



Analytical considerations of arsenic contamination in water

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THE HIGH CONCENTRATIONS of arsenic now being found in ground water in many parts of the world pose an important analytical challenge because of the large number of wells that must be tested. This is particularly true in Bangladesh and other Asian hotspots. Cheap but robust methods of analysis are needed. Training and quality control are also important particularly when the majority of wells are privately owned and testing may be carried out by the private sector. Here, using Bangladesh as an example, we review some of the methods of testing drinking water for arsenic in the field.

Methods suitable for field analysis of arsenic

Arsine gas generation.

Most of the analytical methods for arsenic, including field methods, take advantage of the formation of volatile arsene (AsH_3) gas to separate the arsenic from other possible interferences in the sample matrix. Since the determination of arsenic in drinking water involves trace analysis it is very important to use high purity chemicals. As arsenic is always associated with zinc ores, this is a particular problem. Many of the sources of zinc used for the early arsenic testing in Bangladesh and elsewhere have had relatively high degrees of arsenic contamination leading to poor results.

Most field kits rely on a pre-reduction step but this is not very rapid and increases the time required for a single determination. The approach is also weak due to the necessity to handle dangerous hazards.

The Arsenator however, utilises an efficient method of field hydride generation by using sulphamic acid.

While arsenic species can be detected using various electro chemical methods, it is unlikely that such methods could ever be made robust enough and cheap enough for incorporation into routine field test kits. Electrodes are notoriously fickle and usually expensive and difficult to replace. Other methods involving biosensors are under development but have not yet been demonstrated to be specific enough for the routine testing of arsenic in ground water.

Development and detection of the coloured stain.

Colour stain kits were initially very inaccurate due to poor reproducibility and inability to measure low levels of arsenic. More sensitive kits are now available from Hach, AAN, and Wagtech and these have brought the minimum

detectable concentration down to about 10ug L^{-1} . All of these kits include a calibrated colour scale to enable a semi quantitative estimate of arsenic concentrations, usually based on comparison with a test strip having a graduated colour scale in 6 to 7 steps. Analysis time using these kits is about 30 minutes per sample and with current costs less than US\$1 per sample.

The colour development occurs more efficiently if the gas passes through the reagent paper rather than over it and if the area of paper exposed is small so as to concentrate the available arsene on a small surface area. This approach is adopted by the Wagtech Arsenator.

Photometry

Most photometric methods can in principal be modified for use in the field. A large number of battery powered colorimeters and spectrophotometers are already available commercially. However the most important lab based methods have problems when adapted for field use. To date, the Arsenator is the only photometric instrument commercially available that can be used in the field, whilst producing laboratory accuracies.

The Gutzeit method

Most available field test kits for arsenic are presently based on the Gutzeit method. The test relies on a colour stain reaction giving a yellow colour that then becomes progressively browner as arsenic levels increase. Unfortunately, the human eye is not sensitive to the yellow stain, especially under field conditions. At the beginning of a field survey, the technicians must be tested on their ability to distinguish different intensities of this characteristic colour. Also once the reaction product is formed, the yellow colour gradually fades especially in sunlight. Therefore comparison with a colour chart must be done as rapidly as possible.

The quantification becomes more reliable when an electronic instrument replaces the colour detection. Unlike the human eye, the instrument can use a light source with a narrow range of wavelengths and can therefore be made to be especially sensitive to the yellow colour of the spot. This automation lowers both the detection limit, improves the reproducibility and enables the concentration to be determined on a continuous scale. With the Wagtech Arsenator for instance, detection limits of 0.5ug L^{-1} are possible. The original Kosmus Arsenator used a light-through approach and the Wagtech Arsenator is a miniaturised hand held version.

For most natural groundwaters the Gutzeit method is selective enough. However, there are interferences with this method as is the case with hydrogen sulphide, which can lead to a grey spot on the reagent paper. Therefore, if present, it is necessary to remove this interference. This can be done passing the gas through a piece of cotton wool or filter paper impregnated with lead acetate before the gas reaches the mercuric bromide reagent. Alternatively, the hydrogen sulphide can be oxidised to sulphate before the hydride generation has been done.

Quality assurance and management of large screening programmes.

This is an important aspect, which is necessary not just to confirm blank values but also to test the accuracy of the method periodically and to provide feedback to the survey manager and testers on the quality of the results. The easiest way to do this is to check the results of a standard solution by spiking with different concentrations of arsenic. An alternative approach is to analyse a proportion of samples in duplicate.

Since large field surveys normally involve a large number of people, it is important that there are clear lines of authority and assigned responsibilities. It is also necessary to have reliable sample tracking procedures in place. These management procedures should be documented in the sample protocols.

Sampling and analytical strategy for mass screening

Sampling

Sampling procedures are always a critical part of environmental assessment. The result of a chemical analysis is no better than the sample on which it is based.

Because the time required for the measurement of arsenic is usually less than that required for sampling, it is appropriate to establish a good working place to make the analytical measurement (ie, a temporary "field lab") and to send out samplers to collect samples. The density of tubewells in much of Bangladesh is so high that the distances involved are short and that the delay due to transport of the sample to the "field lab" should not seriously affect the arsenic analysis.

Where there is an interest in the geochemical source of the arsenic, it is also worthwhile collecting ancillary field data, eg, electrical conductivity, alkalinity, pH, dissolved oxygen as well as other chemical parameters such as phosphates etc.

Field testing versus laboratory testing

Field testing have several advantages. There is no need for transport, no storage and therefore no need for preservation. Also, with field testing, the well owner can be informed of the result relatively easily and rapidly. In Bangladesh and other hot climates, attempts to keep sam-

ples cool over a long period of transport to a laboratory can be difficult. On the other hand, laboratory testing has obvious advantages in terms of instrumentation and QA.

There has been considerable expansion in the analytical facilities for arsenic testing in Bangladesh, particularly by the private sector since 1997. While widespread lab testing is advocated by some, there are three major obstacles at present that make this difficult to achieve. Firstly, the lack of laboratories with the analytical capability for sufficient sample throughput and a track record in quality control. Secondly, the lack of management experience to organise the sampling, sample tracking and reporting of results on the scale required and thirdly, logistical problems associated with the transport of samples from the field to the laboratory. This makes field testing more attractive than laboratory testing at least in the short term.

Furthermore, the recent inter-laboratory comparison of arsenic analysis of eight synthetic standards and two groundwater samples by 17 Bangladeshi laboratories has proven disappointing. Less than one third of the participating laboratories were within 20% of the expected values. Not surprisingly, some laboratories were consistently better than others. Therefore, even laboratory testing does not guarantee reliable results. It is clear that there is a need for some kind of continuous quality control programme in Bangladesh to help the laboratories raise their standard of analysis and to give funding agencies confidence in the quality of results obtained. This exercise could be accompanied by a formal accreditation scheme, or could be undertaken more informally. They could even be run on a commercial basis.

Ideally a mass screening programme based on laboratory analysis requires automatic samplers linked to sophisticated instruments such as HG-AAS capable of carrying out several hundred analysis a day. Planning and implementing such a programme raises many new and important issues, including those of responsibility and leadership and requires that many decisions need to be made, both technical and non-technical.

Some desirable features of the analytical approaches apply to both the field and laboratory methods. The most important are reliability and robustness, accuracy including bias and precision, sensitivity and selectivity, cost effectiveness, the time needed for a single determination, personal safety and potential environmental impact. Since field kits have to be used in very large numbers there is relatively little time to train and supervise field workers. Staff turnover of testers can also be high. The hot humid climate found in tropical countries has also to be taken into account in terms of the reliability of the equipment and chemicals, ie, the equipment must be "ruggedised" and the chemicals should be available in individually - sealed and dated packets.

The usefulness of a given test kit is determined in part by the amount of information it provides. At the lowest level such kits only indicate the presence of arsenic above a

certain threshold concentration. The original Merck field test kit widely used in Bangladesh had a stated minimum detected concentration to $100\mu\text{g L}^{-1}$. This is not acceptable for compliance testing where important decisions have to be made. Fortunately the newer field test kits are more sensitive and have a greater resolution than earlier versions. Field instruments such as the Wagtech Arsenator offer a “half-way house” between field and laboratory instruments. In principal, such approaches could have the accuracy and precision generally given by sophisticated laboratory methods whilst being completely portable for field testing.

Conclusions

- The large number of tubewells that need to be tested for arsenic in Bangladesh and elsewhere means that field test kits offer the only plausible approach for mass screening.
- Most existing field test kits for arsenic are based on the classical Gutzeit method. The chance of misclassification is considerably greater with these field kits. There has been a considerable improvement in the field test kits since 1997.
- Other recent improvements include the replacement of liquid acid with sulfamic acid, replacement of zinc by sodium borohydride and the development of a field portable electronic device to measure the yellow brown colour of the stain in a quantitative manner (Wagtech Arsenator).
- The challenge is to produce field test kits that are robust, reliable, cheap and simple enough to be used by relatively unskilled technicians in Bangladesh and elsewhere. These and their supplies should be readily available in the local markets. Wagtech presently has and intends to hold stock within India, Bangladesh, Nepal, Myanmar, Pakistan and further beyond into Indo-china and other areas of concern on a global basis.
- The precision of field or laboratory testing should be established over a range of As concentrations by measuring the precision of a range of standards and by duplicate analysis during screening.
- By establishing a realistic “error” model for the analytical method to be used in a screening survey (field or laboratory based) and having some prior information about the likely distribution of arsenic concentrations expected, it is possible for planners to estimate the likely extent of misclassifications during the screening survey.
- Misclassifications in Bangladesh and other areas are inevitable due to the large number of wells having

arsenic concentrations close to the existing national drinking water standard. However, even with the field test kits now available, these errors could be brought down to no more than 50% of the wells tested on a national scale.

- Giving private well owners as much possible information about the test result will alert them to the likely degree of contamination of their water supply and enable them to make their own decisions accordingly.

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Notes

- ¹ The Wagtech Arsenator is a new electronic instrument developed by Wagtech International and Professor Kosmus for measuring arsenic based on the Gutzeit method.

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