

## Field kits for water quality monitoring–A novel approach



### Engineering

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### ABSTRACT

Monitoring toxic or harmful elements in drinking water is essential for the health and hygiene of population. The levels of elements such as As and F in drinking water are constantly being revised in view of the harmful effects. At present As more than 10 ppb renders the water unsafe. Expensive and sophisticated equipment are required to monitor these elements at the prescribed levels. The instrument requirement is stripped down to basic light source and detector under a micro controller. The chemistry is rewritten so that a field assistant having no background can also produce reliable analytical data. The systems are field tested during the past 18 months and are perfected. As an example the arsenic kit is discussed in detail in this paper.

### INTRODUCTION

Ensuring the quality of drinking water is a major task for the governmental agencies at various levels. Contamination by pollutants from various sources is to be identified, isolated and removed effectively, so that the quality norms prescribed by the authorized agencies is always ensured. In this process elaborate testing procedures are evolved and laboratory and test facilities are created at various levels. To run and maintain such facilities require highly skilled manpower and proper financial outlays. So far in India such facilities are created only at district level. The number of samples to be analyzed in case of a whole district becomes so vast that the labs cannot cope up. As a result, the database is not adequate and accurate. If the methodology is simplified and low cost field operational devices/kits are made available better results are obtained and likely goals are achieved. In fact these facts were realized and in advanced countries also kits are employed for reliability of the data, control and logistics of the operation. However, the scenario in India and third world countries is much different due to financial constraints. The so-called field kits and the equipment available from multinational companies works out to be 2,000 to 3,000 US \$ per unit (i.e) Rs. 1.0 to 1.5 lakhs. A minimum of 20,000 to 30,000 kits is to be developed for the collection of the database, in a state like Andhra Pradesh. This involves heavy financial outlay and hence do not get the required priority. It is appropriate to develop low cost instrumentation, fall safe and foolproof chemistry kits to facilitate government to undertake this work. The developments in electronics (i.e.) micro controllers, high power light sources and integrated light to voltage converter chips made us realize that low cost/disposable instrumentation can be attempted to solve the problem. Spectrochem Instruments Pvt. Ltd in collaboration with JNTU has developed and perfected analytical methods for the characterization of water and wastewater samples down to ppb levels. During the past 2 years work on the analysis of As and F- in a large number of varied samples has resulted in our effort to develop low cost systems. The authors attempted and succeeded in developing such units that are being field tested for the past 18 months. To reduce the cost of instrumentation low cost portable single wavelength spectrophotometer has been developed. The spectrophotometer can be field set for a particular elemental analysis by user. The instrument uses a single wavelength source, microcontroller based electronic and silicon photodetector, powered by four D type torch cells and the total weight of the system is typically less than 500 g. Extensive experimental studies with various reagents and chemicals resulted in a highly sensitive color reaction for the determination of arsenic. The Ag-diethyldithiocarbamate method is found to be satisfactory for the

determination of As down to 5 ppb level. However, to have sufficient sensitivity control of the blank is found to be of utmost importance. To achieve the low and acceptable blank levels highest purity acids and reagents are employed. E-Merck 'suprapure' grade chemicals and sodium borohydride of 98% purity from Aldrich are found to be suitable for determination down to 5ppb levels. In fact these reagents are employed to determine As using vapour generation atomic absorption Spectrophotometric method. Similarly F- free reagents and chemicals are employed in case of field kits for fluoride analysis. Review of the existing methods based on spectrochemical method for the determination of arsenic in aquatic environments arsenic can exist in several oxidation states like -III, 0,III, V as both inorganic and organometallic [2] compounds. Methods are available to identify and determine arsenic, arsenate, methyl arsonic acid, dimethyl arsonic acid, arsine acid, arsenocholine, arsenobetaine and other organic arsenic compounds [3]. Present USEPA approved methods for the determination of arsenic in water are all atomic spectrophotometric method, ICP- AES, Platinum Graphite furnace - Atomic Absorption, Graphite furnace-Atomic Absorption and Hydride generation – Flame Atomic Absorption. The most widely used method is based on hydride generation technique. The economic outlay in capital cost is such that the techniques deter wide spread application in developing countries. The generation of arsine became a standard sample preparation procedure for the arsenic determination. Spectrophotometric determination of arsenic by arsine-Silver diethyldithiocarbamate complex is the classical method for determining traces of arsenic. Holak [4] reported the generation of arsine from zinc – HCl and subsequent use of a liquid nitrogen trap before being passed into an air-acetylene flame for detection by AAS. The method was improved by Yamamoto et al. [5] who used zinc tablets together with stannous chloride and potassium iodide as reductant. Braman et al. [6] used Sodium borohydride in acidic solution to produce nascent hydrogen and this was reported as an efficient method for producing arsines for use in spectrophotometric analysis. A modified sodium borohydride method was reported by Belcher et al. [7] in which the acidified sample was added to pellet of the reductant. M.C Daniel et al. [8] reported the advantage of using a solution rather than pellets. Arsine reacts with a solution of SDDC in pyridine to form a soluble red complex that is the basis for spectrophotometric method for analyzing arsenic. [9] Chatterjee et al. [10] analyzed Arsenic species spectrophotometrically using SDDC/CHCl<sub>3</sub>/Hexamethylenetetramine as absorbing solution. Inorganic materials may interfere with the generation of arsines by sodium borohydride [11]. Potassium iodide - Ascorbic acid is an Efficient prereductant in the hydride generation of arsines by

sodiumborohydride. Tomary et al. [12] presented a new coprecipitation method for the spectrophotometric determination of arsenite and arsenate in ground water. Both studies coprecipitated with thorium (V) hydroxide at pH 9 after centrifugation and dilution with HCl and the absorbance is measured on a spectrophotometer by the usual SDDC method. Fortmann and Riley measured the arsenic by using Arsenomolybdenum - blue complex spectrophotometrically at 866 nm to determine arsenic in seawater. The molybdenum blue spectrophotometric method was used in conjunction with selective reduction and oxidation to determine As (III). Johnson and Pilsen [13] used the same procedure to determine arsenic in seawater following generation of arsine and its oxidation to As (v). Wu and Liu [14] reported As(v) as the arsenoantimonomolybdenum blue - malachite green complex in the presence of Trito X 350 as a solubilizing agent. Arsenite forms a yellow complex with Nphenylbenzohydroxamic acid at pH 4.5 that can be extracted into chloroform and measured spectrophotometrically.[15]. Other spectrophotometric methods for the determination of arsenic have been reported by Stara and Stary [16]. Palnivellu et al. [17] described a highly sensitive determination of arsenite. Absorbance is measured with Carl Zeiss PMQII spectrophotometer with 10mm quartz cell. The determination is made as arsenic tri iodide after an extractive separation into benzene. The results are reported to be more sensitive than those based SDDC and superior to the fluorescence method based on the use of rhodamine B. Arsenic has been determined by several electrochemical techniques. Techniques commonly used include differential pulse polarography [18], Anionic stripping voltameter [19] and cathode stripping voltametry [20]. The differential pulse polarographic technique (DPP) had been used extensively. The polarographic methods are not sensitive for the determination of arsenic at ultratrace concentrations. The anodic stripping methods using platinum and gold electrodes and cathodic stripping voltametry methods are better suited because of their insitu preconcentration capability. Sadana [21] determined arsenic by differential pulse CSV by reducing arsenic (V) to arsenic (III) by heating the sample with conc. HCl and 48% hydrobromic acid in a steam bath at 95–100 c for 45 min. In the determination of arsenic Forsberg et al. [22] reduced As(v) to As(III) by heating with sodium sulfite in conc. acid solutions. Henze et al. [23] studied the As (V) and As (III) by CSV. Arsenic determination by electrochemical techniques is prone to interference. Copper poses serious problem interference from organic matter is also reported. Electrochemistry can be applied to the analysis of arsenic in some marine samples, the techniques are not very sensitive or robust and are not commonly used. Inductively coupled plasma mass spectrophotometry utilizing high temperature plasma, as an ionization source is a very sensitive method for elemental analysis. The arsenic may be atomized by flame [24], in a graphite furnace [25], or in a quartz furnace that may be flame heat [26] or by heating electrically.

## EXPERIMENTAL

### Materials and method

Arsenite containing trivalent arsenic, is reduced selectively by aqueous sodium borohydride solution to arsine in an aqueous medium of pH6. The generated arsine is swept into an absorber tube containing silver diethyldithiocarbamate and morpholine dissolved in chloroform. A red color developed is read at 520 nm. At expected concentration from zero to 50 ppb a sample volume of 50 ml is transferred into the Erlenmeyer flask. To have sufficient sensitivity and to achieve lowest blank levels highest purity grade reagents having arsenic content less than 5ppb (E-MERCK supra pure grade Hydrochloric acid and minimum 98% pure sodium boro hydride pellets) were employed for the generation of arsine.

### Reagents

Arsenic standard solution was prepared using milli Q distilled water. A stock solution containing 1000mg/l (As) was made using AS2O3. 7H2O. the required low concentration standards were prepared daily by dilution of the stock solution. All reagents employed in the experiment, Hydrochloric acid, Silver diethyl dithiocarbamate, were of pure grade.

## Method

To 20 ml of the water sample containing arsenic 2ml of 15% potassium iodide solution is added along with 2 ml 1:3 supra pure Hydro chloric acid (diluted with milli- Q reagent grade water) the sample thus prepared kept aside for 15 min. so that arsenic present in the sample is in the form of trivalent arsenic. The sample is transferred into the reaction vessel and cap is replaced. The boro hydride is dropped into the reaction vessel and cap is replaced. The borohydride decomposition reaction is visible and the nascent hydrogen produced along with the arsine generated bubbles through the reagent vial through the capillary. and arsenic concentration is read by comparing the sample color intensity against the blank. A calibration curve is established by employing As standards between 10 and 100ppb and exactly following the method as cited above.

## INSTRUMENTATION

A single wavelength photometer that works on 6V battery supply is designed and employed in the field kits. The system is based on microcontroller electronics having all the required functional electronic components in a single chip. This approach is specifically developed so that the equipment density, hence the power requirements are met from a battery source. A specific light emitting diode and silicon photo detector are employed in the design of the spectrometer.

## FIELD KITS

The chemistry and the reagents required to carryout the color reaction are designed so that very little knowledge base is required for the operator. Infact, the operator is as followed. A measured sample of 20ml is taken and added to the reaction vessel, 5 drops of reagent (A) (i.e.) HCl is added and then a tablet called reagent (B) is dropped into the vessel. The cap is quickly replaced. The outlet tube is kept in vial containing reagent (C) till the bubbling is stopped. Then the vial is pushed into the sample compartment and the reading is noted. The system is factory calibrated to read the ppb As. The disposal as well as storage instructions of the system and the reagents are also given in the illustrated manual of the kit.

## CONCLUSION

The kits that are designed for the analysis of various polluting elements such as As, Hg, F etc based on the instruments designed and the chemistry/ reagents developed are safe, rugged and reliable. They provide cost effective analytical facilities and the field analysis makes the analysis foolproof and accurate.

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