American Industrial Hygiene Association Journal

ISSN: 0002-8894 (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/aiha20

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P.H. DAVIS , F.J. BERLANDI , G.R. DULUDE , R.M. GRIFFIN , W.R. MATSON & E.W. ZINK

To cite this article: P.H. DAVIS , F.J. BERLANDI , G.R. DULUDE , R.M. GRIFFIN , W.R. MATSON & E.W. ZINK (1978) Analysis of total arsenic in urine and blood by high speed anodic stripping voltammetry, American Industrial Hygiene Association Journal, 39:6, 480-490, DOI: 10.1080/0002889778507793

To link to this article: https://doi.org/10.1080/0002889778507793

A method for the measurement of parts per billion levels of total arsenic in urine and blood is described. Samples are wet ashed with a mixture of HNO_3, $HClO_4$, and H_2SO_4 acids. Ashed materials are subjected to a reductillation™ procedure to reduce As (V) to As (III) and to separate arsenic from the sample matrix. Collected arsenic is then quantitated by anodic stripping voltammetry (ASV) at a gold film electrode. ASV analysis time is only 2 minutes. By simultaneous reductillation of 4 samples, ppb arsenic determinations can be accomplished at a rate of about 12 per hour. The method is as accurate, precise and reliable at the nanogram level as the more universally accepted colorimetric techinques are at the microgram and milligram levels. For replicate analysis of real samples, method precision ranged from ±1.4 ppb at the 5 ppb level to ±0.96 ppb at the 25 ppb level. Accuracy is estimated at ±6% over the range 5 to 500 ppb arsenic.

Analysis of total arsenic in urine and blood by high speed anodic stripping voltammetry

P.H. DAVIS, F.J. BERLANDI, G.R. DULUDE, R.M. GRIFFIN, W.R. MATSON and E.W. ZINK
Environmental Sciences Associates, Inc., Bedford, Massachusetts

introduction

The recently renewed interest in levels of arsenic in the work environment has reemphasized the need for a highly sensitive and precise analytical method for this element. Sensitivity is of special concern in the analysis of biological samples where sample size and preparation time are often limiting factors. Most currently employed procedures for arsenic analysis are relatively insensitive, have marginal precision, and are frequently time consuming. Instrumentation for the more sensitive techniques is often expensive and elaborate. Spectrophotometric (colorimetric) methods are the most widely employed procedures for arsenic determination. This is true primarily because of their apparent simplicity and their low cost. Again, however, these methods are limited in terms of sensitivity, and they require considerable skill and attention on the part of the analyst. An excellent review of methods for the determination of arsenic has been published.[1]

OSHA's recently enacted standard for arsenic in air in the work environment sets an "action level" of 5 μg As/m^3. When exposure reaches this level, the employer must begin to measure and record exposure and implement certain medical surveillance requirements. Measurement of arsenic concentrations in workers' urines is the most commonly employed procedure for ascertaining undue arsenic exposure. The current NIOSH recommended method (P & CAM 140)[2] for determining arsenic in urine is an arsine generation-colorimetric (silver diethyldithiocarbamate) technique. The range of this method for 25 ml of urine is from 0.01 mg/l to 1.0 mg/l. Evolution time for arsine generation is 30 minutes per sample, thus necessitating the use of several pieces of apparatus for multiple samples. Also, this procedure employs the use of pyridine, a foul-smelling solvent, for collection of arsine although it has been shown that l-ephedrine in chloroform may be used as a solvent for the silver diethyldithiocarbamate in arsenic determinations.[3]

The determination of arsenic concentrations in workers' blood specimens may also serve as a monitor of arsenic exposure. Arsenic in whole blood has been measured[4] by an arsine generation atomic absorption procedure and a level of 4 ppb by weight has been reported. The investigators claimed that the level compares favorably with cited levels of "normal" blood arsenic content.[5] This technique required 5 ml of whole blood in order to obtain enough arsenic to fall within the sensitivity range of their

method. Drawing quantities of blood of this volume or larger (10 ml for duplicate analyses) is an undesirable feature for any screening program or routine monitoring system when other tests may also be necessary. Duplicate measurements of normal levels of arsenic in blood would require 30-300 ml of sample per individual for most spectrophotometric methods.

This paper describes a new analytical method for the determination of total arsenic in biological samples, such as urine and blood, at ppb concentration levels. The method described requires only 2 ml of blood and 1 ml of urine and is based on anodic stripping voltammetry (ASV), an electroanalytical technique. A detailed discussion of ASV is beyond the scope of this paper. Several excellent review articles and books have been written on the techinque.[6-9]

Basically, anodic stripping voltammetry is an electroanalytical technique consisting of two distinct steps. The first step is a preconcentration procedure and consists of the electro-deposition of metal ions of interest in the solution onto an electrode for a fixed period of time while the solution is stirred to increase the efficiency of collection by the electrode. Following the preconcentration step, the potential applied to the electrode is scanned in a positive direction and metals deposited at the electrode are reoxidized into solution giving a resulting peak-shaped oxidation current-time curve. Analytic concentration factors of several thousand fold are routinely achieved during the deposition step. Consequently, the magnitudes of the oxidation (stripping) currents are considerably greater than the corresponding currents which would result from the direct reduction of the metal ions in solution. Analysis is accomplished by a direct correlation of the peak-shaped stripping signal (area or peak height) with the amount of analyte in solution.

Determinations of part-per-million (ppm) levels of arsenic by anodic stripping voltammetry were pioneered by investigators in the U.S.S.R.[10,11] In the U.S., one investigator[12,13] has determined arsenic at the part-per-billion (ppb) level by anodic stripping voltammetry using a small-area gold wire electrode. His detection limit was 0.02 ng/ml (0.02 ppb) for inorganic standards prepared with deionized water when using a plating time of 20 minutes. Other workers[14] have employed a gold film plated on a wax-impregnated cylindrical graphite rod to quantitatively measure arsenic in fish samples and the N.B.S. Standard Reference Material, Orchard Leaves. These latter workers reported that their method gave results for arsenic in the acid-digested samples which agreed favorably with results obtained by hydride evolution-atomic absorption spectroscopy and neutron activation analysis. All of the ASV procedures described above were subject to varing levels of interference which could become significant in real samples.

The electroactive form of arsenic under the conditions employed for anodic stripping voltammetry is the arsenic (III) ion. Therefore, prior to analysis, arsenic (V) ions must be reduced to arsenic (III). The analysis of very low levels of arsenic by anodic stripping may be subject to interferences from other materials in the sample solution. Thus, a scheme for the separation of arsenic from its matrix is also highly desirable. One procedure which simultaneously accomplishes both goals is the distillation of arsenic trichloride ($AsCl_3$) from a solution of cuprous chloride (Cu_2Cl_2) in concentrated hydrochloric acid (HCl). In this method reduction and distillation are carried out in essentially a single process in a simple apparatus, and we have termed the procedure "reductillation". The volatilized $AsCl_3$ and HCl are collected in deionized water and this resulting solution is then analyzed for its arsenic content by ASV. Development and verification of the arsenic reductillation-ASV analysis procedure has been presented elsewhere.[15]

experimental

apparatus and chemicals

An Environmental Sciences Associates, Inc., Model 3010A Trace Metals Analyzer (TMA) was used throughout this study for all ASV measurements. This instrument utilized a special staircase potential scan for the stripping scheme in which the potential of the electrode was advanced in a series of discrete voltage steps in a

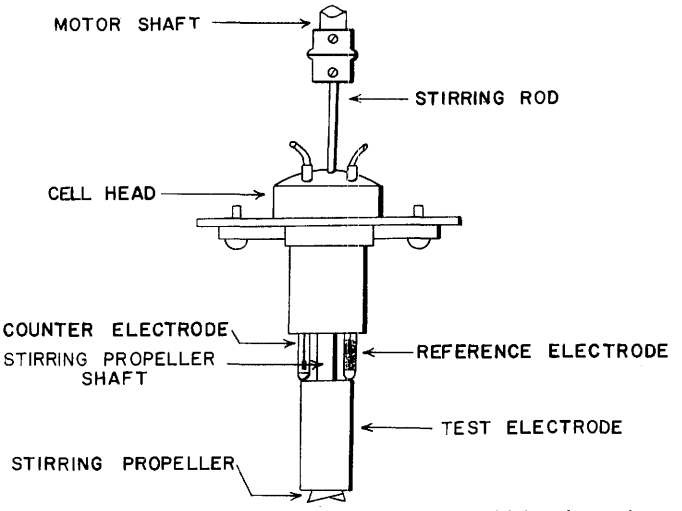

Figure 1 – Schematic diagram of the high-sensitivity electrode.

positive-going direction. Staircase stripping effectively resolved the analytical stripping signal from the total current which can contain considerable "noise" due to current associated with the capacitive charging of the electrode-solution interface. The Model 3010A TMA was capable of integrating the peakshaped stripping signal and providing a direct digital readout of the integrated signal and could be calibrated to give a digital display in any desired units of arsenic concentration.

The electrode employed in this work was the ESA 3010/3010A High Sensitivity Electrode Assembly (ESA Part No. 3600-01). Figure 1 is a schematic drawing of the electrode assembly. The insolubility of arsenic in mercury precluded the use of the mercury film electrode commonly employed in ASV analysis of heavy metals. The best electrode material found to date for the ASV analysis of arsenic is gold. Thus, the working electrode for arsenic ASV consisted of a thin film of gold plated on the upper, inner surface of the pyrolytic graphite tube. The useable life-times of gold electrodes prepared in this manner ranged from days to weeks. When the electrode could no longer provide a useable signal (i.e., when it had limited sensitivity), it was possible simply to replate the thin gold film. The gold film was plated following instructions of the electrode manufacturer.[16]

Basically, 1 mg of gold as $AuCl_3$ (100 μl of 10^{-2} g Au/ml stock solution) was plated onto the graphite substrate from a matrix of 0.5 *F* HCl at a plating potential of -0.150 V *vs.* Ag/AgCl (sat'd. NaCl) reference electrode. Total plating time was about 90 minutes with plating from an unstirred, quiescent solution except for short 10-15 second periods of stirring at 20 minute intervals. The surface area of the active portion of the High Sensitivity Electrode was approximately 3 cm^2.

The reference electrode was a Ag/AgCl (sat'd. NaCl) electrode isolated from the analyte solution by a porous Vycor® plug. The reference compartment was filled with saturated sodium chloride and some sodium chloride crystals to maintain saturation.

The counter electrode was a platinum wire which was also separated from the sample matrix solution by a porous Vycor plug. The counter electrode compartment was filled with 0.1 *F* $N_2H_4 \cdot 2HCl$.

Analytical solutions were stirred by a Teflon® stirring propeller and shaft which extended down through the electrode structure and rotated about its longitudinal axis. This stirring geometry produced highly efficient stirring of the solution thus leading to rapid electrodeposition of analyte.

The apparatus used for the reductillation process is illustrated schematically in Figure 2. The digestion-reductillation tube was an 85 mm x 20 mm borosilicate glass tube outfitted with a

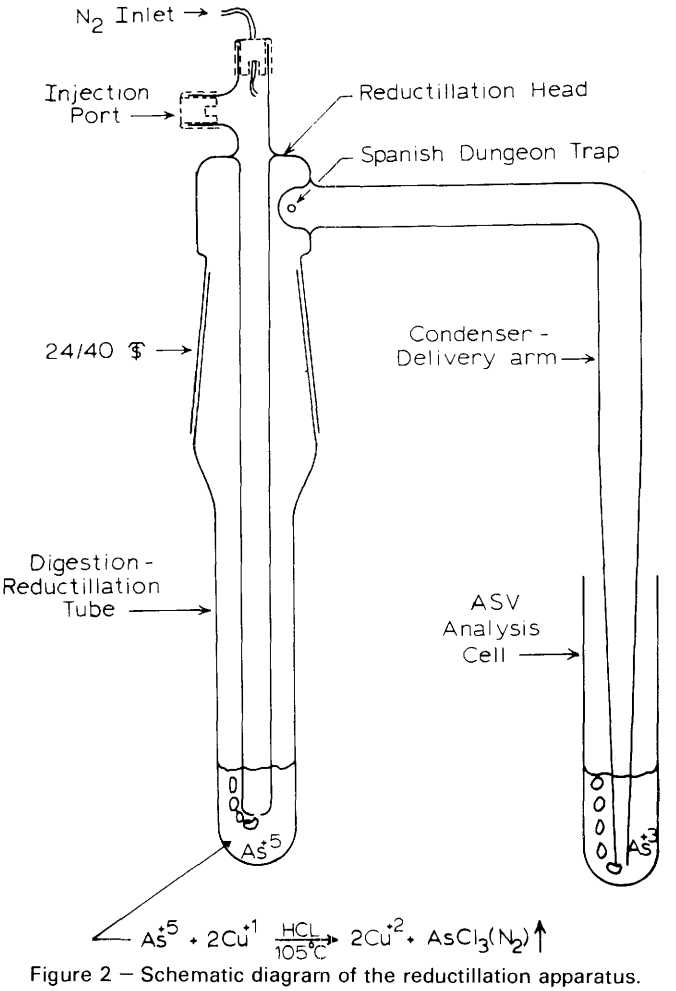

Figure 2 – Schematic diagram of the reductillation apparatus.

24/40 male ground glass joint. The nitrogen delivery tube was an 8 mm O.D. glass tube with the submerged end drawn to an I.D. of about 2 mm. The injection port and nitrogen inlet were outfitted with rubber septums. A Teflon tube forced through a small puncture in the rubber septum and terminated on the opposite end by a Kel-F brand plastic female luer fitting was connected to a supply of nitrogen gas. A length of platinum wire inside the Teflon tubing, with its diameter nearly equal to the I.D. of the Teflon tube, acted as a flow restrictor to the nitrogen. The rate of nitrogen flow was then regulated by adjusting the pressure of the nitrogen supply. Initially, the flow rate was measured by means of a Dwyer Model RMA-11-SSV flow meter which was calibrated by measuring the rate of displacement of water from an inverted graduated cylinder. After these initial measurements, an optimal flow rate of 144 cc/min (STP) was reproducibly obtained by operating at 10 psig nitrogen pressure. The condenser-delivery arm was an 8 mm I.D. glass tube tapered to an I.D. of about 2 mm at the delivery end. The "Spanish Dungeon" trap was a 2-4 mm hole which acted to prevent physical carry-over of fine droplets produced by the bubbling action of the nitrogen. The reductillation head was outfitted with a female 24/40 ground glass joint which matched with the joint of the digestion-reductillation tube. The ASV analysis/collection cell was a 75 mm x 18 mm electrochemical cell (ESA Part No. 3010-41). The analysis/collection cell contained four milliliters of deionized water which served to trap the $AsCl_3$ and HCl vapors swept from the

reductillation apparatus by the flow of nitrogen gas.

Deionized water was produced by a train of commercial Culligan brand carbon filters and ion exchange beds. Deionization efficiency of this system was monitored by conductivity measurements. Reagent grade hydrochloric acid was purchased from J.T. Baker Chemical Co., Phillipsburg, N.J. "Electrolytic purified" grade copper metal powder and reagent grade arsenic trioxide, sodium chloride, and hydrazine dihydrochloride were obtained from Fisher Scientific Co., Fairlawn, N.J. Cuprous chloride, 95%, was obtained from Ventron Corporation, Danvers, Mass. High purity gold metal, 99.99%, was purchased from Research Organic/Inorganic Chemical Corp., Sun Valley, CA. Reagent grade sodium arsenate was from Mallinckrodt Chemical Works, St. Louis, MO. Sodium hydroxide (Mallinckrodt Chemical Works) used in titrations of HCl solutions was standardized against potassium hydrogen phthalate (Fisher Scientific Co.). Nirtic, perchloric, and sulfuric acids used in the wet digesion of samples were obtained from G.F. Smith Chemical Co., Columbus, Ohio.

A stock solution 10^{-2} g Au/ml was prepared by dissolving 1 g of high purity gold in a minimum of aqua regia. Then, an excess of HCl was added and the solution gently deaerated with N_2 gas to expel chlorine from the liquid. The resulting gold solution was diluted to 100 ml with deionized water.

A standard solution containing 10^{-2} g As(III)/ml was made by dissolving 1.320 grams of As_2O_3 in 5 ml of 10 *F* NaOH, adding 25 ml of 37% HCl, and diluting the solution to 100 ml with deionized water.[17] Standard solutions at the 10^{-4} g As(III)/ml and 10^{-6} g As(III)/ml levels were prepared as required. The 10^{-4} g As(III)/ml standard was stable for at least one month, the latter for at least one week.

4.164 g of $Na_2HAsO_4 \cdot 7H_2O$ was dissolved in 40 ml of deionized water, acidified with 0.5 ml of 95% H_2SO_4 (G.F. Smith Chemical Co., Columbus, Ohio; doubly distilled from Vycor glass) and diluted to 100 ml with deionized water. This gave a stock solution of 10^{-2} g As(V)/ml.[17] Working standard solutions (10^{-4} g and 10^{-6} g As(V)/ml) were prepared as required from the 10^{-2} g As(V)/ml stock solution.

10% cuprous chloride in HCl was prepared and purified according to available instructions.[18] The Cu_2Cl_2 solution was stored in a capped, clear pint bottle containing some copper metal (about 10-40 g) and a stirring bar coated with Teflon TFE Fluorocarbon Resin. The solution, which became dark and opaque due to oxidation of Cu(I) ions to Cu(II) ions on exposure to air, was placed on a magnetic stirrer and stirred for about 1 hour. During this time the solution became clear or slightly straw colored since the excess Cu metal reduced Cu(II) ions back to Cu(I). The solution was then ready for use.

To use the solution, the bottle was uncapped and about 0.7 ml of the reagent was quickly pipeted into each reductillation tube containing the ashed sample reconstituted with 6 ml of 37% HCl. Exposure of the Cu_2Cl_2 solution to air again caused it to darken each time the bottle was opened. However, the solution could be cleared again by recapping the bottle and stirring the solution with copper metal. The Cu_2Cl_2 reducing reagent may be used with a slight or mild coloration, but it should not be used when it is dark and opaque. Repeated opening of the storage bottle and subsequent air oxidation of the Cu(I) will accelerate the slow dissolution of copper metal in the bottle. This process can lead to a slowly increasing blank due to arsenic present in the copper metal.

During the latter part of our investigations, prepackaged vials were obtained from ESA, Inc., 45 Wiggins Ave., Bedford, MA, 01730, containing 6 ml of arsenic free 1% Cu_2Cl_2 in 37% HCl. Each vial provided the reagent necessary to reconstitute and reduce one wet-ashed sample.

procedure

Aliquots of blood, 2 ml, were wet ashed prior to reductillation and analysis. First, 2 ml of concentrated nitric acid were added to the 2 ml blood sample in a digestion/reductillation tube. The blood-acid mixture was immediately swirled vigorously in the tube to break up precipitated protein globules. The tube was then heated cautiously on a hot plate with a surface temperature of about 150° C. As foam developed and rose toward the top of the tube, the bottom

of the tube was cautiously tapped against the workbench surface to break up the foaming action. After about 10 minutes of this process, the rapid foaming ceased. Then, the sample was allowed to boil for about 5 minutes and finally 2 ml of an acid mix consisting of HNO_3, $HClO_4$, H_2SO_4 (23:23:1) were added. The tube was then placed in a specially constructed aluminum heating block (ESA Part No. 3600-12). This block had 30 round wells, each of which accepted one digestion/reductillation tube. The wells were deep enough that almost the entire length of the digestion/reductillation tubes were in contact with the well walls. This arrangement provided for an even heating of the walls of the tubes with a resultant decrease in reflux action and a faster rate of liquid evaporation. The samples were heated to near dryness and then allowed to cool to room temperature.

Following wet ashing of the blood samples, the As(V) residue in the digestion/reductillation tubes was reductillated to convert As(V) to As(III) and to separate the As(III) from other ions in the sample matrix. First, the As(V) residue was dissolved by adding 6 ml of 37% HCl to each tube. This was followed by 0.7 ml of 10% cuprous chloride reagent. Each of 4 reductillation tubes were then fitted to a reductillation head and each reductillation apparatus placed in a four-place reductillation/digestion block (ESA Part No. 3600-13). At the same time, the tip of each condenser arm was immersed to near the bottom of a 4 ml volume of deionized water in the analysis/collection cell. Adjustment of the depth to which the condenser tips extended in the collection tubes was accomplished by means of a lab jack on which the collection tubes were positioned.

The reductillation heating block was heated to a steady-state optimal temperature of 105° C prior to beginning reductillation of samples. However, the process of evaporation of HCl and water from the reductillation tube and heating of the N_2 gas during reductillation removed considerable heat from the heating block. Thus, it was necessary to adjust the hot plate setting upward from its initial equilibrium setting while reductillating samples.

The reconstituted samples were heated for 1 minute without any nitrogen flow through the solutions to allow time for the solutions in the tubes to come to temperature more rapidly. Then, the nitrogen flow was initiated and continued for 11 minutes. At the end of the 12-minute reductillation process, the delivery tube was removed from the collection liquid while the reductillation apparatus was removed from the heating block, and then the nitrogen flow was stopped.

The solution in the analysis/collection cell was then analyzed for its arsenic content by first adding 0.50 ml of 37% HCl (to adjust the volume and HCl concentration (see below) of the collection liquid) and then performing an ASV analysis on the solution with the Model 3010A TMA. Analysis time on the TMA was 2 minutes. Deposition potential was -0.150 V *vs.* Ag/AgCl and stripping potential scan rate was 100 mv sec^{-1}. The Model 3010A TMA was calibrated [18] to give a direct digital readout in nanograms arsenic in 7 *M* HCl.

The analysis of urine, water, and wine samples followed the digestion of 1 or 2 ml aliquots of the liquid with an equal quantity of HNO_3, $HClO_4$, H_2SO_4 (23:23:1) acid mix. National Bureau of Standards Orchard Leaves and Bovine Liver standard reference materials and the collaborative ketchup sample were digested with enough acid mix to affect destruction of all organic matter. The digested samples were then reconstituted with 37% HCl and an aliquot was taken for analysis.

results and discussion

Arsenic is not amenable to analysis by anodic stripping voltammetry at the hanging mercury drop or mercury film electrodes because of the insolubility of arsenic in mercury. The best electrode material found to date is gold. In this study, a thin film of gold plated on a pyrolytic graphite substrate served as a working (sensing) electrode. Use of this electrode in conjunction with a supporting electrolyte of hydrochloric acid resulted in analytically useful stripping signals such as those shown in Figure 3 for the analysis of arsenic in wine. The spikes on either side of the stripping peaks are integration markers indicating the "window" within which the signals are integrated.

Table I shows that the analytical stripping signal morphology is a function of the

TABLE V
ASV Analysis of Arsenic in Standards and Collaboratively Studied Samples

Sample	Sample Designation	ASV Results (ppm As)	Certified Value or Group Average (ppm As)
Orchard Leaves	N.B.S. S.R.M. no. 1571	10.14	10.0±2.0
Bovine Liver	N.B.S. S.R.M. no. 1577	0.057	0.055
Collaborative Ketchup	"Control"	0.006	0.011
Collaborative Ketchup	"Spiked" +0.13 ppm	0.12	0.11
E.P.A. no. 1	U.S. E.P.A.	0.024	0.026
E.P.A. no. 2	U.S. E.P.A.	0.102	0.109
E.P.A. no. 3	U.S. E.P.A.	0.147	0.154
E.R.A.	Commercial Standard no. 1762	0.097	0.110
E.P.A. no. 1	Diluted 1:10	0.0025	0.0026
E.P.A. no. 2	Diluted 1:10	0.010	0.011
E.P.A. no. 3	Diluted 1:10	0.014	0.015

levels of arsenic requires some knowledge of the efficiency of the reductillation of several levels of arsenic. Reductillation efficiency was determined by reductillating quantities of arsenic from 10 ng to 1 mg. Dilutions of the collection solution with 7 *M* HCl were made where necessary. The data in Table IV show the excellent collection efficiency of the 4 ml of deionized water in the collection/analysis cell over the wide range of arsenic levels used.

The accuracy of the reductillation-ASV technique was evaluated by analyzing several samples of "known" arsenic content (Table V). Samples analyzed were National Bureau of Standards Standard Reference Materials (S.R.M.), Environmental Protection Agency water standards, and a ketchup sample which was analyzed in conjunction with a round robin arsenic analysis. The agreement between values obtained by the method under development and the accepted, or target, values for the standards was excellent. In addition, the freedom from interferences from numerous cations and anions is evident since rather high levels of potential interferants were present in these standards.

TABLE VI
Recovery of Biologically Important Species of Arsenic from Whole Blood

Chemical Species	ppb As Added	ppb As* Found	%Recovery
Arsenic III	5.0	5.0	100
Arsenic III	10.0	9.8	98
Arsenic III	16.7	16.5	99
Arsenic III	50.0	49.8	100
Arsenic III	100.0	97.2	97
Arsenic V	27	28	105
Dimethylarsinic Acid (Cacodylic Acid)	22	23	105
Methylarsonic Acid	13	13	100

*Average of Duplicate Determinations

results of blood and urine analyses

Recoveries of arsenic (both inorganic and organoarsenicals) added to 2 ml aliquots of whole blood (Talbe VI) were excellent, even for a 5 ppb over-spike. The precision of the technique for the analysis of total arsenic in whole blood is shown by the data in Table VII. Tabulated results are for eight replicate runs of each sample. The data in these two tables indicate that the reductillation-ASV technique is definitely applicable to the measurement of arsenic in the blood of industrial workers since only four milliliters of blood would be necessary, even for duplicate analyses.

The most commonly employed method for monitoring the exposure of personnel to arsenic is the quantitative determination of the arsenic level in workers' urines. Evidence has been presented that the human body methylates ingested arsenic and that the primary forms of arsenic in urine are dimethylarsinic acid (cacodylic acid) and methylarsonic acid, with lower levels of inorganic As(III) and As(V) species. The applicability of the reductillation-ASV technique to the analysis of total arsenic in

TABLE VII
Precision of ASV Reductillation Measurements of Arsenic in Blood

	ppb As Found	S.D. (σ)	R.S.D.	%Recovery
Blank	6	2.6	43%	--
Base Blood (B.B.)	0	--	--	--
B.B. + 5 ppb As (III)	5.4	1.6	29%	108
B.B. + 25 ppb As(III)	27	0.9	3%	108
B.B. + 5 ppb As(DMAA)	5.2	1.1	21%	104
B.B. + 25 ppb As(DMAA)	23.9	1.03	4.3%	96

Results are for eight (8) replicate runs of each sample

TABLE VIII
Recovery of Arsenic in Urine Spiked with Dimethylarsinic Acid

Sample[a]	ng As	Avg. ng As	%Recovery
1 ml urine	9, 10	10	--
1 ml urine + 50 ng As	59, 55	57	94
1 ml urine + 100 ng As	100, 103	102	92
1 ml urine + 200 ng As	195, 190	192	91
1 ml urine + 400 ng As	387, 381	384	94
1 ml urine + 600 ng As	557, 554	555	91
		AVG. = 92±2	

[a]ng As added as dimethylarsinic acid, sodium salt

only 1 ml of urine is demonstrated by the data in Table VIII. Percent recovery of arsenic in this case is acceptable in light of the uncertainty in the assay of the dimethylarsinic acid, sodium salt, used to spike the urine and of the uncertainty of the stability of stock solutions of this compound.

conclusions

The effectiveness of a reductillation-ASV procedure for the measurement of total arsenic in blood and urine has been demonstrated. The method is relatively rapid, requiring only 12 minutes for reductillation and a two-minute ASV analysis time. The per sample analysis time can be reduced considerably by reductillating 4 to 8 samples in the same 12-minute interval. Excluding sample wet ashing time, samples can be routinely analyzed for arsenic at the ppb level at a rate of about 12 per hour when 4 reductillations are accomplished simultaneously. The sensitivity of the ASV technique allows the use of small volumes of blood and urine. This is especially important in the case of blood analysis since only a few milliliters are needed, even for duplicate analyses.

The reductillation-ASV procedure has proven to be as accurate, precise, and reliable at the nanogram level as the more universally accepted colorimetric techniques are at the microgram and milligram levels.

acknowledgment

We wish to acknowledge the National Institute for Occupational Safety and Health, NIOSH Contract No. HSM 99-72-107, for financial support during the initial phase of the investigations necessary for the development of this method.

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Accepted December 6, 1977