

Design and Development of Low Cost, Simple, Rapid and Safe, Modified Field Kits for the Visual Detection and Determination of Arsenic in Drinking Water Samples

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Abstract: Arsenic is naturally found in surface and ground waters and the inorganic forms of arsenic are the most toxic forms. The adverse health effects of arsenic may involve the respiratory, gastrointestinal, cardiovascular, nervous, and haematopoietic systems. Arsenic contamination in drinking water is a global problem widely seen in Bangladesh and West Bengal of the Indian sub continent. As there is a great demand for field test kits due to the anticipated reduction of the US EPA arsenic standard from 50ppb to 10ppb a field kit which offers rapid, simple and safe method for precise estimation of arsenic at 10ppb in drinking water samples is developed. Field methods, based on the mercuric-bromide-stain, consist of three different major parts, which are carried out stepwise. The first part of the procedure is to remove serious interference caused by hydrogen sulphide. In commercially available kits either the sulphide is oxidized to sulphate and the excess oxidizing reagent removed prior to the hydride generation step or, the hydrogen sulphide is filtered out by passing the gas stream through a filter impregnated with lead acetate during the hydride generation step. The present method employs cupric chloride in combination with ferric chloride or Fenton's reagent for the removal of hydrogen sulphide, which is rapid, simple and more efficient. Other interferences at this step of the analyses are normally not expected for drinking water analysis. In the second step, the generation of the arsine gas involves the classical way of using zinc metal and hydrochloric acid, which produce the 'nascent' hydrogen, which is the actual reducing agent. Hydrochloric acid can be replaced by sulfamic acid, which is solid and avoids a major disadvantage of having to handle a corrosive liquid in the field. The arsine gas produces a yellowish spot on the reagent paper. Depending on the arsenic content, either, Yellow – H (HgBr)₂ As (10-50ppb), Brown – (HgBr)₃ As (50-100ppb) or Black – Hg₃ As₂ (>100ppb) are formed which can be precisely estimated by visual comparison with standard color chart. The results obtained by field kits agree well with the data obtained through I.C.P.AES methods. The most important characteristic for field measurement is that analytical results can be obtained on the site where the sample is taken with high precision and can be conveniently utilized for monitoring arsenic rapidly in a highly contaminated large geographical area.

Keywords: arsenic, field kit, and drinking water.

Introduction

Arsenic, a common contaminant of ground water, has been found to adversely affect human health at levels as low as 10 micro grams per liter. The quantification of trace amounts of arsenic in water samples has always been a problem. The current methods rely on expensive apparatus, complicated procedures, and dangerous chemicals reagents [1] Low cost test kits, available in the past had a working range of 100 to 3000µg/L, which is not sensitive enough to monitor drinking water supplies.

The method employed here addresses many of these problems.

Field Measurement of Arsenic in Water

Field methods play an important role in environmental analytical chemistry. The most important characteristic for field measurement is that analytical results can be obtained on the site where the sample is

taken [2]. This can be done using relatively simple field-testing kits or very sophisticated instrumental methods.

Field-testing methods are normally the method of choice in a number of cases such as:

- Emergencies, when analytical results are required in a hurry. Inadequately developed country infrastructure; where the number of laboratories with competent personnel and equipment is small; where the sampling sites are too far away and where poor logistics do not guarantee that the sample results can be made available in a timely fashion to responsible persons who have to take or recommend a course of action.

A further reason to choose a field method could be the extent of the monitoring programme in a highly contaminated geographical area, where the lower quantification limit specifications of field equipment would be sufficient for a major part of the samples. For example, the present demand to monitor a huge number of possibly contaminated tube wells in areas like Bangladesh, and in India, West Bengal, Bihar States etc is a strong argument for the development of reliable field methods.

In the present paper we are reporting a rapid, simple, safe and precise modified field kit method for the estimation of arsenic in drinking water samples by visual colorimetric method.

Materials and Materials

Reagents

- 1) **Stock Arsenic Solution:** The Stock solution was prepared by dissolving 1.320 gm of Arsenic Trioxide in 10 ml double distilled Water containing 4 gm NaOH and diluted to 1000 ml with Distilled water. (1ml = 1mg As)
- 2) **Arsenic Standard Solution:** An intermediate standard solution was prepared by 100-fold dilution of stock solution with distilled water. Working standard solution was prepared by diluting the intermediate solution.
- 3) **Sulfamic Acid:** 2gm of sulfamic acid is weighed and added for reaction.
- 4) **Zinc Powder:** 1 gm of zinc powder is to be added for each reaction.
- 5) **Mercuric Bromide strips:** Cold-pressed what man drawing-paper gives better results than filter paper. It should be cut into strips of 4mm. in width, which are sensitized by being drawn repeatedly through a 5 per cent solution of recrystallised mercuric bromide, then dried on a horizontal rack of glass rods, cut into lengths of 7 cm., and kept in the dark in a bottle containing anhydrous calcium chloride, covered with a layer of cotton-wool until required for use.
- 6) **Cupric Chloride:** 0.2682gm of cupric chloride was dissolved in 100 ml of de-ionized water to get 1000ppm of cupric solution.
- 7) **Ferric Chloride:** 0.2904gm of ferric chloride was dissolved in 100ml of de-ionized water to get 1000ppm of ferric solution.
- 8) **Sulphide Standards:** Standards are prepared by dissolving 0.2433gm of sodium sulphide in 100ml

of de-ionized water to get 1000ppm of sulphide solution. The solutions containing 1000ppm are further diluted as per requirement. Tests were carried out to determine the levels at which sulphide interfered. Sodium sulphide standards were prepared and the concentrations were verified using methylene blue method. To 0.3ml of 1000ppm sodium sulphide, 5ml of 0.05ppm arsenic solution, 5ml of cupric chloride, 10ml of ferric chloride were added and the total volume was made up to 100ml with de-ionized water. (Color of the solution was light brown).

Procedure

Fill the reaction vessel with sample water (35 to 50 ml). Add 5 to 10mg of cupric chloride to mask the interference of sulphide, and then ferric chloride solution. After the addition of cupric chloride a light blue precipitate will be formed, this will turn to brown after the addition of ferric chloride, which dissolves after the addition of sulfamic acid and zinc powder (1 gm). Seal the reaction vessel immediately and swirl to mix. The seal of the reaction vessel contains a flap, which can be removed for the test strip to slide into the groove so that the reactible pad faces the small opening and completely covers it (Fig 1). Replace the flap securely back. Expose 0.5x0.5 inch mercuric-bromide-coated reaction pad to the gas through a hole only 3/16 inches in diameter. This arrangement allows all of the generated gas to come into contact with the mercuric bromide and be reacted. The excess paper around the hole provides sufficient reactant to absorb the excess generated arsine. Keep the duration of the reaction for 30 minutes, swirling twice during the reaction period. Addition of KI and SnCl₂ is necessary as a preliminary step if arsenic is present in arsenate instead of arsenite.

In just 30 minutes, a color develops on the Arsenic Test Strip based on how much arsine gas was generated in the reaction. Remove the test strip and compare the developed color immediately to that of the standard chart. Compute concentration of arsenic in water by comparing the test strip to the color chart. The semi-quantitative "steps" of this test are 0, 10, 30, 50, 70, 300 and 500 ppb, providing an overall range of 0-500 ppb. This kit being developed under Department of Atomic Energy sponsored project with Electronic Corporation of India, Hyderabad, as collaborating institute, it is named as JNTU-ECIL Arsenic kit.



Figure 1: Experimental set up for strip test method used for detection of arsenic.

Results and discussions

Methods Based on the Mercuric-Bromide Stain

Field methods, based on the mercuric-bromide-stain [3], consist of three different major parts, which are carried out stepwise.

The first part of the procedure is to remove serious interference caused by hydrogen sulphide. As most of the water samples from arsenic rich areas originate from reducing environments they are likely to contain various amounts of sulphur in its lowest oxidation state (hydrogen sulphide). This odoriferous compound reacts with mercuric-bromide to form a greyish-black precipitate, which makes the determination of arsenic ambiguous. Field kits that do not have a way to negate this interference are useless.

Two methods to remove hydrogen sulphide are currently in use; either the sulphide is oxidized to sulphate and the excess oxidizing reagent removed prior to the hydride generation step or, as is done in the larger number of available kits, the hydrogen sulphide is filtered out by passing the gas stream through a filter impregnated with lead acetate during the hydride generation step. The lead salts, which react with hydrogen sulphide, form insoluble lead sulphide, while the arsine gas passes the filter unchanged. Other interferences at this step of the analyses are normally not expected for drinking water analysis. When the kit is used for wastewater analysis then the larger concentrations of heavy metals (such as copper and nickel) may interfere with the hydride generating process and/or other hydride generating elements, e.g. antimony and selenium.

The second step, the generation of the arsine gas, is the most important one. The classical way is the use of zinc metal and hydrochloric acid, which produce the 'nascent' hydrogen, which is the actual reducing agent. The zinc metal has to be of a definite grain size (20-60 mesh) to ensure that the reaction progresses at a certain rate: not too fast – in order to ensure the maximum yield at the reagent paper, and not too slow – in order to allow the determination to be completed in a practicable time. At room temperature arsenate is reduced to arsenite, which is then reduced to arsine gas. The reduction of arsenate to arsenite is accomplished by adding a small amount of potassium iodide and stannous chloride and, depending on temperature, needs at least 15 minutes to be completed. Hydrochloric acid could be replaced by sulfamic acid, which is solid and avoids a major disadvantage of having to handle a corrosive liquid in the field. Sulfamic acid is a dry, non-volatile, non-hygroscopic, odorless, white crystalline, stable solid acid. It is moderately soluble in water by forming strongly acidic aqueous solution that is comparable in acidity to the common strong mineral acids but may be easily handled and stored in the dry form. Its solution is less corrosive towards metals than other mineral acids. It also removes any interference [4] due to NO_2^- as represented by the following equation:

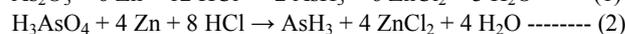


Further sulfamic acid is non-flammable and non-explosive and requires no special safety measures during

storage. To prevent from absorption of moisture and possible caking, it should be stored in a cool, dry place.

Evolution of Arsine

The following reactions will take place in the evolution of arsine:



Generally, two systems are in common use for the reaction of the arsine gas with the reagent paper impregnated with mercuric-bromide. The original version from 1907, still being sold, inserts a small reagent strip into a tube and the arsine gas passes over the surface of this paper. As the contact between the two reactants is not very intense, this method lacks sensitivity and has low reproducibility. Many tests, both in laboratories [5] and in the field [6], have shown that this method is not sufficiently reliable to test for low arsenic concentrations. If the flow of the arsine gas passes through, rather than over, the reagent paper then lower detection limits can be reached.

The third methodological step is the quantification of the arsenic concentration. The arsine gas produces a white to yellow to tan to brown spot on the reagent paper, which can be used for the quantification of the arsenic concentration, by visual comparison with a standard color chart (Fig 2).

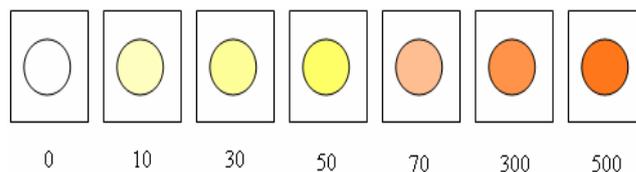
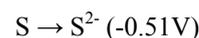


Figure 2: Standard Color Chart of Arsenic in ppb by Strip method.

Sulphide Interference

The main interference caused in the estimation of arsenic by hydride technique is sulfur, which gets reduced under the potential where arsenic gets reduced to arsine.



During the reduction of arsenic to arsine gas, sulphides are also reduced to form hydrogen sulphide (H_2S). Hydrogen sulphide reacts with the mercuric bromide test strip in the same way as the arsine gas, leading to erroneous results. Current methods for removing sulphide interference entail passing the arsine gas stream through a scrubber containing lead acetate to remove the hydrogen sulphide as lead sulphide. Even zinc and copper scrubbers are also used but they have been found to be less efficient. There are many drawbacks to these methods. Handling and disposal of

hazardous lead acetate and lead sulphide is harmful, apart from this the rate of gas evolution has to be controlled to allow adequate contact time for the entire sulphide to react with the scrubber.

The new method eliminates the need to rely on these harmful chemicals to remove sulphide interference. Use of a desulphurizing agent for removal of sulphide interference and the desensitizing effect of the reagent is counter balanced [7] by the use of ferric chloride [8,9] which increases the rate of evolution of arsine, so complete evolution of arsine takes place with in the reaction period and giving precise results.

Assessment of Optimum levels of cupric chloride and ferric chloride for removal of sulphide interference

In all these field kits hydrogen sulphide is usually the most serious interferent. This can occur as a dissolved gas in ground waters that are strongly reducing. A second source of hydrogen sulphide is the dissolved organic matter in the water, containing sulphur compounds, which may reduce to hydrogen sulphide during hydride generation step. So the amount of CuCl₂ required to remove the interference of sulphide in the range 3-5ppm is systematically studied. The appearance of white color in the lead acetate strip indicates the removal of sulphide interferences, which indicates nearly

50ppm of CuCl₂, is sufficient for removing sulphide interference. So in all the tests 50ppm of CuCl₂ is recommended. Water samples containing different ppms of arsenic were analyzed by adding 50ppm of CuCl₂ and this was found to be sufficient for arsenic concentrations in the range of 0.01ppm-1.0ppm. Further when CuCl₂ is used to suppress the sulphide interference, it is observed that it also suppresses the release of AsH₃ to certain extent. However it is observed that ferric salts (FeCl₃) enhance the arsenic evolution and compensates the suppression effect of CuCl₂ in arsine evolution. The amount of FeCl₃ required to be added along with CuCl₂ to attain maximum sensitivity for the detection of arsenic is systematically examined.

From all the tests run 50ppm of CuCl₂ and 100ppm of FeCl₃ are found to be effective in removing the sulphide interference and also in development of spots (Fig.3) in the estimation of arsenic in ground water. With this method, it was found that as much as 3ppm of S²⁻ could be tolerated before the acceptance criteria of 10ppb arsenic level. Clearly the presence of Copper (II) at normal levels cannot be tolerated in the determination of bismuth, selenium and tellurium as their hydrides, although the interference effect has been reported to diminish in the presence of iron.



Figure 3: Mercuric bromide strips exposed to arsine in the presence of cupric chloride and ferric chloride

For evaluating the merits and demerits of determination of arsenic by this method, tests were carried out and compared with other methods for the estimation of arsenic in drinking water samples, and the corresponding data are presented in the Table 1. Here the concentration

of the arsenic is taken in the range of 0.05-1.0ppm for reference only because the data related to other kits cited in the literature falls in this range. The results obtained by field kits were found to agree well with the data obtained through ICPAES method also (Table 1B).

Table 1: Comparison of arsenic determination by JNTU-ECIL Kits and other methods

Concentration of Arsenic	JNTU-ECIL Method	HACH Method
0.05ppm	Yellow	Yellow
0.1ppm	Dark yellow	Dark yellow
0.3ppm	Light orangish yellow	Light orangish yellow
0.5ppm	Orange yellow	Orange yellow
1.0ppm	Brown	Brown

A

Sample	JNTU-ECIL Strip test method	ICPAES Method
Sample 1	0.05ppm	0.045ppm
Sample 2	0.1ppm	0.1ppm
Sample 3	0.5ppm	0.51ppm
Sample 4	0.7ppm	0.68ppm

B

Ion or Substance	Concentration
Sulphide (S ²⁻)	5 mg/L
Selenium (Se)	1 mg/L
Antimony (Sb)	0.25 mg/L
Tellurium (Te)	0.25 mg/L

The following were found to interfere at concentration greater than those listed.

C

Ion or Substance	Level Tested
Hardness	1000 mg/L CaCO ₃
Alkalinity	1000 mg/L CaCO ₃
Iron (Fe)	50 mg/L
Temperature	10 to 40 degrees C
Copper	100ppm

The following did not interfere at the levels tested.

D

Table 2: Effect of various metal salts in determination of arsenic by strip test

Metals 10 ppm	(CH ₃ COO) ₂ Pb Strip (lead acetate strip)	HgBr ₂ Strip (Distilled Water) JNTU-ECIL Method	HgBr ₂ Strip (Arsenic 0.05 ppm) JNTU-ECIL Method	Matching with the standard arsenic solution- HgBr ₂
Co(NO ₃) ₂	Black	Light Yellow	Orange	Increase
CoCl ₂	No Change	No change	Orange	Increase
(NH ₄) ₆ Mo ₇ O ₂₄	Black	Light Yellow	Orange	Increase
(NH ₄) ₂ SO ₄ NiSO ₄	No Change	No Change	Orange	Increase
CdSO ₄	No Change	No Change	Yellow	Matched
Ce(SO ₄) ₂	No Change	No Change	Dark Yellow	Slight Increase
Pb(NO ₃) ₂	No Change	No Change	Light Yellow	Slight Decrease
(CH ₃ COO) ₂ Pb	No Change	No Change	Light Yellow	Slight Decrease
Cu(NO ₃) ₂	No Change	No Change	Yellow	Matched
NiSO ₄	No Change	No Change	Orange	Increased
MnCl ₂	No Change	No Change	Dark Yellow	Slight Increase
FeCl ₃	No Change	No Change	Orange	Increased
CuCl ₂	No Change	No Change	Yellow	Matched

Other Interferences

Various substances likely to interfere with the method were evaluated using the same acceptance criterion (5µg/L As). The interferences due to various metal salts in the determination of arsenic were studied by taking distilled water and arsenic solution and the corresponding results are presented in the Table 2. The concentrations of the metal salts were fixed to 10ppm and were individually added to the arsenic solution to check their interference.

Based on the above table, the increase in color development of the mercuric bromide strip is attributed to the catalytic properties of the metals under consideration and further does not result in any interference due to their presence.

Cost Evaluation for the Strip Test

The cost of the chemicals required for analysis of arsenic in 100 water samples comes to about Rs.500 (approximately US\$10), the details of which are presented in the Table 3. The cost of labor for each test comes to about to \$5.

Table 3: Cost estimation for analysis of arsenic in water samples

S.No	Item	Quantity	Indian Rupees
1	Rubber caps	2 pieces	60
2	Plastic bottles	2 pieces	60
3	Arsenic Test papers (HgBr ₂ paper)	100 pieces	220
4	Sulfamic acid	250G	38
5	Zinc powder	100G	46
6	Copper chloride	100G	54
7	Ferric chloride (anhydrous)	100G	22
Cost of 100 tests			500(US\$10)

Conclusions

- 1) JNTU-ECIL Arsenic field kits will be useful for investigating large number of samples as they are simple, reliable and cost effective and are suitable for mass screening.
- 2) These field-test kits can also in principle be used to determine the arsenic speciation, specifically the concentration of As (III) and As (V) species, albeit only at a semi-quantitative level. This depends on different kinetics of hydride formation between As (III) and As (V) species. As (III) forms the hydride

more rapidly than As (V). Therefore, the As (V) species are often reduced to As (III) species in a separate pre-reduction step. This is usually carried out by adding a few drops of concentrated potassium iodide and stannous chloride solution.

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