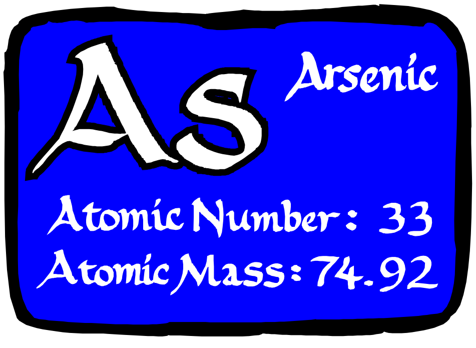
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

# Monitoring Arsenic in the Environment:
## A Review of Science and Technologies for Field Measurements and Sensors



EPA 542/R-04/002
April 2004
http://www.epa.gov/tio
http://cluin.org

# Monitoring Arsenic in the Environment: A Review of Science and Technologies for Field Measurements and Sensors

Dan Melamed
Office of Superfund Remediation and Technology Innovation
Now with the U.S. Department of Energy

Office of Solid Waste and Emergency Response
U.S. Environmental Protection Agency
Washington, DC 20460

# Notice

Preparation of this report has been funded in part by the U.S. Environmental Protection Agency (EPA) under contract number 68-W-03-038. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. A limited number of printed copies of *Monitoring Arsenic in the Environment: A Review of Science and Technologies for Field Measurements and Sensors* is available free of charge by mail or by facsimile from:

U.S. EPA/National Service Center for
Environmental Publications (NSCEP)
P.O. Box 42419
Cincinnati, OH 45242-2419
Telephone: (513) 489-8190 or (800) 490-9198
Fax: (513) 489-8695

A portable document format (PDF) version of the report is available for viewing or downloading from the Hazardous Waste Cleanup Information (CLUIN) web site at http://clu-in.org/. Printed copies can also be ordered through that web
address, subject to availability.

# Monitoring Arsenic in the Environment: A Review of Science and Technologies for Field Measurements and Sensors

## Abstract

This report reviews field assays and other technologies with the potential to measure and monitor arsenic in the environment. The strengths and weaknesses of the various assays are discussed with respect to their sensitivity, ability to detect the chemical states of arsenic, performance in various media, potential interferences, and ease of operation. The report, which relies mainly on government documents and the published literature, examines the state of the science and development efforts of selected technologies.

## Table of Contents

## TABLES

## Introduction

Arsenic is a well-known toxic chemical that the Environmental Protection Agency (EPA) and the World Health Organization (WHO)[1] list as a known carcinogen. Arsenic is found in a wide variety of chemical forms throughout the environment and can be readily transformed by microbes, changes in geochemical conditions, and other environmental processes.[2] While arsenic occurs naturally, it also may be found as a result of a variety of industrial applications,[3] including leather and wood treatments,[4] and pesticides.[5] Man-made arsenic contamination results mainly from manufacturing metals and alloys, refining petroleum, and burning fossil fuels and wastes. These industrial activities have created a strong legacy of arsenic pollution throughout the United States.

The combination of high toxicity and widespread occurrence has created a pressing need for effective monitoring and measurement of arsenic in soil and groundwater. Toxic levels of arsenic have been detected in water supply wells in the United States[6] and abroad,[7] creating a health risk for a large fraction of the world's population and a direct, Superfund-driven need to monitor and measure arsenic for the effective remediation of waste sites. Arsenic is second only to lead as the main inorganic contaminant in the original National Priority List (NPL) of Superfund sites.[8] It also is one of the toxic materials regulated under the Resource Conservation and Recovery Act (RCRA). Therefore, the need exists for arsenic monitoring at Superfund sites, RCRA landfills, facilities handling arsenic-containing wastes, and sites where arsenic is found at toxic levels in groundwater.

Unlike organic pollutants, arsenic cannot be transformed into a non-toxic material; it can only be transformed into a form that is less toxic when exposed to living organisms in the environment. Because arsenic is a permanent part of the environment, there is a long-term need for regular monitoring at sites where arsenic-containing waste has been disposed of and at sites where it occurs naturally at elevated levels. A range of analytical field assay methods for pollutants, such as arsenic, provide valuable tools to support improved site characterization initiatives, such as the Triad method from EPA,[9] and the Adaptive Sampling and Analysis Programs (ASAP) from the Department of Energy (DOE).[10]

This paper presents a brief overview of the scientific literature on existing technologies that are available for detecting arsenic in soil, waste, and groundwater and includes research developments that may affect those technologies. The focus is on fieldable technologies, including those that could be used as long-term remote sensors and in hand-held or readily portable devices for detecting arsenic in the field. This review intends to provide a critical overview of existing methods and technologies under development and offers insights into the most plausible future developments for detecting arsenic in the field.

One of the main sources of information on current analytical technologies is EPA's publication SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,"[11] which is a compendium of analytical and sampling methods that have been evaluated and approved for use in complying with RCRA regulations. EPA's Environmental Technology Verification (ETV) Program is another source of information on current analytical technologies. The ETV program verifies the performance of innovative, commercially available environmental technologies. Lastly, the Department of Defense (DOD) through the Environmental Security Technology Certification Program (ESTCP) demonstrates and validates promising innovative technologies for the military's environmental needs. Although the scope of this paper emphasizes the relevant technologies for arsenic detection and measurement listed in SW-846 or evaluated by the ETV and ESTCP programs, non-government research is also included.

This review also draws on publicly available information from two major government programs that fund research on technologies, including those dedicated to arsenic detection and related applications. DOD has developed a wide variety of technologies to address environmental problems, such as arsenic, at military sites through its Strategic Environmental Research and Development Program (SERDP). The Small Business Innovation Research (SBIR) Program, which is associated with every federal agency, fosters a science and technology research effort for small businesses that develop commercial technologies that assist government agencies to achieve their mission.

## The Environmental Chemistry of Arsenic

Arsenic is commonly found throughout the environment in a wide array of chemical species that vary in toxicity and mobility. Many of these chemical species can be transformed due to biological activity or other changes in the environment, such as a change in oxidation-reduction potential and pH. This prospect for natural environmental change creates the possibility that a wide variety of arsenic species are constantly transforming at any time. To determine the potential transformation and risk of arsenic in the environment for remedy decisions, the analysis of environmental samples should include identifying and quantifying both the total quantity of arsenic present and the specific chemical forms present, a procedure known as speciation.[12, 13]

However, speciation by a laboratory is expensive and the sample collection methods to ensure the preservation of in situ conditions are difficult and expensive. As a result, speciation may be cost-effective only when it is important to the fate and transport analysis or the risk assessment, but always should be considered when it does not add too much to the cost. Although the goal of most of the techniques examined in this paper is to measure all of the arsenic present in a sample, when possible the applicability of specific techniques to determine the speciation of an arsenic sample is also discussed.

The main species of arsenic found in the environment are the arsenic (III) and arsenic (V) oxyacids. In many environments, the arsenic (V) is often deprotonated as an arsenic (V) or arsenate anion; in contrast the arsenic (III) oxyacid remains in its neutral form as arsenite. Arsenate, arsenate anions, along with neutral arsenite constitute the main targets for field analytical assays. In contaminated soils, inorganic arsenate is the predominant species.[14] In general, the arsenate and other arsenic (V) specie[7] are immobilized on geologically available surfaces, usually as iron oxides.[15] Although arsenic (V) compounds are considered a low risk, bacterial[16] and other environmental activities can readily convert them back into more mobile and more toxic forms of arsenic.

Groundwater and soil also contain organoarsenic species: monomethylarsenic acid, dimethylarsenic acid, trimethylarsine oxide, and trimethyl arsine. In general organoarsenic compounds are less toxic than their corresponding oxyacids.[17] Although usually found in lower concentrations, under the right conditions, they can be found in very high concentrations. In freshwater lakes, methylated arsenic can make up to 60% of the total arsenic.[18] There are also arsenic sulfur species that constitute a sizable portion of arsenic geology[7] and reducing environments in sediment and in solution.[2, 19, 20] Although all of these species are not as common or currently believed to be as toxic as arsenic oxyacids they constitute a sizable fraction of the naturally occurring arsenic and should be a target in field measurements.

Another important key to understanding the environmental risk from arsenic is bioavailability, defined as the measure of the amount of arsenic that can be absorbed by a living organism. Although bioavailability is likely to play a strong role in future environmental regulatory decisions,[21] it has not received widespread regulatory and public acceptance.[22] Also, the techniques for measuring bioavailable arsenic are varied and the subject of ongoing research, which goes beyond the scope of this review.

## Current Methods and Requirements for Measuring Arsenic in the Environment

### Currently Available Laboratory Assays to Measure Arsenic

Fixed laboratory assays are generally required to accurately measure arsenic in an environmental sample to parts per billion (ppb) levels, defined here as μg/L for water or μg/kg for solids. The preferred laboratory methods for the measurement of arsenic involve pretreatment, either with acidic extraction or acidic oxidation digestion of the environmental sample. Pretreatment transfers all of the arsenic in the sample into an arsenic acid solution, which is subsequently measured using any one of several accepted analytical methods, such as Atomic Fluorescence Spectroscopy (AFS),[23] Graphite Furnace Atomic Absorption (GFAA), Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).[24] These instruments are bulky, expensive to operate and maintain, and require fully equipped laboratories to maintain and operate. Field assays, in which lower sensitivities may be acceptable for purposes of sample screening or site surveys, strive for similar detection goals as fixed lab methods, are relatively inexpensive, and can produce a large number of screening results in a short time.

### Current Requirements for Measuring Arsenic

The current maximum contaminant level (MCL) for all forms of arsenic in groundwater is 50 μg/L (50 ppb), set by EPA in 1975 based on a Public Health Service standard originally established in 1942. On January 22, 2001 EPA adopted a new standard for arsenic in drinking water at 10 ppb, to be enforced by January 2006.[25] Arsenic contaminated waste is restricted under RCRA as a hazardous waste and must be treated to meet limits determined by a prescribed extraction protocol, the toxicity characteristic leaching procedure (TCLP). Arsenic contaminated soil is often treated as a hazardous waste with the same limitations on treatment or disposal although other regulations may also apply.[26, 27] The new groundwater limits may affect disposal procedures for waste containing arsenic, increasing the pressure to monitor RCRA waste sites for the potential leaching of arsenic into groundwater.

### Currently Available Field Assays to Measure Arsenic

#### Colorimetric Test Kits

Field kits have been used extensively to test for arsenic in groundwater, and in many cases, it is the only assay applied. The current baseline methodology involves a variety of technologies that are all variations of the “Gutzeit” method, developed over 100 years ago.[28] These assays have been applied almost exclusively to water samples, although they may be applied to testing solid waste and soil, using either an acidic extraction or an acidic oxidation digestion of the sample.

### *A General Description of the Technology*[28]

The “Gutzeit” method and its variants involve treating the water sample with a reducing agent that transforms the arsenic compounds present in the water into arsenic trihydride (arsine gas). This separates the arsenic from the sample. The arsenic trihydride diffuses out of the sample where it is exposed to a paper impregnated with mercuric bromide. The reaction with the paper produces a highly colored compound. The concentration of the arsenic can be approximated using a calibrated color scale. This test method is inexpensive, and minimally trained personnel can readily perform it and read the results in the field. However, sulfur, selenium, and tellurium compounds have the potential of interfering with this assay. Organoarsenic species, such as monomethylarsonate and dimethylarsinate, cannot be directly detected using this assay.[28] Although these compounds are transformed into $CH_3AsH_2$ and $(CH_3)_2AsH$ in the presence of reducing agents like sodium borohydride,[2] it is not clear if these compounds react with the mercuric bromide in the test strip.

One of the most dramatic cases of a population at risk from naturally occurring arsenic in groundwater exists in Bangladesh and Eastern India where millions of people are affected. The enormous scale of the arsenic problem in one of the world’s largest populations at risk brought full-scale public concern and international aid to find a remedy for the problem. One of these studies demonstrated the shortcomings of field analytical capabilities. Beginning in 1997, the World Bank, WHO, and other international agencies used field kits extensively to test local groundwater wells. However, display problems affecting the accuracy and reproducibility of the available field test kits occurred. Rigorous comparisons of three field kits that were used in Bangladesh have all shown significant variations when compared with accepted laboratory methods, and they were prone to producing a high fraction (up to 50% in some cases) of false negative and false positive readings that could not readily be attributed to any external factor.[29, 30] All of the test kits rely on the Gutzeit method that generates highly toxic arsine gas.

An independent study had shown that performing these three field tests will generate arsine gas well above the threshold limiting value (TLV) of 0.05 parts per million by volume (ppmv) recommended by the Occupational Safety and Health Administration (OSHA).[31] Therefore, the workers operating the field assays may require specific protective equipment to operate this assay. Also, these assays generate toxic mercury solid waste because the test strips contain mercuric bromide.

## Portable X-ray Fluorescence

Portable X-ray fluorescence has recently been accepted as a field technique to measure arsenic in dry solid samples, such as soil and dried sludge. A current draft EPA test method, SW-846 6200, has reportedly performed with an interference free detection limit of 40 mg/kg (40 ppm) in quartz sand. The main interferents listed in this method were variations in particle size, moisture, and lead co-contamination.[11]

### *A General Description of the Technology*[32]

Environmental samples are irradiated with high-energy photons (x-rays when generated by an electronic device or gamma rays when generated from a radioisotope). For arsenic detection, a sealed $Cd^{109}$ radioisotope source is used. After the sample is irradiated, the sample atom may absorb the photon, dislodging an electron from the inner shell of the atom. In this process, known as the photoelectric effect, the resulting vacancy is filled by an electron that cascades in from outer electron shells. This rearrangement of electrons results in emission of x-rays characteristic of each atom, termed x-ray fluorescence (XRF). This combination uses a specific energy photon for the photoelectric effect while precisely measuring the energy of the XRF photon emitted by the sample to allow for an accurate identification of the elements in a sample. In field investigations, EPA often requires a fixed laboratory analysis of duplicates to verify the performance of the field technology. Typically, verification is performed using acid digestion followed by any of the accepted analytical methods, such as GFAA, ICP, or HGAAS. However, caution should be applied when comparing the results from these two techniques. XRF measures the bulk concentration of arsenic in the solid sample, while acid extractions are limited to the arsenic that can be removed from a sample using any of a number of standardized extraction procedures (e.g., EPA Methods 3050, 3051, and 3052).[11] Therefore, the two results should not be compared directly.

## Science and Technology Developments for Arsenic Analyses

In this section, technologies at various stages of development will be discussed for arsenic detection in the field. The discussion includes a description of current field assay technologies, the technology development efforts, and a survey of scientific and technology research obtained from the published literature.

### Colorimetric Test Kits

The poor performance of the test kits during the Bangladesh crisis created a strong incentive to improve the performance of the colorimetric field kit technology. In one study, a close examination of the baseline technology gave way to several low-cost improvements. Investigators changed the reducing agent used to transform arsenate and arsenite into arsine gas from powdered zinc metal to sodium borohydride, because zinc metal displayed slow reactivity and had the potential of being contaminated with arsenic. They changed the acid from a hydrochloric acid solution to a solid acid (sulfamic acid), which is more easily transported and safer to use. They changed the reaction chamber that maximizes the exposure of the test strip to arsine to minimize the possibility for operator exposure. They also found that in a preliminary step, sulfide contaminants that are known to interfere with this test could be oxidized to sulfates that did not interfere with the assay. Lastly, electronic devices were introduced to read the colored test strip, thereby eliminating errors from visual inspection.[28] Many of these improvements were incorporated into the next generation field kits.

#### Commercially Available Colorimetric Field Kits

The ETV Program tested a variety of arsenic field kits in July of 2002 and four more in August of 2003 under field conditions, using both technically trained and untrained users. All of the field assays were viewed as semiquantitative, unless the field kit was equipped with a portable colorimeter that allows for a fully quantitative determination of arsenic. Some of these colorimeters were computer operated, which allowed for greater accuracy and reproducibility albeit at higher cost. One of these assays, the As75, is specified by the manufacturer to have a Method Detection Limit (MDL) of 10 ppb, although the ETV program users were able to obtain a MDL of ~30 ppb. The arsenic field kits tested in August of 2003 were all capable of measuring low concentrations of arsenic, ranging from 15 ppb down to 4 ppb, which was independently verified by the ETV program. Improved protocols appeared to have minimized many of the problems with sulfide interference.[33]

While improvements to this technology have occurred since their highly criticized field performance in Bangladesh, their reliability still lags behind laboratory studies. Also, these assays do not detect any of the organic arsenates that may be found in groundwater.[34] Lastly, these assays are not benign; they generate poisonous arsine gas that poses a hazard to the operator, and the test strips constitute mercury solid wastes.

### Technology Development Efforts for Colorimetric Field Kits

EPA awarded an SBIR grant in September 2000 to ADA Technologies. The researchers successfully developed a test kit with a detection limit of 10 ppb arsenic in a 20 ml sample. The results are read as a colorimetric change in the filter held within the cap. The device typically responds to both arsenate and the more toxic, and mobile arsenite ions, but the design also allows for an alternative chemical system that responds only to arsenite ions. Unlike the currently available technology, the products of the reaction in ADA Technologies test kit are not hazardous and do not require any special disposal. At present, ADA Technologies is seeking to develop this technology in collaboration with other companies involved with water testing.[35]

### Research Efforts for Colorimetric Field Kits

A considerable amount of research has been dedicated to developing an arsenic-detection colorimetric solution that matches or exceeds the sensitivity of the Gutzeit method while improving safety, accuracy, and reproducibility.

One research group electrochemically reduced the arsenite ion into arsine gas. These investigators found that the arsenic reduction by this electrochemical method compared favorably to reduction by the chemical reducing agent sodium borohydride. In this study, the arsine gas reacted with a silver compound to give a highly colored complex that can be measured quantitatively. The investigators were able to achieve detection limits up to 50 ppb arsenite using this method. Gold, copper, and iron (III) species were found to interfere with the sample reduction.[36]

One direction for this research involves developing arsenic chemistry that will react with a dye in a way that can be measured and quantified. One such system reduces arsenic compounds into arsine gas, which then bleaches a dye in a solution containing detergents and metal particles. This system has been shown to be effective, with limits of detection for arsenic as low as 30 ppb.[37, 38] Although this system generates arsine gas, it is not clear if any of it leaves the solution. Further testing in the field and a more rigorous analysis of applicability for environmental measurements remain to be done.

Another possible approach involves developing arsenic chemistry that directly forms a highly colored material. Under the right conditions, arsenate (V) anions will react with molybdenum oxide to form a coordination compound, known as an arsenic polyoxomolybdate complex. When reduced, the arsenic polyoxomolybdate complex becomes an arsenomolybdate anion with an intense blue color that can be measured easily. However, this reaction has not been applied to environmental measurements in the field for several reasons. Iron, phosphate, and silicate, common constituents in groundwater and soil, interfere with the assay. Although the arsenomolybdate anion has a well-defined absorbance band, it is not very strongly colored when compared to conventional dyes. Arsenic polyoxomolybdate complexes can also be assayed electrochemically. The results of one such study showed a limit of arsenic detection down to 1 ppm.[39] Although the detection limit demonstrated in this study is too low for environmental analyses it demonstrates the possibility of combining colorimetric and electrochemical assays, which offers the possibility to develop a sensor with increased accuracy and dynamic range.

Despite these potential problems, scientists have been able to apply arsenic polyoxomolybdate complexes to environmental analysis with some success. Key to this method is the development of a protocol that effectively oxidizes available arsenite into arsenate and subsequently measures the absorbance of the resultant arsenate-molybdenum complex. A recent study examined several of these protocols and measured arsenic levels in natural waters up to 20 ppb with no substantial interference from high concentrations (up to 10-30 ppm) of silicate or sulfate, although phosphate and iron are still potential interferents.[40] It should also be noted that molybdenum oxide solutions have a low toxicity, [41] and their use on the scale appropriate for these assays should not create waste disposal problems.

Another strategy for improving the sensitivity and selectivity of an assay uses separation technologies to concentrate and purify the samples. One such development involves the use of a solid state fibrous anion exchanger to concentrate the arsenate or the arsenomolybdate anion. The researchers were able to lower the arsenate detection limit to 4 ppb using this method.[42] Several groups have developed solutions to potential interferents by separating out the arsenic ions from the rest of the environmental sample. One group reduced the arsenic in industrial samples to arsine gas, which was separated from the sample using a permeable membrane. The arsine gas was then oxidized to arsenate, transformed into its molybdenum complex, and analyzed. With this method, detection limits of arsenic levels down to15 ppb could be obtained from unfiltered samples without interference from phosphate, nickel, copper, and iron, which interfere with the molybdenum blue assay as well as the conventional SW-846 laboratory analytical methods.[43]

Two other research groups have developed trace-level detection technologies for using ion chromatography or ion exchange columns to isolate arsenic compounds. Arsenic speciation may be possible with chromatography. Both methods use ion chromatography, either before or after a complete oxidation of the arsenic to arsenate occurs in the sample. After this, arsenate is converted into the arsenate-molybdenum complex, which is than analyzed. One group, using ion chromatography on surface and groundwater achieved a detection limit of ~1.0 ppb along with some speciation of inorganic arsenic.[44] The other group used an anion exchange column and achieved a detection limit of less than 8 ppb for total arsenic.[45]

The current state of the science and technology for colorimetric assays is summarized in Table 1. All of these assays are limited to detecting inorganic arsenic, and all arsenic species must be converted to arsenate, or arsenite, depending on the specific assay applied. A promising arsenic detection assay in terms of sensitivity, reproducibility, and accuracy involve the combination of separation technologies with polyoxomolybdate chemistry.

Table 1. Summary of Colorimetric Assays

| Method | Media | MDL | Positives | Negatives | Comments |
|---|---|---|---|---|---|
| Current Technology | | | | | |
| Test Strips "Gutzeit"-based assay[28, 30] | Liquid | 0.5 ppb | Easily performed | Generates arsine gas and mercury waste[31]<br>Prone to both false positive and false negative readings<br>Inaccurate<br>Interference from sulfur compounds | Accurate, quantitative readings can be obtained with the use of an absorption device[33] |
| Technology Developments | | | | | |
| EPA SBIR[35] | Liquid | 10 ppb | Easily performed | Generates arsine gas | Modest improvements on current technology. Reports of the development of a mercury-free test strip. Potential arsenite/arsenate speciation capability |
| Research Efforts | | | | | |
| I. Dye Based Systems [37, 38] | Liquid | 30 ppb | | Generates arsine gas | Only performed in laboratory |
| II. Molybdoarsenate chemistry coupled with separation technology[40, 42, 43, 44, 45] | Liquid | 1-15 ppb | Relatively inexpensive, commercially available equipment required<br>Low toxicity[41] | Requires sample preparation; all arsenic must be converted to arsenate anion | Potential interferents are eliminated by separation protocols<br>The separation technologies allowed for the possibilities for arsenic speciation[44]<br>Electrochemical measurement of the molybdoarsenate could also be used to enhance sensitivity as well as selectivity[39] |

## X-ray Fluorescence (XRF)

X-ray fluorescence is a promising technology for detecting arsenic in the field. It is one of the few techniques that can directly measure arsenic in soil without requiring aqueous soil extractions. Improvements continue on the initial application of this field technology. In one published study, a portable XRF instrument was used for an in situ analysis of arsenic from an arsenic-contaminated abandoned industrial site in England.[46] The extent of contamination of the abandoned buildings at the site measured down to MDL (~120 ppm in this study) and compared to laboratory analyses. Isolated building materials, debris, as well as unidentified deposits found at the site were examined for arsenic This gave a better understanding of the potential reuse of the site as well as the proper disposal of the building debris.

### Commercially Available XRF Equipment

The ETV program tested a number of XRF field units in 1997.[47] Each tested instrument was portable, field-ready (i.e., battery-powered for up to 8 hours), and weighed less than 20 pounds. A radioactive $Cd^{109}$ source was used to irradiate samples. Each device was able to measure a MDL ~100 mg/kg of arsenic in soil (100 ppm) with an average of ± 15% drift. Drift is defined as the variation of an instrument to measure a known quantity of arsenic after a period of time, usually corrected by frequent calibration of the instrument. A recent study lists the MDL for arsenic with portable XRF field units at 60 ppm.[46] Other examples of XRF field units have improved the software and thus the signal, calibration, and ability to convert x-ray intensities to concentration. Also, radioactive isotopes are beginning to be replaced with miniature x-ray tubes.[48] This change offers the possibility for greater power and analyses of different wavelengths, as well as increased federal regulatory relief because it eliminates the use of radioactive materials.[49]

### Technology Development Efforts for XRF Equipment

The SERDP [50] and ESTCP [51] programs have developed the Site Characterization and Analysis Penetrometer System (SCAPS) that combines traditional cone penetrometer technology with XRF technology to rapidly delineate the subsurface distribution of contaminants. Although the equipment is capable of measuring arsenic in the laboratory, it had not been tested in the field. All of the sites evaluated in the studies are co-contaminated with lead, which interferes with XRF arsenic measurements. However, given that XRF has shown strong sensitivity and utility for direct measurement of arsenic in other field applications, the potential exists for XRF in combination with a cone penetrometer to measure arsenic under conditions where interference from lead would not be a problem.

### Research Efforts Dedicated to XRF Technologies

Current research has explored the use of XRF to analyze arsenic in aqueous solutions after preconcentration of the sample on a suitable solid substrate. This method appears to work well for aqueous samples,[52] and has been performed on actual groundwater samples with satisfactory results with arsenic concentrations measured down to 50 ppb.[53] A recent study of a series of metals (Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, but not arsenic) preconcentrated on a resin and analyzed using a portable XRF gave a detection limit of 20-40 ppb.[54] All of these studies indicate that XRF has good potential for measuring arsenic directly in water in the field. Other studies have shown that using specific resins for preconcentrating arsenic in the field may make arsenic speciation possible.[17]

The current state of the science and technology for XRF field assays is summarized in Table 2. Although the sensitivities are not as high, the capability to measure a wide variety of metals is a definite strength. The ability to sample both solid and liquid samples also provides considerable sampling flexibility.

Table 2. Summary of the Use of XRF in Arsenic Field Assays

| Method | Media | MDL | Positives | Negatives | Comments |
|---|---|---|---|---|---|
| Current Technology | | | | | |
| Hand-held devices[47] | Solids | 60 ppm[46] | Possibility for analyses of a wide spectrum of metals from a single sample | Interference from lead<br>Sample preparation usually required<br>Many models contain a radioactive source | The radioactive source has been replaced with a miniature x-ray tube in some newer models[48] |
| Research Efforts | | | | | |
| Use of portable XRF devices to measure arsenic in groundwater [53, 54] | Liquids | 50 ppb | Possibility for analyses of a wide spectrum of metals from a single sample | Interference from lead<br>Sample preparation required<br>Samples must be preconcentrated onto a solid matrix | Preconcentrating samples onto a solid matrix may allow for arsenic speciation |

## Anodic Stripping Voltammetry (ASV)

Electrochemical assays for the detection of arsenic have demonstrated promise for detecting arsenic in the field. These methods work best for liquid samples, such as groundwater. Solid samples must be digested or extracted before testing. EPA has already approved analytical method SW-846-7063 for ASV which is capable of measuring from 0.1 to 300 µg/L of free (i.e., not adsorbed or bound to any other species in solution) arsenic. Although not designed specifically for field use, commercially available versions of the laboratory equipment for this method may be readily transported and used in the field.

### *A General Description of the Technology* [11]

Anodic stripping voltammetry provides an alternative analytical technique for measuring dissolved arsenic in drinking water. The ASV method is equally sensitive for As (III) and As (V) and is suitable for measuring low levels of arsenic. This method uses anodic stripping to quantify free dissolved arsenic [as As (III) and/or As (V) ions] at a potential of +145 mV with respect to the saturated calomel electrode from a conditioned gold-plated electrode. The analysis by ASV involves three major steps. First, a glassy carbon electrode (GCE) is prepared by plating a thin film of gold onto the electrode, which is then conditioned. The samples are made acidic and rendered conductive by adding hydrochloric acid. The electrode is placed in the sample solution, and a fraction of the dissolved arsenic is reduced onto the electrode surface. The arsenic removed from solution forms a layer of arsenic on the gold electrode that is subsequently oxidized off. A careful measurement of the amount of electrical current required to remove (or strip) the arsenic oxidatively (an anodic process) gives a quantitative measure of the amount of material that was removed from solution. The arsenic concentration in the sample is determined by comparing the electrochemical response from the sample to external standards. Dissolved antimony and bismuth are positive interferences. Dissolved cooper at concentrations greater than 100 times the arsenic concentration is also an interferent.

### Commercially Available ASV Equipment

In 2002, the ETV program tested an Anodic Stripping Voltammetric field apparatus called the Nano-Band™ Explorer. The instrument is portable, lightweight, and field ready with battery power up to 40 hours. However, the ETV program tested the instrument solely in the laboratory and did not assess its field performance. The MDL levels of ~13 ppb were achieved, but the operators felt that using the Nano-Band™ Explorer required technical ability beyond those of the non-technical operator. In August 2003, the ETV program tested the PDV 6000, another Anodic Stripping Voltammetric field apparatus. MDL levels ~7 ppb were achieved, and the instrument tested well for both laboratory and field studies. However, the ETV staff reported that the manual was difficult to follow and that the some operations required professional judgement.[33]

In January 2003, the ESTCP program reported the results of its testing of the Metalyzer™ 5000. This instrument reportedly measured multiple toxic metal concentrations in water using the ASV technique with detection limits below ppb levels. The technology worked as expected in terms of sensitivity and accuracy in the laboratory; however, when arsenic samples were spiked with other metals (Aluminum, Antimony, Bismuth, Cadmium, Copper, Chromium, Iron, Lead, Magnesium, Manganese, Mercury, Nickel, Selenium, Tin, and Zinc), at twenty and forty times the analyte concentration, the sensitivity for arsenic detection dramatically decreased. Given this performance, arsenic should only be measured using relatively clean, well-defined samples, such as drinking water or relatively clean well water, thereby reducing its flexibility for field use. It also should be noted that commercial production of the Metalyzer 5000™ was discontinued.[55]

### Research Efforts Dedicated to ASV

As described in method SW-846-7063, ASV should be able to detect and quantify both arsenite and arsenate. Recent studies have shown that this technique is limited to measuring only the arsenite in an environmental sample. The arsenate in the sample had to be chemically reduced to arsenite and then measured electrochemically to give a total arsenic measurement. This method was used to measure the arsenic content of the groundwater from a series of wells in Bangladesh and demonstrated a detection limit of 0.5 ppb, verified with established laboratory methods and techniques.[56] Another group has developed a field-deployable ASV instrument that can directly measure arsenite and arsenate electrochemically without the need for chemical reduction. The detection limit was 0.5 ppb for both arsenic species. However, comparable concentrations of copper, mercury, or large concentrations of zinc interfered with the measurement.[57] Later field studies using this instrument suffered interference from many species, such as surfactants in the water samples.[58]

Recently, microelectrodes have become affordable and readily available. Microelectrodes offer a distinct advantage over the previously mentioned ASV methods (including SW-846-7063) in which a new gold electrode must be prepared for each new set of experiments. In contrast, gold microelectrode arrays can be readily mass-produced using photolithographic methods. Gold microelectrode arrays have been used to create a field-portable ASV with a detection limit of 0.05 ppb for arsenite, but again, the arsenate had to be reduced chemically before measurement. The main interferents were copper, mercury, and lead. Field-testing of this instrument on contaminated groundwater sites in Maine and New Jersey showed it could accurately measure arsenic compared to laboratory studies using the standard laboratory methods.[59, 60]

A common criticism of using electrochemical methods in the field is electrode fragility.[45] However, in one study, a gold microelectrode array lasted 30 days.[60] This experiment is a good first step in developing this technology in rugged field instruments as well as remote long-term sensors. However, much more development of instruments, including independent field-testing (such as the ETV program), will be required before this goal will be achieved.

A summary of ASV efficacy for detecting arsenic is shown in Table 3. In general, this technology requires well-trained personnel to operate it and to interpret the data. Also, the durability of the

Table 3. Performance of ASV Equipment for the Detection of Arsenic

| Method | Media | MDL | Positives | Negatives | Comments |
|---|---|---|---|---|---|
| Current Technology | | | | | |
| ESTCP Testing of ASV field-ready equipment[55] | Liquid | Less than 1 ppb | High sensitivity | Requires technically trained personnel<br>Interference from copper, mercury and zinc | The specific unit tested is no longer manufactured |
| ETV Testing of ASV field-ready equipment[33] | Liquid | 13 ppb | High sensitivity | Requires technically trained personnel<br>Interference from copper, mercury and zinc | Experienced operators required[33] |
| Research Efforts | | | | | |
| Newly-designed field equipment [57, 59, 60] | Liquid | 0.05-0.5 ppb | High sensitivity<br>Possibilities for arsenic speciation | Durability of the electrodes has been questioned<br>Interference from copper, mercury and zinc | There is some controversy about whether ASV is limited to arsenite analysis or able to measure both arsenic and arsenite directly. It is not clear if this technique can detect arsenic species other than the oxyacids |

electrode is questionable, and the variable performance of this technique calls for some caution. The performance problems identified during the ETV and ESTCP demonstrations all point to a technology that can be challenging to use despite the promise of very low sensitivities. The utility of this technique for the detection of both arsenite and arsenate is important. Most of the research indicates that it is only possible to directly measure arsenite with ASV; arsenate has to be chemically reduced to arsenite, followed by another ASV measurement. Although this procedure can be readily performed it definitely allows for uncertainty to enter into the measurements and does not reflect well on the utility of the method.

## Biological Assays: Using Bacteria and Plants for Arsenic Detection

### *A General Description of the Technology* [62,65]

All cell-based organisms have intricate mechanisms for detoxifying arsenic compounds that involve a wide variety of proteins that chemically modify, transport and extrude the arsenic from the cell.[61] The biological synthesis and activation of these proteins is regulated by the presence of arsenic, often through specific genetic mechanisms (the identity of which depends on the organism, the type of detoxification mechanism, and the analyte). In one commonly employed mechanism, activation of the genes that encode the proteins for arsenic resistance depends on the reversible binding of a regulatory protein to a Deoxyribonucleic acid (DNA) control sequence associated with that gene. When the regulator is bound to the analyte it can switch the gene on to synthesize the required proteins to activate the arsenic detoxification system. Understanding the identity, specificity, and sensitivity of the genetic elements and their corresponding regulatory proteins is key to technologies employing biosensors. When creating an arsenic biosensor, the arsenic-responsive DNA control sequences are linked to an additional gene. This gene, called a reporter gene, produces a protein whose properties can be readily observed: as an enzyme that generates a highly colored material or a fluorescent protein. Using techniques developed from molecular biology, it is possible to develop a microbe that generates a visible signal, usually fluorescing bright yellow, when it comes in contact with arsenic compounds.

## Science and Technology Research Efforts for Biological Assays

A recent study using microbes has been shown to detect arsenic down to ppb levels.[62] However, far less research involving the use of plants to detect arsenic has been conducted than for the use of microbes. A strong research effort involving the study of plants that accumulate and store arsenic, primarily for the remediation of arsenic-contaminated sites, is underway.[63] A recent study demonstrated changes in color pigmentation of two water plants upon exposure to arsenic. This effect requires an incubation period of three days and can be quantified with a series of standards.[64] Although this is a very good "low tech" assay, it requires more study to rule out, for instance, the effect of other stresses, such as nutrient levels or microbial infection, that can generate the same pigment change as arsenic absorption. Genetically modified microbes were used in another recent study to develop a set of semi-quantitative assays for potable water. The investigators also developed an assay that produced a visible blue color with arsenite concentrations above 8 ppb.[65]

Despite the fact that biological systems have good potential for assaying arsenic, there are a few reasons for caution. The coloration changes in plant systems may be due to factors other than arsenic detection. The bacterial systems apply only to water assays and have had only limited success actually quantifying arsenic. Also, it is not clear whether the microbes are measuring all of the arsenic in a sample or just the bioavailable arsenic. This application of microbes as a biosensor for bioavailable arsenic is the subject of another review. [66]

## Other Assays for Arsenic in the Environment

This section discusses several techniques for the measurement of arsenic that have achieved some success in the laboratory but have not been widely applied to field applications. Research in this area has been comparatively sparse

### Electrophoresis Techniques

Capillary electrophoresis is a technique that can only extract and separate ions species from an environmental matrix; it cannot detect or measure the concentration of these species. However, when combined with a sensitive detection technique, it has potential as an analytical technique. Often this technique, which is combined with instruments, such as ICP-MS, is used for arsenic speciation in the laboratory. The draft EPA Method, SW 846-6500, assays the following inorganic anions: fluoride, bromide, chloride, nitrite, nitrate, ortho-phosphate, and sulfate in aqueous matrices using capillary ion electrophoresis with absorption spectroscopy. In some cases, the anion can be directly measured by its absorbance spectrum; in other cases, indirect detection is required. In indirect absorbance detection, a strongly absorbing species is placed in the buffer. As the anion of interest migrates down the capillary, it displaces the buffer, changing the absorption spectrum for that region of the capillary and allowing the anion to be detected and quantified.

#### *A General Description of the Technology*[11]

An UV-light absorbing electrolyte is placed in a 75 μm diameter fused silica capillary. Voltage is applied through the capillary causing electrolyte and anions to migrate towards the anode and through the capillary's UV detector window. Anions are separated based upon differential rates of migration in the electrical field directly related to the local ion concentration.

Capillary electrophoresis has been used to detect arsenic by direct absorbance of the arsenic species with detection limits in the ppm range, which is several orders of magnitude above the required sensitivity levels.[67, 68] However, with indirect UV, detection limits below 1 ppb have been achieved. The technology has been applied successfully to arsenic spiked water samples and soil extracts. In one study, organoarsenic compounds were analyzed directly.[69] A similar study that used indirect laser-induced florescence detection showed detection limits for arsenic in the range of 250 ppb.[70]

A recent study developed miniaturized detection devices using isotachophoresis, which is closely related to the electrophoresis technique. A miniature sensor (8-cm long, 8-cm wide and 6-mm thick) was fabricated and fitted with a conductivity detector. This device was able to measure arsenic species to a range of 2-5 ppm for arsenite and arsenate, respectively. It also successfully measured the arsenic content of an industrial effluent.[71] This technology's size, durability, and ease of use make it a strong candidate for a sensor technology, provided greater sensitivity can be achieved.

## Laser Induced Breakdown Spectroscopy (LIBS) for the Detection of Arsenic

### *A General Description of the Technology* [72]

Laser-induced breakdown spectroscopy can determine the elemental composition of aerosols, liquids, gases, and solids qualitatively and quantitatively in real time with a single laser pulse. A high-powered, pulsed laser beam is focused directly into the targeted sample to form a small laser-induced breakdown, called a laser spark. The resulting high-temperature plasma is sufficient to vaporize, atomize, and electronically excite a small amount of the sample matter. The electrons within these atoms gain energy, and subsequently emit light at characteristic wavelengths as the plasma cools and the electrons relax to their original condition (i.e., ground state). This process, which is known as atomic emission, forms the basis of LIBS as an analytical technique. The resulting emissions frequency spectrum is a fingerprint of the elemental composition of the sample but not its speciation. After calibration, the intensity of each peak in the spectrum can be used to quantify elemental concentrations.

LIBS has become very useful for the detection of a wide variety of RCRA metals in soil. It has been combined with a cone penetrometer, in combination with XRF into the SCAPS system, for the in situ analyses of RCRA metals in subsurface soils.[50, 51] The DOE Environmental Management program has combined a similar system with a cone penetrometer equipped with a LIBS system.[72] Typical detection limits for the SCAPS LIBS sensor are 1-10 ppm for lead, chromium, and cadmium, making it a good complement to the XRF capabilities of the SCAPS system.[51] Recently, a portable LIBS field unit successfully measured lead contamination in soils with a detection limit on the order of 100 ppm,[73] making this technique a good complement to the hand-held XRF devices for lead detection. However, the LIBS detection limits for arsenic preclude its successful application for arsenic analysis. Detection limits for LIBS are a function of several variables, including the intensity of the emission line(s) for a specific metal, plasma temperature, soil moisture, and grain size, as well as detector signal to noise. Reported detection limits for arsenic, such as the 705 ppm achieved in contaminated Los Alamos soil, are considered poor when compared with other techniques.[74] A final detection limit of 530 ppm was reported for the SCAPS equipped with LIBS in laboratory studies; the device was not tested on arsenic in the field.[75] Although improvements to this technique have reportedly brought this limit down to 400 ppm,[76] the technology requires more research to improve the detection limits for arsenic.

Table 4 contains the summary of the assays discussed in this section. Although LIBS may become a promising analytical technique, current studies indicate poor sensitivity, and because the technique vaporizes the sample arsenic, speciation is not possible while electrophoresis techniques show great potential for field applications and sensors.

## New Analytical Technologies with Possible Applications for Arsenic Analysis

Analytical techniques that have been successfully applied to other environmental species could be applied to arsenic detection in the field. In general, this section considers only those techniques that have successfully detected low levels (below ppm) of inorganic oxyanions that have a similar structure, and chemical behavior to their arsenic counterparts, e.g., chromate, phosphate, and perchlorate.

Table 4. Miscellaneous Assays for the Detection of Arsenic

| Method | Media | MDL | Positives | Negatives | Comments |
|---|---|---|---|---|---|
| Electrophoresis Techniques | | | | | |
| Capillary electrophoresis [67, 68, 69, 70] | Liquid | Less than 1 ppb | High sensitivity | Requires indirect measurement methods for arsenic detection | Good separation capabilities allow for arsenic speciation<br>Capable of wider application with other assays |
| Isotachophoresis[71] | Liquid | 2-5 ppm | Highly compact | Poor sensitivity | Strong possibilities for sensor development |
| Laser Techniques | | | | | |
| Laser Induced Breakdown Spectroscopy[72, 73, 74, 75, 76] | Solid | 400 ppm | Fast<br>Remote sensing possibilities<br>Multiple species can be measured | Requires highly trained personnel<br>No speciation possible<br>High-powered laser requires safety precautions | Has been attached to a cone penetrometer [50, 51, 72]<br>Portable unit available[73]<br>Low sensitivity precludes wider use |

## Microcantilever Sensors

### *A General Description of the Technology*[77, 78]

Recently, a new set of environmental sensors has been developed from Atomic Force Microscopy (AFM) technologies, permitting atomic and molecular scale resolution of surfaces. These sensors use the micrometer scale cantilever (microcantilever) or springboard that is fabricated for AFM. These miniature cantilevers are coated with a "detector film" that interacts with the desired species. When the desired species adsorbs onto this film, it causes one of several changes: surface stress, a temperature change, or increased mass. These surface changes all result in the microcantilever deforming (bending). Although this deformation can be measured in several ways, laser reflection is the standard method.

At present, this technology has been applied to sensors for the detection of chromate[79] and cesium.[80] These sensors all demonstrated excellent sensitivity, capable of ppb detection limits, and high selectivity. It may be possible to design a coating capable of selectively binding arsenic. Preliminary results from this technology indicate excellent potential for developing a highly specific, highly sensitive arsenic sensor.

## Surface Enhanced Raman Spectroscopy

### *A General Description of the Technology*

Surface Enhanced Raman Spectroscopy (SERS) is a powerful tool for classifying unknown chemicals by their vibrational spectra. A molecule is adsorbed onto a specially prepared metal surface (usually silver), and laser light is reflected off the adsorbed molecule. The change in wavelength of the scattered light is dependent on the vibrational spectrum of a target molecule and is an indication of its structure. The Raman spectrum can uniquely "fingerprint" the desired molecular species, and with computer assistance, it can specifically identify and quantify a single chemical species in a large sampling environment. Raman spectra of arsenite and arsenate in solution[20, 81] and soils,[82] are known, although MDLs have not been determined.

Raman spectroscopy identifies and quantitates the concentration of molecules by carefully measuring the wavelength and intensity of the laser light scattering. Researchers developed a sensor that uses cationic-coated silver particles as substrates to detect perchlorate, chromate, dichromate, and cyanide anions. The coating attracts the anions to the SERS substrate where they are identified and quantified by their characteristic Raman scattering. The investigators were able to detect chromate anions to levels of 60 ppb.[83] If SERS technology demonstrates similar sensitivity and selectivity for detecting arsenic compounds in environmental field studies, it can be developed into a possible field portable detection system.

## Conclusions

Accurate, fast measurement of arsenic in the field remains a technical challenge. Technological advances in a variety of instruments have met with varying success. However, the central goal of developing field assays that reliably and reproducibly quantify arsenic has not been achieved. Table 5 identifies and comments on technologies that have demonstrated promise. For instance, the XRF methods have the capability of measuring a variety of metals in addition to arsenic. XRF also is noted for being able to measure both solids and aqueous samples (groundwater) in the field. The colorimetric methods, when combined with separation technologies and spectrometers, also have reliable sensitivities with potential for measuring arsenic speciation. ASV appears to be very promising except for the limitations on whether arsenate can be directly measured and for possible interference from other metals.

The literature review for this report suggests that a lack of capability for the field measurements of organoarsenic compounds. Although acknowledged to be less acutely toxic than inorganic arsenic, these compounds still comprise an important fraction of the total environmental arsenic and should not be discounted from environmental arsenic analysis. Similar efforts should also be applied to arsenic sulfur species.

Minimal research and development has occurred on an independent, field ready sensor technology for arsenic. Although one compact sensor unit has been developed, its sensitivity is inadequate.[71]

Microcantilever-based sensors offer strong potential for use in arsenic detection. However, a cantilever-based sensor for arsenic has not been developed. SERS-based field analytical systems show similar potential, but neither of these technologies has been applied to arsenic detection in either the laboratory or the field.

Table 5. A General Summary of Arsenic Detection Techniques

| Method | Media | MDL | Comments |
|---|---|---|---|
| Current Technologies | | | |
| Colorimetric Assays[28,30] | Liquid | 1-30 ppb | Quantitative readings can only be obtained with the use of an absorption spectrometer<br>Limited to arsenite and arsenate, some promise for speciation |
| XRF hand held devices[47] | Solids | 60 ppm | Measures a wide spectrum of metals in addition to arsenic |
| ASV[33, 55] | Liquids | 0.1 ppb | High sensitivity |
| Research Efforts for Technologies | | | |
| Colorimetric Assays[37, 38, 42, 43, 44, 45] | Liquid | 1 ppb | The use of separation technologies with a spectrometer can greatly enhance the sensitivity and reliability of the assay. Some possibilities for arsenic speciation.<br>Electrochemical measurement of the polyoxometallate could also be used to enhance sensitivity as well as selectivity |
| Electrophoreses Techniques[67, 68, 69, 70, 71] | Liquid | 2 ppm to 0.25 ppb | Some possibilities for a compact sensor unit<br>One of the few techniques that has directly measured organoarsenic compounds |
| LIBS[72, 73, 74, 75, 76] | Solids | 400 ppm | Poor sensitivity |
| ASV[57,59, 60] | Liquid | 0.5-0.05 ppb | There is some debate in the literature about the capability to measure both arsenite and arsenate<br>Interference from other environmental metals a concern |
| XRF[53, 54] | Liquids | 50 ppm | Capable of measuring a wide spectrum of metals in a sample |
| Bioassay[62, 64, 65] | Liquids | 10 ppb | Mainly a semiquantitative assay for arsenate and arsenite in water. There are uncertainties about true measurements as opposed to determining bioavailabile arsenic |
| Analytical Technologies Not Yet Applied to Arsenic | | | |
| Microcantilever Based Sensors[79, 80] | Liquid | NA | Has not been applied to arsenic but outstanding selectivity and sensitivity for a wide variety of other systems are promising |
| Surface Enhanced Raman[83] | Liquid | NA | Has not been applied to arsenic but outstanding selectivity and sensitivity for chromate and other anions are promising |

## Appendix: List of Acronyms

| | |
|---|---|
| AFM | atomic force microscopy |
| AFS | atomic fluorescence spectroscopy |
| ASAP | adaptive sampling and analysis programs |
| ASV | anodic stripping voltammetry |
| DNA | deoxyribonucleic acid |
| DOD | Department of Defense |
| DOE | Department of Energy |
| EPA | Environmental Protection Agency |
| ESTCP | Environmental Security Technology Certification Program |
| ETV | Environmental Technology Verification |
| GFAA | graphite furnace atomic absorption |
| HGAAS | hydride generation atomic absorption spectroscopy |
| ICP-AES | inductively coupled plasma-atomic emission spectrometry |
| ICP-MS | inductively coupled plasma-mass spectrometry |
| LIBS | laser induced breakdown spectroscopy |
| MCL | maximum contaminant level |
| MDL | method detection limit |
| NPL | National Priority List |
| OSHA | Occupational Safety and Health Administration |
| ppb | parts per billion |
| ppm | parts per million |
| ppmv | parts per million by volume |
| RCRA | Resource Conservation and Recovery Act |
| SBIR | small business innovation research |
| SCAPS | site characterization and analysis penetrometer system |
| SERDP | Strategic Environmental Research and Development program |
| SERS | surface enhanced Raman spectroscopy |
| TCLP | toxicity characteristic leaching procedure |
| TLV | threshold limiting value |
| WHO | World Health Organization |
| XRF | x-ray fluorescence |

## References

[1] World Health Organization. *Arsenic in Drinking Water*. Fact Sheet No. 210, May 2001. (http://www.who.int/inf-fs/en/fact210.html)
[2] Cullen, W.R.; and Reimer, K.J. Arsenic Speciation in the Environment. *Chem. Rev*., 1989, 89, 713-784.
[3] U.S. Environmental Protection Agency. *Locating and Estimating Air Emissions from Sources of Arsenic and Arsenic Compounds*. U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA-454-R-98-013. June 1998.
[4] Hingston J.A.; Collins, C.D.; Murphy, R.J.; and Lester, J.N. Leaching Chromated Copper Arsenic Wood Preservatives: a Review. *Environ. Pollution*, 2001, 111, 53-66.
[5] Kristen, K. Arsenic in Old Herbicides Comes Back to Haunt Denver. *Environ. Sci. and Technol*., 2000, 34, 376A,
[6] Ayotte, J.D.; Montgomery, D.L.; Flanagan, S.M.; and Robinson, K.W. Arsenic in Groundwater in Eastern New England: Occurrence, Controls, and Human Health Implications. *Environ. Sci. and Technol*., 2003, 37, 2075-2083.
[7] Kumar, B.; and Suzuki, K.T. Arsenic Round the World: a Review. *Talanta*, 2002, 58, 201-235.
[8] Davis, A.; Sherwin; D.; Ditmars, R.; and Hoenke, K.A. An Analysis of Arsenic Records of Decision. *Environ. Sci. and Technol.*, 2001, 35, 2401-2406.
[9] Crumbling, D.M.; Groenjes C.; Lesnik, B.; Lynch, K.; Shockley, J.; Vanee, J.; Howe, R.; Keith, L.; McKenna, J.; and Peck, D. Managing Uncertainty in Environmental Decisions. *Environ. Sci. and Technol*., 2001, 33, 3686-3688.
[10] U.S. Department of Energy. *Adaptive Sampling and Analysis Programs (ASAPs)*. DOE/EM-0592. OST/TMS ID 2946. August 2001.
[11] U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)*. (http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm)
[12] Gong, Z.; Lu, X.; Ma, M.; Watt, C.; and Le, C. Arsenic Speciation Analysis. *Talanta*, 2002, 58, 77-96.
[13] Jain, C.K.; and Alli, I. Arsenic: Occurrence, Toxicity and Speciation Techniques. *Water Res*., 2000, 34(17), 4304-4312.
[14] Garcia-Manyes, S.; Jimenez, G.; Padro, A.; Rubio, R.; and Rauret, G. Arsenic Speciation in Contaminated Soils. *Talanta*, 2002, 58, 97-109.
[15] Matera, V.; LeHecho, I.; Laboudigue, A.; Thomas, P.; Tellier, S.; and Astruc, M. A Methodological Approach for the Identification of Arsenic Bearing Phases in Polluted Soils. *Environ. Pollution*, 2003, 126, 51-64, and references cited therein.
[16] Macur, R.E.; Jackson, C.R.; Botero, L.M.; McDermott, T.R.; and Inskeep, W.P. Bacterial Populations Associated with the Oxidation and Reduction of Arsenic in an Unsaturated Soil. *Environ. Sci. Technol*. 2004, 38,104-111.
[17] Le, X.C.; Yalscin, S.; and Ma, M. Speciation of Submicrogram per Liter Levels of Arsenic in Water: On Site Species Separation Integrated with Sample Collection. *Environ. Sci. and Technol*., 2000, 34, 2342-2347.
[18] Anderson, L.C.D. and Bruland, K.W. Biogeochemistry of Arsenic in Natural Waters: The Importance of Methylated Species. *Environ. Sci. and Technol*., 1991, 25, 420-427.
[19]Floroiu, R.M.; Davis, A.P.; and Torrents, A. Kinetics and Mechanism of $As_2S_3$ (am) Dissolution under $N_2$. *Environ. Sci. Technol.,* 2004, 38,1031-1037.
[20] Wood, S.A.; Tait, C.D.; and Janecky, D.R. A Raman Spectroscopic Study of Arsenite and Thioarsenite Species in Aqueous Solution at 25°C. *Geochem. Trans.*, 2002, 3(4), 31-39.
[21] Hogue, C. Metal Matter, As EPA Looks at Regulation of Metals, It Faces Issues Not Found with Organic Chemicals. *Chemical and Engineering News*, 2002, 80, 40.
[22] Ehlers, L.J.; Luthy, R.G. Contaminant Bioavailability in Soil and Sediment. *Environ. Sci. and Technol*., 1999, 33, 3686-3688.
[23] Gomez-Ariza, J.L., Sanchez-Rodas, D., Giraldez, I. and Morales, E., 2000. A Comparison Between ICP-MS and AFS Detection for Arsenic Speciation in Environmental Samples. *Talanta*, 2000, 51, 257-268.
[24] U.S. Environmental Protection Agency. *Analytical Methods Support Document for Arsenic in Drinking Water*. U.S. EPA, Office of Water, Targeting and Analysis Branch. EPA-815-R-00-010. December 1999.
[25] 40 CFR Parts 9, 141, and 142, National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring: Final Rule.
[26] U.S. Environmental Protection Agency. *Arsenic Treatment Technologies for Soil, Waste, and Water.* EPA-542-R-02-004. September 2002.

[27] U.S. Environmental Protection Agency. *U.S. EPA Workshop on Managing Arsenic Risks to the Environment: Characterization of Waste, Chemistry, and Treatment and Disposal*, May 1-3, 2001, Denver, CO. (http://www.epa.gov/ttbnrmrl/arsenictech.htm).

[28] Kinniburgh, D.G.; and Kosmus, W. Arsenic Contamination in Groundwater: Some Analytical Considerations. *Talanta*, 2002, 58, 165-180.

[29] Erickson, B.E. Field Kits Fail to Provide Accurate Measure of Arsenic in Groundwater. *Environ. Sci. and Technol.*, 2003, 37, 35A-38A.

[30] Rahman, M.M.; Mukherjee, D.; Semgupta, M.K.; Chowdury, U.K.; Lodh, D.; Chanda, C.R.; Roy, S.; Selim, M.D.; Quamruzzaman, Q.; Milton, A.H.; Shahidullah, S.M.; Rahman, T.; and Chakraborti, D. Effectiveness and Reliability of Arsenic Field Testing Kits: Are the Million Dollar Screening Projects Effective or Not? *Environ. Sci. and Technol.*, 2002, 36, 5385-5394.

[31] Hussam, A.; Alauddin, M.; Khan, A.H.; Rasul, S.B.; and Munir, A.K.M. Evaluation of Arsine Generation in Arsenic Field Kit. *Environ. Sci. and Technol.*, 1999, 33, 3686-3688.

[32] U.S. Environmental Protection Agency. *Field Analytic Technologies Encyclopedia: X-Ray Fluorescence*. (http://fate.clu-in.org/xrf.asp?techtypeid=49)

[33] U.S. Environmental Protection Agency. Verifications: Arsenic Test Kits. U.S. EPA, Environmental Technology Verification Program. (http://www.epa.gov/etv/verifications/vcenter1-21.html)

[34] Hach Company. Arsenic Test Kit. Lit. No. 3778. (http://ecommerce.hach.com/stores/hach/pdfs/literature/L3778.pdf)

[35] Bognar, John A.. *Final Report: Rapid, Accurate, Single-Step Test Strip for Low Level of Arsenic in Water*. U.S. EPA, National Center for Environmental Research, 2001. (http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/1719/report/F)

[36] Arbab-Zavar, M.H.; and Hashemi, M. Evaluation of Electrochmical Hydride Generation for Spectrophotometric Determination of As(III) by Silver Diethyldithiocarbamate. *Talanta*, 2000, 52, 1007-1014.

[37] Kundu, S.; Ghosh, S.K.; Mandal, M.; Pal, T.; and Pal, A. Spectrophotometric Determination of Arsenic via Arsine Generation and In-Situ Color Bleaching of Methylene Blue (MB) in Micellar Medium. *Talanta*, 2002, 58, 935-942.

[38] Kundu, S.; Ghosh, S.K.; Mandal, M.; and Pal, T. Micelle Bound Redox Dye Marker for Nanogram Level Arsenic Detection Promoted by Nanoparticles. *New J. of Chem*., 2002, 26(8), 1081-1084.

[39] Metelka, R.; Slavkova, S.; and Vytras, K. Determination of Arsenate and Organic Arsenic via Potentiometric Titration of Its Heteropoly Anions. *Talanta*, 2002, 58, 147-151.

[40] Lenoble, V.; Deluchat, V.; Serpaud, B.; and Bollinger, J.C. Arsenite Oxidation and Arsenate Determination by the Molybdene Blue Method. *Talanta*, (2003, in press, 10 pp.).

[41] Fairhall, L.T., Dunn, R.C.; Sharpless, N.E.; and Pritchard, E.A. *The Toxicity of Molybdenum*, U. S. Public Health Service, Public Health Bulletin, 1945, 293.

[42] Dedkova, V.P.; Shvova, O.P.; and Savvin, S.B. Determination of Arsenic(V) as a Heteropoly Acid After its Adsorption on a Fibrous Anion Exchanger. *J. Anal. Chem*., 2002, 57(4), 298-302.

[43] Rapasinghe, T.; Cardwell, T.J.; Cattrall, R.W.; Luque de Castro, M.; and Kolev, S.D. Pervaporation-Flow Injection Determination of Arsenic Based on Hydride Generation and the Molybdenum Blue Reaction. *Anal. Chim. Acta*, 2001, 445, 229-238.

[44] Johnson, R.L.; and Aldstadt III, J.H. Quantitative Trace Level Speciation of Arsenite and Arsenate in Drinking Water by Ion Chromatography. *Analyst*, 2002, 127, 1305-1311.

[45] Dasgupta, P.K.; Huang, H.; Zhang, G.; and Cobb, G.P. Photometric Measurement of Trace As(III) and As(V) in Drinking Water. *Talanta*, 2002, 58, 153-164.

[46] Potts, P.J.; Ramsey, M.H.; and Carlisle, J. Portable X-Ray Fluorescence in the Characterization of Arsenic Contamination Associated with Industrial Buildings at a Heritage Arsenic Works Near Redruth, Cornwall, UK. *J. Environ. Monit*., 2002, 4, 1017-1024.

[47] U.S. Environmental Protection Agency. Verifications: X-Ray Fluorescence Analyzers (Field Portable). U.S. EPA, Environmental Technology Verification Program. (http://www.epa.gov/etv/verifications/vcenter1-18.html)

[48] Thomsen, W. and Schatzlein, D. Advances in Field Portable XRF. *Spectroscopy*, 2002, 17(7), 14-21.

[49] U.S. Nuclear Regulatory Commisssion. 10 CFR Parts 30, 31, and 32: Requirements for Certain Generally Licensed Industrial Devices Containing Byproduct Material, Final Rule. Also, *Guidance About Licenses Authorizing Distribution to General Licensees*, NUREG-1556, Vol. 16. (http://www.nrc.gov/reading-rm/doc-collections/nuregs/staff/sr1556/v16/index.html#_1_2)

[50] Cespedes, E.R.; Lieberman, S.H.; Nielsen, B.J.; and Robitaille, G.E. *Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) Accelerated Sensor Development Project, Final Report*. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. Technical Report SERDP-99-3, September 1999.

[51] Environmental Security Technology Certification Program. Site Characterization and Analysis Penetrometer System (SCAPS) Heavy Metal Sensors. (http://www.estcp.org/projects/cleanup/199716o.cfm)

[52] Peraniemi, S.; and Ahlgren, M. Optimized Arsenic, Selenium and Mercury Determinations in Aqueous Solutions by Energy Dispersive X-Ray Fluorescence After Preconcentration in Zirconium-Loaded Activated Charcoal. *Anal. Chim. Acta*, 1995, 302, 89-95.

[53] Sbareto, V.M. and Sanchez, H.J. Analysis of Arsenic Pollution in Groundwater Aquifers by X-ray Fluorescence. *Appl. Rad. and Iso*., 2001, 54(5), 37-740.

[54] Driscoll, J.N. Determination of ppb Levels of Metals in Water by XRF. *Am. Lab. News*, March 2002, 16-18.

[55] Environmental Security Technology Certification Program. Heavy Metals Analyzer. (http://www.estcp.org/projects/compliance/199606v.cfm)

[56] Rasul, S.B.; Munir, A.K.M.; Hossain, Z.A.; Khan, A.H.; Alauddin, M.; and Hussam, A. Electrochemical Measurement and Speciation of Inorganic Arsenic in Groundwater of Bangladesh. *Talanta*, 2002, 58, 33-43.

[57] Huang, H. and Dasgupta, P.K. A Field-Deployable Instrument for the Measurement and Speciation of Arsenic in Potable Water. *Anal. Chim. Acta*, 1999, 380, 27-37.

[58] Dasgupta, P.K , personal communication.

[59] Feeney, R. and Kounaves, S.P. On Site Analysis of Arsenic in Groundwater Using a Microfabricated Gold Microelectrode Array. *Anal. Chem*., 2000, 72(10), 2222-2228.

[60] Feeney, R. and Kounaves, S.P. Voltammetric Measurement of Arsenic in Natural Waters. *Talanta* , 2002, 58, 5823-5831.

[61] Rosen, B.P. Biochemistry of Arsenic Detoxification. *FEBS Lett*., 2002, 529(1), 86-92.

[62] Roberto F.; Barnes, J.; and Bruhn, D. Evaluation of a GFP reporter Gene Construct for Environmental Arsenic Detection. *Talanta*, 2002, 58, 181-188.

[63] Ma, L.Q.; Komar, K.M.; Tu, C.; Zhang, W.; Cai, Y.; and Kennelley, E.D. A Fern that Hyperaccumulates Arsenic. *Nature*, 2001, 409, 579.

[64] Aziz, A. Azolla Filculoides Lam. and A-pinnata R. Brown to Measure Arsenic Pollution in Groundwater. *Bangladesh J. Bot*., 2001, 30(1), 7-24.

[65] Stocker, J.; Balluch, D.; Gsell, M.; Harms, H.; Geliciano, J.; Daunert, S.; Malik, K.; and Van de Meer, J. Development of a Set of Simple Bacterial Biosensors for Quantitative and Rapid Measurements of Arsenite and Arsenate in Water. *Environ. Sci. and Technol*., 2003, 37, 4743-4750.

[66] Strosnider, H. *Whole-Cell Bacterial Biosensors and the Detection of Bioavailable Arsenic*. U.S. EPA, Technology Innovation Office, National Network of Environmental Management Studies Fellow Program. August 2003. (http://www.clu-in.org/download/char/bacterial_biosensors.pdf)

[67] Chen, Z.L.; Lin, J.M.; and Naidu, R. Separation of Arsenic Species by Capillary Electrophoresis with Sample Stacking Techniques. *Anal. and Bioanal. Chem.*, 2003, 375(5), 679-684.

[68] Sun, B.G.; Macka, M.; and Haddad, P.R. Separation of Organic and Inorganic Species by Capillary Electrophoresis Using Direct Spectrophotometric Detection. *Electrophoresis*, 2002, 23(15), 2430-2438.

[69] Casiot, C.; Alonso, M.C.B.; Boisson, J.; Donard, O.F.X.; and Potin-Gautier, M. Simultaneous Speciation of Arsenic, Selenium, Antimony, and Tellurium Species by Capillary Electrophoresis and UV Detection. *Analyst*, 1998, 123, 2887-2893.

[70] Zhang, P.D.; Xu, G.W.; Xiong, J.H.; Zheng, Y.F.; Yang, Q.; and Wei, F.S. Capillary Electrophoresis of Arsenic Species with Indirect Laser Induced Detection. *J. Sep. Sci*., 2002, 25(3), 1555-1559.

[71] Prest, J.E.; Baldock, S.J.; Fielden, P.R.; Goddard, N.J.; and Treves Brown, B.J. Miniaturized Isotachophoretic Analysis of Inorganic Arsenic Speciation Using a Planar Polymer Chip with Integrated Conductivity Detection. *J. Chrom. A*, 2003, 990, 325-334.

[72]U.S. Department of Energy. *Fiber Optic/Cone Penetrometer System for Subsurface Heavy Metals Detection: Innovative Technology Summary Report*. DOE/EM-0508, March 2000.

[73]Wainner, R.T.; Harman, R.S.; Mizolek, A.W.; Nesby, K.L.; and French, P.D. Analysis of Environmental Lead Contamination: Comparison of LIBS Field and Laboratory Instruments. *Spectrochem. Acta B*, 2001, 56, 777-793.

[74]Koskelo, A. and D.A. Cremers. *RCRA Metals Analysis by Laser-Induced Breakdown Spectroscopy: Detection Limits in Soils*. LA-UR-94-1544, Los Alamos National Laboratory, Los Alamos, NM, 1994.

[75]Cespedes, E.R.; Lieberman, S.H.; Nielsen, B.J.; and Robitaille, G.E. *Tri-Service Site Characterization and Analysis Penetrometer System (SCAPS) Accelerated Sensor Development Project, Final Report*. U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS. Technical Report SERDP-99-3. September 1999.

[76]Fisher, B.T.; Johnsen, H.A.; Buckley, S.G.; and Hahn, D.W. Temporal Gating for the Optimization of Laser-Induced Breakdown Spectroscopy Detection and Analysis of Toxic Metals. *Appl. Spec*., 2001, 55(10), 1312-1319.

[77]Sepaniak, M.; Datskos, P.; Lavrik, N.; and Tipple, C. Microcantilever Transducers: A New Approach To Sensor Technology. *Analytical Chemistry*, 2002, 74, (21), 568A-575A.

[78]Anderson, J.E.T.; Zhang, J.-D.; Chi, Q.; Hansen, A.G.; Nielson, J.U.; Friis, E.P.; Ulstrup, J.; Boissen, A.; and Jensenius, H. In-Situ Scanning Probe Microscopy and New Perspectives in Analytical Chemistry. TrAC - *Trends in Anal. Chem*., 1999, 18(11), 665-674.

[79]Ji, H.F.; Thundat, T.; Dabestani, R; Brown, G.M.; Britt P.F.; and Bonnesen, P.V. Ultrasensitive Detection of $CrO_4^{2-}$ Using a Microcantilever Sensor. *Anal. Chem*., 2001, 73(7), 1572-1576.

[80] Ji, H.-F.; Finot, E.; Dabestani, R.; Thundat, T.; Brown, G.M.; and Britt, P.F. A Novel Self-Assembled Monolayer (SAM) Coated Microcantilever for Low Level Cesium Detection. *Chem. Comm*., 2000, 457-458.

[81]Rochette, E.A.; Bostick, B.C.; Li, G.; and Fendorf, S. Kinetics Of Arsenate Reduction by Dissolved Sulfide. *Environ. Sci. Technol*., 2000, 34(22), 4714-4720.

[82]Frost, Ray L.; Kloprogge, T.; Weir, M.L.; Martens, W.N.; Ding, Z.; and Edwards, H.G.H. Raman Spectroscopy of Selected Arsenates: Implications for Soil Remediation. *Spec. Acta A*, 2003, 59(10), 2241-2246.

[83]Mosier-Boss, P.A.; and Lieberman, S.H. Detection of Anions by Normal Raman Spectroscopy and Surface-Enhanced Raman Spectroscopy of Cationic-Coated Substrates. *Appl. Spec*. 2003, 57(9), 1129-1137.