling method' involves estimation around one colour only. For samples lying between 0 and 100 ppb the doubling method correspondingly provides results of between 0 and 200 ppb which are then halved. In this range the colour comparator chart only shows colours for 0 and 100ppb (the next colour is at 500ppb). Thus the method effectively gives a Yes/No result relying on the operator to determine whether the colour development is above or below 100ppb (50ppb when halved). At this concentration of arsenic the colour development is a light yellow and this must lead to some operator bias and inaccuracies.

2. The Merck ' doubling method' is also quite expensive. As double the amount of 'Reagent 1' is required the kit will only have a lifetime of 40 tests. At 2500Tk. ($50) per kit this equates to 62.5 Tk ($1.25) per test. As the composition of the reagents is not given it is not possible to replace them. Thus the entire kit must be replaced once the reagents are finished.

3. The means by which the arsine gas contacts with the test strip is not ideal. The strip is suspended in the test tube and the gas circulates around it rather than passing directly through a porous test paper as is the case with the AAN kit.

4. The glass test tubes in the Merck kit are very fragile and easily broken.

5. The tests take a long time to complete. The total time required to complete one test is about 45 minutes.

6. The dropper in the cap of the HCl bottle (Reagent 2) does not work well and the fumes produced by the HCl can be strong.

3.2 Asian Arsenic Network (AAN) Method
3.2.1 Advantages

The advantages of the AAN kit are:

1. The AAN kit supposedly provides more accurate results than the Merck kit. The colour comparator chart is divided into gradations of 10 ppm.

2. The tests are also quicker, taking only about 10-15 minutes per test.

3. Testing with the AAN kit is slightly cheaper. The kit costs 1600 Tk ($32) and can complete 30 tests. This equates to 53 Tk ($1.06) per test. However, as the composition of the reagents is known it is possible to replace them.

3.2.2 Disadvantages

The disadvantages of the AAN kit are:

1. The procedure is fairly complicated. It has more steps than the Merck kit and the potential for error is greater.

2. The colour chart has many gradations but these are very similar and it is often hard to judge which is correct

3. The Mercury Bromide paper is fiddly and does not work if it becomes wet

4. The instructions detail the weight of reagents to be added but give no indication of the number of spoonfuls

5. Waiting '5-10 minutes for colour development' is recommended in the instructions, but gradually increasing colour development is observed between 5 and 10 minutes

6. The kit is limited to 30 tests by the amount of hydrochloric acid provided.

4. Results

On consideration of the following results it is important to remember that this study was only done on those wells which tested as between 0 and 100ppb in the field using the Merck normal method. The figures given are not for all wells tested.

4.1 Merck Doubling Method

The matrix in Table 1 shows the correct and incorrect results given by the kit compared to the laboratory results. This is ordered using the Bangladesh standard of 50ppb. Figure 1 is a scatter plot of the exact field and laboratory results.

Table 1 - Comparison of Merck doubling method results with laboratory results

		AAS Laboratory Analysis	
Merck		**< 50 ppb (green)**	**> 50 ppb (red)**
Doubling	**< 50 ppb (green)**	**95 (39%)**	**9 (4%)**
Method	**> 50 ppb (red)**	**87 (36%)**	**50 (21%)**
	Total	**182 (75%)**	**59 (25%)**

Total = 241 samples

It can be seen from Table 1 that the Merck 'doubling method' incorrectly identified 4% of the total wells tested as green when they should have been red (false negatives) - this is a 'dangerous identification' (i.e. it could lead to people drinking water from wells which are actually above the Bangladesh standard).

Milton also found that the Merck kit incorrectly identified 4% out of a total of 200 wells as false negatives (Milton, 1999).

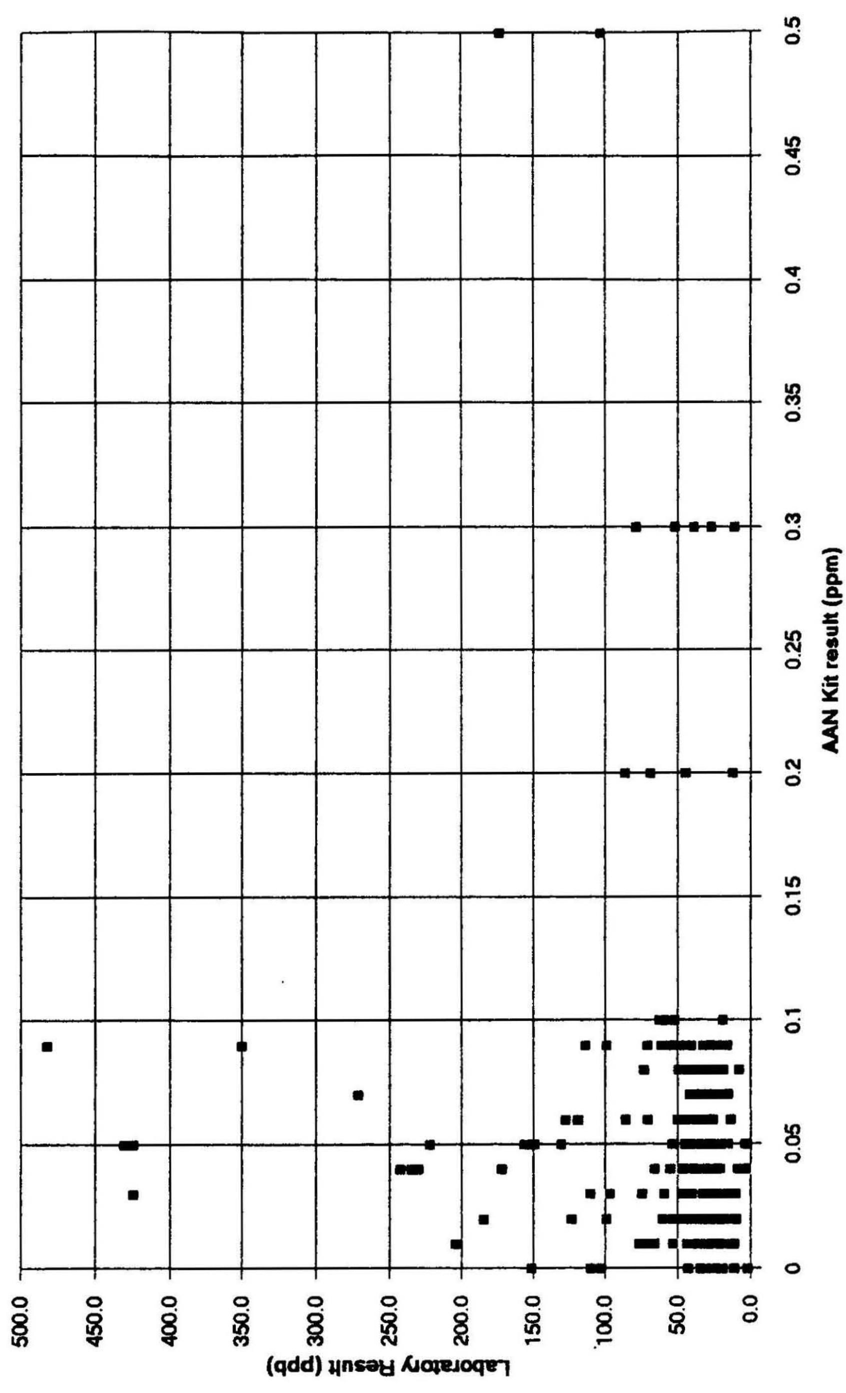
36% of the total wells tested were incorrectly identified as red when they should have been green (false positives) - these are 'wasted wells' (i.e. they would be put out of service when actually they are below the Bangladesh standard).

A total of 60% were correctly identified as green or red.

4.2 Asian Arsenic Network (AAN) Method

The matrix in Table 2 shows the correct and incorrect results given by the kit compared to the laboratory results. This is ordered using the Bangladesh standard of 50ppb. Figure 2 is a scatter plot of the exact field and laboratory results.

Figure 2 - AAN method results v AAS laboratory results



5. Discussion of Results

Firstly it is important to remember that this study was only done on those wells which tested as between 0 and 100ppb in the field using the Merck normal method. As these wells are currently being marked with a red cross they are also referred to as 'cross-marked' wells. The figures given are not for all wells tested.

Of these 'cross-marked' wells the kits correctly identified around 60% of the samples. However, the important figure to consider is the number of times the kits gave a result of less than 50ppb when the laboratory testing showed that the actual concentration was greater than 50ppb. This was 4% of the total tests with the Merck 'doubling method' and 10% of the total tests with the AAN method.

Under the current testing program in Jhikorgachha Thana and in Sonargaon Thana, the percentage of tubewells with arsenic levels of between 0 and 100ppb ('cross-marked' tubewells) is around 11% and 4% respectively. This figure is likely to vary widely across Bangladesh.

If the Merck 'doubling method' was used for testing of these wells in Jhikorgachha Thana, the results of this study suggest that 4% of that 11% may be incorrectly marked as green when they actually should be red. This is 0.5% of the total tubewells of Jhikorgachha Thana .

In actual figures the total number of tubewells is around 28 000 so this equates to about 140 tubewells being incorrectly painted. Whether this level of error is acceptable given the enormous number of wells to be tested and the emergency nature of the situation is a matter for national policy makers.

Furthermore, continuing with this example, use of the Merck 'doubling method' would lead to a large number of false positives or 'wasted' tubewells. 36% of the cross-marked tubewells would be incorrectly painted as red when they actually should be green. This is 4.3% of the total tubewells. In actual figures this equates to around 1080 tubewells.

The Merck 'doubling method' was found to be easier to use than the AAN kit, however, it is slightly more expensive. A locally made version of the AAN kit (manufactured by NIPSOM) is available for 900 Tk and can complete 100 tests. This has been used previously by BRAC (Chowdhury and Jakariya, 1999).

6. Conclusions

At present wells which are tested with the Merck normal method and show a slight stain, but not enough to be 100ppb, are marked with a cross. In the two thanas where BRAC is working, Jhikorgachha Thana and Sonargaon Thana, these wells are 11% and 3% respectively of the total number of wells.

This study was undertaken to determine whether a field method would be sufficiently accurate to definitively mark these wells either red (>50ppb) or green (<50ppb).

The results of this study are basically in agreement with other work done by organisations such as the NGO forum (Milton, 1999) and the BGS (BGS, 1999). The conclusion is that if a standard such as 50ppb (GoB, 1991) or 10ppb (WHO, 1993) is to be followed, field kits do not possess the required accuracy to consistently determine whether the arsenic concentration of a sample is above or below this level. Theses results show that the field kits will correctly identify the majority of wells with arsenic concentration of between 0 and 100ppb (around 60%), however, some 'false negatives' (wells incorrectly identified as <50ppb when they are actually >50ppb) will always occur.

In general the Merck 'doubling method' was found to be easier to use than the AAN kit, however, it is slightly more expensive. The reagents of the AAN method can be replaced but the entire Merck kit must be replaced. A locally made version of the AAN kit (manufactured by NIPSOM) is available for a much lower price.

In summary, to accurately and consistently determine the arsenic concentration in water at concentrations of >0 ppb and < 100ppb the only method currently available is laboratory testing by Atomic Absorption Spectrophotometry. The 'Arsenator' which is being developed by Walter Kosmos may have potential as a field instrument in future.

Appendix 1: Field and laboratory quality checks

All testing on wells identified as having between 0 and 0.1 ppm was undertaken by the degree-qualified BRAC supervisors, not the village health workers. Where there were unusual results or a large discrepancy between the two methods samples were re-analysed. The supervisors also re-tested 10% of the wells tested by the VHW's as a check on original accuracy for sample selection.

Samples for analysis in the laboratory were acidified on site before transportation to Dhaka.

Blank samples were sent to the laboratory for arsenic analysis. Results of this analysis is given below.

Sample No.	Composition	Expected Result	Result
1	De-ionised water	0	0
71	BRAC treated tap water	0	0
94	De-ionised water (acidified)	?	6.9
145	BRAC treated tap water	0	0.5
217	BRAC treated tap water	0	11.5
384	BRAC treated tap water	0	0
421	BRAC treated tap water	0	10.7
Average			4.2

Although these results are not ideal they show that the laboratory is operating at a reasonable standard in the context of Bangladesh.

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