CONSIDERATIONS FOR THE DETERMINATION OF TRACE CONCENTRATIONS OF ARSENIC IN ENVIRONMENTAL WATER SAMPLES

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Studies of the occurrence, distribution and aqueous geochemistry of arsenic in the environment requires accurate and sensitive analytical measurements. In addition to the determination of total arsenic concentrations, speciation of the form in which arsenic occurs plays a major role in its chemical reactivity and toxicity. Determination of speciation includes: the distribution of oxidation states (i.e. AsO_2^{-1}, arsenite and AsO_4^{-3}, arsenate); the nature of molecular compounds incorporating arsenic; and physical forms of arsenic, such as, dissolved, colloidal or particulate. Because of its normally low concentration in natural systems, analytical methodology usually requires both high sensitivity and specificity.

Gutzeit Method

Traditionally, trace analysis of arsenic in aqueous systems involved the use of a Gutzeit procedure, involving the formation of arsine gas by reaction with hydrogen under the catalytic action of elemental zinc. This is followed by reaction of the evolved arsine with mercuric chloride, impregnated in filter paper. The intensity of the colored (black) compound formed on the paper was compared with arsenic standards treated by the same procedure. Alternately, the gaseous arsine is reacted with silver diethyldithiocarbamate (AgDEDTC) in pyridine to form an intense red solution. A spectrophotometric absorption measurement is made at a wavelengh of 535 nm. A variation of this method that is more sensitive and accurate involves the absorption of the arsine gas in a sodium hypobromite solution, where the arsenic is oxidized to the pentavalent state. The arsenate formed by this process then reacts with ammonium molybdate in the presence of hydrazine sulfate (reducing agent) for the formation of a heteropoly-molybdenum blue complex. A spectrophotometric measurement at a wavelength of 840 nm is then used to quantitatively determine the amount of arsenic (Sandell, 1959). This general approach to trace arsenic determinations is more laborious and less suitable for rapid and accurate analysis than more modern analytical techniques, although a variation of the Gutzeit method has been more recently used for a rapid field analysis procedure (Kosmos, 2001)

PIXIE, NAA and DPASV

A highly sensitive technique that has found utility in the determination of trace arsenic, involves a x-ray emission procedure using a 3-5 MeV proton induced excitation source. This technique, commonly known as PIXIE, demonstrates high sensitivity (Taylor, 1982), although it requires a rather elaborate instrumental setup.

Trace concentrations of arsenic can also be determined by neutron activation analysis. Bombardment of the sample by a large neutron flux (about 1012 n/cm2 sec) in a nuclear reactor produces measurable activity from elements present down to subnanogram quantities. However, significant interferences can result in poor accuracy. In the case of arsenic, radioactive ^{76}As (γ emitter) can be created by the activation of natural ^{75}As. However, 76As can also be formed by the activation of ^{76}Se and ^{74}Ge. These interferences can be minimized by an undesirably time-consuming chemical separation prior to the irradiation step (Taylor, 1982).

An electrochemical technique employing differential pulse anodic stripping voltammetry uses a gold working electrode (Forsberg and others, 1975). Since As^{+5} is not electrolytically active in most supporting electrolytes, a prereduction to As^{+3} using Na2SO3 is required. Mercury and copper seriously interfere with this determination.

Detection Limits

Gutzeit			
Spot test	0.5 µg	DPASV	0.02 µg/L
AgDEDTC color	1 µg	HG-AAS	0.1 µg/L
Mo-blue color	0.1 µg	HG-ICP-AES	0.1 µg/L
NAA	Sub ng	GFAAS	0.5 µg/L
PIXIE	0.2 µg/L	ICP-MS	0.03 µg/L

HG-AAS and HG-ICP-AES

One of the more widely used analytical procedures for the determination of arsenic involves a combination of hydride generation (arsine) and atomic absorption spectrophotometry (Thompson and Reynolds, 1978). Typically the hydride is formed by reaction with either metallic zinc-stannous chloride in an acidic solution; or sodium borohydride in acidic solution. The sodium borohydride reduction procedure instantaneously converts As^{+3} to arsine gas; however, at room temperature, the reduction of As^{+5} to arsine occurs relatively slow. Therefore, a total arsenic determination requires a prereductant such as KI to convert all arsenic to the +3 oxidation state prior to the arsine formation step. The use of arsine gas formation provides both a way to separate the analyte from potential chemical interferences in the sample and to preconcentrate to improve analytical sensitivity. Atomization prior to the atomic absorption measurement is performed with either a argon-hydrogen-entrained air flame, or a heated quartz cell. Usually better precision is obtained with the cell because noise from flame flicker is eliminated. The same hydride generation procedure coupled with inductively coupled plasma-atomic emission spectrometry has also been used for the trace determination of arsenic (Edwards and others, 1998). The same basic characteristics and limitations reported for the hydride generation-atomic absorption procedure are observed with this technique. The primary advantage of this approach is the ability to simultaneously determine other hydride forming elements such as antimony, selenium, etc.

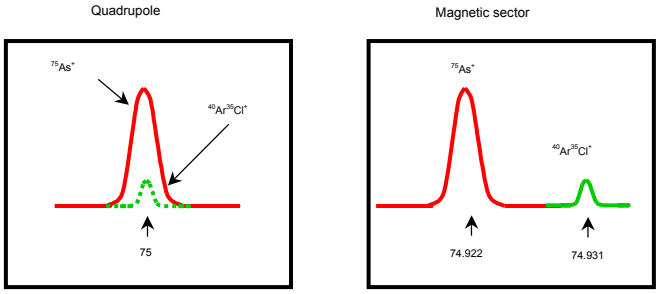
GFAAS

Graphite furnace-atomic absorption spectrophotometry (GFAAS) is currently one of the most accepted technologies for the determination of trace arsenic in aqueous samples. The U.S. Environmental Protection Agency method 200.9 calls for the use of a stabilized temperature platform and a palladium-magnesium nitrate matrix modifier. To obtain maximum sensitivity, samples are often preconcentrated 5:1 by an evaporation process. For maximum sensitivity, electrodeless discharge lamps are used for the primary excitation source.

ICP-MS

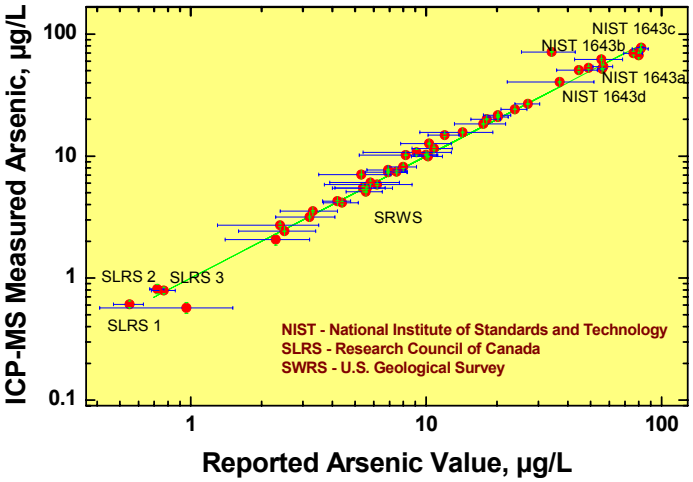
The most recently developed technique for the trace determination of total arsenic utilizes inductively coupled plasma-mass spectrometry (ICP-MS). This procedure uses the ion current measurement of monoisotopic $^{75}As^{+}$. Quantitation is performed by ratioing to the ion current of 103Rh, which is added as an internal standard at a concentration of about 4 µg/L. Unfortunately, a common molecular interference, $^{40}Ar^{35}Cl^{+}$ also appears at this same location in the mass spectrum. The magnitude of this interference is proportional to the concentration of Cl in the analysis sample. As seen below, this interference can be resolved using a high-resolution magnetic sector mass spectrometer to make the measurement, however, most laboratories do not currently have this instrumentation, and therefore, cannot make uninterfered direct ion current measurements of the resolved species. Laboratories utilizing quadrupole mass

spectrometry, which nominally operates at unit mass resolution, must use a correction technique when there is appreciable chloride is present in the sample. Therefore, a mathematical correction for the spectral interference from the $^{40}Ar^{35}Cl^{+}$ molecule is required (Taylor, 2001).



Mass spectral interference at m/e 75

An analysis by ICP-MS of a set of U.S. Geological Survey Standard Reference Water Samples, National Institute of Standards and Technology, and the National Research Council of Canada, Certified Reference Materials are shown. The error bars represent the spread in the Most Probable Values reported for the standards. The linearity and slope of this correlation plot demonstrates the accuracy of the ICP-MS direct analysis procedure for total arsenic concentration.



Speciation

Speciation analysis of arsenic and arsenic containing compounds have been performed by a variety of methods. These usually employ the use of chemical processes such as selective formation of a volatile compound followed by physical separation prior to measurement (Andreae, 1977). An example of this approach would include the discrimination of As^{+3} and As^{+5} prior to hydride generation. Although these methods can often be tedious, they have been shown to produce accurate results.

Other approaches to arsenic speciation include the use of chromatographic techniques to isolate specific compounds so that they can be selectively measured (Harrison and Rapsomanikis, 1989). These techniques include primarily ion exchange and liquid chromatography. Compounds such as monomethylarsonate, dimethylarsonate, trimethylarsonate arsenobetaine, and arsenocholine, are separated and independently quantified.

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