Determination of Arsenic(III) and Selenium(IV) Using an On-Line Anodic Stripping Voltammetry Flow Cell with Detection by Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry

Jack R. Pretty,* Elmo A. Blubaugh, and Joseph A. Caruso

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172

An on-line anodic stripping voltammetry (ASV) flow system, interfaced with inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICPMS) detectors, has been used for determination of arsenic(III) and selenium(IV) and for elimination of polyatomic interferences which arise from chloride in sample matrices. Details of the working electrode preparation are discussed. Arsenic signals in ICP-AES were enhanced by as much as 10 times through preconcentration of sample volumes up to 5 mL. Using ICP-AES detection, recoveries for analyte spikes in 1:10 diluted urine were 102% for As(III) (matrix-matched standards) and 91% for Se(IV) (standards in electrolyte). Using ICPMS detection, determination of certified Se(IV) and Se(IV) spikes in diluted NIST SRM 2670 elevated urine gave recoveries of 92–103%, while recoveries of As(III) spikes in diluted NIST SRM 2670 urine ranged from 94 to 113%. High levels of chloride matrix exhibited little effect on the arsenic signal with ICP-AES or ICPMS detection. Elimination of the polyatomic interference $ArCl^+$ in ICPMS was very efficient for diluted NIST SRM 2670 urine and for a synthetic matrix of 1000 μg/mL chloride.

INTRODUCTION

There is a continuing demand for analytical methods which allow determination of arsenic and selenium at trace levels in environmental and biological samples. Arsenic exists in various states, with As(III) being the most toxic, followed by the more stable pentavalent form and various organic derivatives.[1,2] Selenium is found in several oxidation states, most commonly Se(IV) or Se(VI). It is apparently a nutritional requirement at trace levels.[3] Selenium deficiency in animal feed results in a variety of diseases in livestock and the populations they supply,[3,4] while an excess produces chronic selenosis resulting in severe toxic symptoms and death. Selenium has been suspected of carcinogenic activity at high levels, although its true role is still disputed.[3]

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is now widely accepted as a method for determination of trace elements. Arsenic and selenium emission lines are relatively weak and are mainly in the near-ultraviolet region of the spectrum,[5] where the photomultipliers and monochromator gratings in ICP-AES units often exhibit less than optimal performance. Detection limits of less than 100 pg/mL have been quoted for arsenic in inductively coupled plasma mass spectrometry (ICPMS)[6]. However, the common matrix constituent chloride gives rise to polyatomic ions including $^{40}Ar^{35}Cl^+$ at $m/z = 75$,[7] which overlaps monoisotopic arsenic and interferes with its determination at trace levels. Most selenium isotopes are overlapped by polyatomic ions derived from argon, with the most abundant isotope at $m/z = 80$ suffering severe interference from the dimer of ^{40}Ar.[7] The Ar_2H^+ signals at $m/z = 77$ and 82 are less intense, but the corresponding selenium isotopes are of lower abundance (7.58 and 9.19%, respectively). They are also subject to interferences from sulfur trioxide, CCl_2^+ and Kr^+ at $m/z = 82$,[8] and $^{40}Ar^{37}Cl^+$ at $m/z = 77$.[7]

The relative insensitivity of arsenic and selenium in ICP-AES has prompted investigation of signal enhancement techniques. The method of hydride generation can provide much lower detection limits,[1,9-12] but requires considerable operator attention.[9,13] Various modifications permit state-specific detection of arsenic with the hydride method.[1] Arsine generation has also been used in tandem with ICPMS for signal enhancement and matrix elimination.[14] Selenium has been analyzed in a similar manner, but can be rendered inactive to reduction to the hydride by interaction with various metals.[10] Methods which combine chromatography with ICP, designed for arsenic speciation, can sometimes also eliminate matrices.[15,16] However, chloride can saturate some types of chromatographic column at moderate levels, leading to incomplete elimination of $ArCl^+$ and influencing chromatographic resolution.[16]

Previously, an anodic stripping voltammetry (ASV) flow system incorporating a reticulated vitreous carbon (RVC)

* To whom correspondence should be addressed. Present address: National Institute of Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226.

(1) Cullen, W. R.; Dodd, M. *Appl. Organomet. Chem.* **1988**, *2*, 1.
(2) Stojanovic, R. S.; Bond, A. M.; Butler, E. C. V. *Anal. Chem.* **1990**, *62*, 2692.
(3) Andrews, R. W.; Johnson, D. C. *Anal. Chem.* **1975**, *47*, 294.
(4) Jarzabek, G.; Kublik, Z. *Anal. Chim. Acta* **1982**, *143*, 121.
(5) Winge, R. K.; Peterson, V. J.; Fassel, V. A. *Appl. Spectrosc.* **1979**, *33*, 206.
(6) Horlick, G.; Tan, S. H.; Vaughan, M. A.; Shao, Y. In *Inductively Coupled Plasmas in Analytical Atomic Spectrometry*; Montaser, A.; Golightly, D. W., Eds.; VCH Publishers, Inc.: New York, 1987.
(7) Tan, S.; Horlick, G. *Appl. Spectrosc.* **1986**, *40*, 445.
(8) Lyon, T. D. B.; Fell, G. S.; Hutton, R. C.; Eaton, A. N. *J. Anal. At. Spectrom.* **1988**, *3*, 265.
(9) Hwang, J. D.; Huxley, H. P.; Diomiguardi, J. P.; Vaughn, W. J. *Appl. Spectrosc.* **1990**, *44*, 491.
(10) Dennis, B. L.; Moyers, J. L.; Wilson, G. S. *Anal. Chem.* **1976**, *48*, 1611.
(11) Thompson, K. C.; Thomerson, D. R. *Analyst* **1974**, *99*, 595.
(12) Thompson, M.; Pahlavampour, B.; Walton, S. J.; Kirkbright, G. F. *Analyst* **1978**, *103*, 568.
(13) Davis, P. H.; Dulude, G. R.; Griffin, R. M.; Matson, W. R.; Zink, E. W. *Anal. Chem.* **1978**, *50*, 137.
(14) Heitkemper, D. T.; Caruso, J. A. *Appl. Spectrosc.* **1990**, *44*, 228.
(15) Morita, M.; Uehiro, T.; Fuwa, K. *Anal. Chem.* **1981**, *53*, 1806.
(16) Sheppard, B. S.; Shen, W. L.; Caruso, J. A.; Heitkemper, D. T.; Caruso, J. A. *J. Anal. At. Spectrom.* **1990**, *5*, 431.

0003-2700/93/0365-3396$04.00/0

working electrode was developed for on-line use with ICP-AES and ICPMS detectors.[17] This system has been successfully used for quantitation of several transition metals and provides efficient elimination of various undesirable matrix species, along with enhancement of analyte signals up to 65 times above continuous nebulization levels via preconcentration from sample volumes up to 20 mL.[18,19] These capabilities would clearly be beneficial in the analysis of arsenic and selenium by ICP-AES or ICPMS. The ASV flow system was therefore adapted for this purpose.

As(III) and Se(IV) are electrochemically responsive in most electrolytes while As(V) and Se(VI) are not,[20-24] permitting state-specific determination. Acidic media are recommended for both analytes, which deposit as the elements.[3,20,24] Solid electrodes are used, since the stripping currents of the analytes appear at positive potentials equal to or greater than that of mercury.[25] Arsenic is also insoluble in mercury.[13,26] Gold electrodes are often chosen over platinum for ASV of arsenic, because the enhanced reversibility of the As(III)/As(0) couple and the superior overvoltage of gold at low pH provide higher sensitivity.[20] Most ASV of selenium has also been performed at gold electrodes.[3,23,24] The working electrode of the ASV flow cell was therefore plated with gold as described below.

EXPERIMENTAL SECTION

Apparatus. Previous reports have described construction and use of the ASV flow cell and the supporting manifold of valves and tubing.[17,18] All potentials are reported relative to Ag/AgCl. After deposited analytes are stripped from the electrode, the output of the ASV cell was monitored using ICP-AES (ICP-2500, Plasma-Therm, Kresson, NJ) and ICPMS (VG PlasmaQuad, VG Elemental, Winsford, Cheshire, UK). Further information on these instruments and their support hardware has previously been provided.[17,18,27] Parameters of operation for both ICP units are listed in Table I. Voltammograms for ASV–ICP-AES work were traced on an x–y recorder (Omnigraph 2000, Houston Instruments, Houston, TX).

Reagents and Standards. Distilled deionized water from a purification system (Barnstead, Boston, MA) was used for all solutions. Stock solutions (1000 μg/mL) wee prepared using sodium arsenite(III) and sodium arsenate(V) (Fisher Scientific, Cincinnati, OH). Selenium(IV) stock solution (10 000 μg/mL) was prepared by dissolving 1.000 g of powdered metal (Fisher) in 1 mL of nitric acid, with immediate dilution to 100 mL to minimize further oxidation of the metal. Stock solutions were diluted as necessary to prepare samples. Ammonium chloride or sodium chloride (reagent grade, Fisher) was used in matrix elimination studies. The electrode was plated with 200 μg/mL gold chloride (atomic absorption standard, Fisher) in 0.1 mol/L hydrochloric acid (reagent grade, Fisher). Nitric acid (doubly distilled, No. 621, GFS Chemicals, Columbus, OH) was used for the samples, the ASV cell supply electrolyte, and the bypass solution that was directed to the ICP unit while ASV cell output was diverted to waste.[18,27] The supply electrolyte and bypass solution were 0.1 mol/L HNO_3.

Procedure. Operation of the anodic stripping voltammetry flow system was as previously described,[18] with one simplification; the ASV cell supply electrolyte was continually degassed with helium but was used at room temperature. Flow rate for delivery of sample to ASV cell was 1.02 mL/min, and flow rate for washout of cell and for delivery of cell output to the ICP was 1.70 mL/min, unless otherwise noted. Volume of sample injected into the flow system was 1 mL, except as noted during signal enhancement studies.

Table I. Operating Conditions for ICP Instruments

ICP-AES	
radio frequency power	
forward	1.0 kW
reflected	<5 W
gas flows	
coolant	14.4 L/min
auxiliary	0.7 L/min
nebulizer	1.05 L/min
observed wavelengths	
arsenic	228.82 nm
selenium	206.27 nm
observation height	15 mm above load coil
monochromator slits	50 μm (entrance and exit)
integration time	1 s for each data point
ICPMS	
radio frequency power	
forward	1.3 kW
reflected	<5 W
gas flows	
coolant	13.0 L/min
auxiliary	1.0 L/min
nebulizer	0.658 L/min
spray chamber	Scott-type double pass, cooled
sampling cone	nickel, 1.0-mm orifice
skimmer cone	nickel, 1.0-mm orifice
sampling distance	10 mm from load coil
data acquisition	
single ion monitoring	
sweeps	1
dwell time	655, 360 μs
channels	4095
run time	2684 s
time resolved acquisition	
dwell time	1280 μs
channels	512
mass range	74–78 m/z units

Gold was plated onto the working electrode of the ASV cell using a procedure adapted from the literature.[13] Since the gold deposited on carbon as a brown powder from stirred solution and as a finer yellow plate from quiescent solution, the plating was done in cycles. Gold chloride (200 μg/mL in 0.1 mol/L HCl) was pumped into the ASV cell with the potentiostat at open circuit. Flow was halted and the circuit closed (potential at −0.15 V). When the reductive current dropped to a low level, the circuit was opened and more plating solution was pumped into the cell. Twenty cycles were run with solution delivered to the ASV cell in forward direction and 20 cycles with solution delivered in the reverse direction to try to distribute gold more evenly through the RVC, as had been done for mercury plating in earlier studies.[17]

Viewing the electrode through the plastic ASV cell half showed that gold was not plated evenly regardless of how many cycles were used. Some portions of the RVC plated well while others had an uneven, less lustrous appearance. The heavy gold deposit is difficult to remove electrolytically due to oxide formation, so plated electrodes were removed from the ASV cell when analytical sensitivity declined (see below). When these were examined, it was evident that pockets within the RVC disk were virtually gold-free. This may be due to deposition being blocked by contamination or to uneven distribution of plating solution within the ASV cell. Alternatively, the very high current present during plating may have resulted in Ohmic potential drops, so that not all parts of the electrode experienced the same potential.

After plating, any remaining gold solution was flushed from the cell with the supply electrolyte. Potential was cycled between +1.0 and −0.5 V, the latter being the most negative potential for which hydrogen gas generation was not observed at the RVC. Once the current response of these scans became reproducible,

(17) Pretty, J. R.; Evans, E. H.; Blubaugh, E. A.; Shen, W. L.; Caruso, J. A.; Davidson, T. M. *J. Anal. At. Spectrom.* **1990**, *5*, 437.
(18) Pretty, J. R.; Evans, E. H.; Blubaugh, E. A.; Caruso, J. A.; Davidson, T. M. *J. Anal. At. Spectrom.* **1992**, *7*, 1131.
(19) Pretty, J. R. and Caruso, J. A. *J. Anal. At. Spectrom.*, in press.
(20) Forsberg, G.; O'Laughlin, J. W.; Megargle; Koirtyohann, S. R. *Anal. Chem.* **1975**, *47*, 1586.
(21) White, M. C.; Bard, A. J. *Anal. Chem.* **1966**, *38*, 61.
(22) McCrory-Joy, C.; Rosamilla, J. M. *Anal. Chim. Acta* **1982**, *142*, 231.
(23) Adeloju, S. B.; Bond, A. M.; Briggs, M. H.; Hughes, H. C. *Anal. Chem.* **1983**, *55*, 2076.
(24) Hamilton, T. W.; Ellis, J.; Florence, T. M. *Anal. Chim. Acta* **1979**, *110*, 87.
(25) Holak, W. *Anal. Chem.* **1980**, *52*, 2189.
(26) Sadana, R. S. *Anal. Chem.* **1983**, *55*, 304.
(27) Pretty, J. R. Ph.D. Dissertation, Department of Chemistry, University of Cincinnati, 1991.

the potential was set at −0.3 V. Current dropped over the next few minutes, and when the current level became steady, the electrode was assumed to be ready for use. This conditioning was performed at the start of every experimental session using gold-plated electrodes. The ASV cell was filled with deionized water when not in use to prevent air from entering the porous electrode.[17]

RESULTS AND DISCUSSION

Aging of Gold-Plated Electrodes. The highest sensitivity for either analyte was always obtained shortly after freshly plating a new RVC electrode. On subsequent days, the ICP-AES analyte peak signals and stripping currents obtained with the same electrode progressively decreased. Plating more gold onto the electrode did not restore response to the original level. Changes in sensitivity have been widely reported with gold electrodes (solid and plated film) in ASV, and many workers apply pretreatments (chemical, potential cycling, polishing) prior to experimental sessions or between sample runs.[13,20,24,28,29] Reports vary concerning the useful lifetime of a gold electrode, but despite pretreatments, declining sensitivity usually forces eventual replacement.[13,24,28,29]

Passivation may have involved oxidation of the gold surface during storage,[20,30] which was not fully eliminated by the potential cycling treatment, gradually reducing the active surface area. Adsorption of organic species, present at ultratrace levels in electrolyte and at higher levels in samples (below) may have played a role,[2,30] although drops in sensitivity occurred regardless of whether complex matrices had been investigated on the previous day. It has also been reported that gold deposits in discrete particles at active sites of a carbon surface and that the condition of the substrate can affect the activity of the gold deposit.[24] Should some portions of the RVC become passivated (by oxidation during use), gold particles plated onto or surrounded by these regions would be electrically isolated. Potential cycling would not restore gold lost in this way, even if effective for reducing oxide films and releasing adsorbed contaminants.[2,28,30] Replating the electrode would not restore original activity, since new metal would plate only at sites that remained active, and the increase in active gold surface area would be small.

Results for Arsenic Using ICP-AES Detection. Many familiar electrolyte media may be used for ASV of arsenic.[20] Preliminary ASV tests indicated that 0.1 mol/L nitric acid was suitable, so this medium (innocuous for use with ICPMS) was used as the sample electrolyte, except in a few tests (below). Dilute perchloric and hydrochloric acids could be tolerated as sample media if completely swept out of the ASV cell by the flow of dilute nitric acid supply electrolyte prior to stripping of deposited arsenic. They are unsuitable as cell supply electrolytes when the ASV cell output is monitored by ICPMS due to resulting $ArCl^+$ signals. Arsenic stripping current peaks appeared at approximately +0.300 V, and stripping potential scans were carried out to +0.600 V.

As(III) at 10 μg/mL was used in the initial tests. As deposition potential was made more negative the arsenic peak response in ICP-AES increased, indicating higher analyte deposition efficiency as others have observed[20] (Figure 1). Because hydrogen gas generation occurred at −0.600 V, −0.500 V was chosen as deposition potential for all arsenic work. ICP-AES peak signals for several replicate runs gave precision of ~1% RSD. Stripping scan rate had little effect since the deposited analyte was stripped into quiescent solution (flow through the ASV cell was briefly halted with a valve while

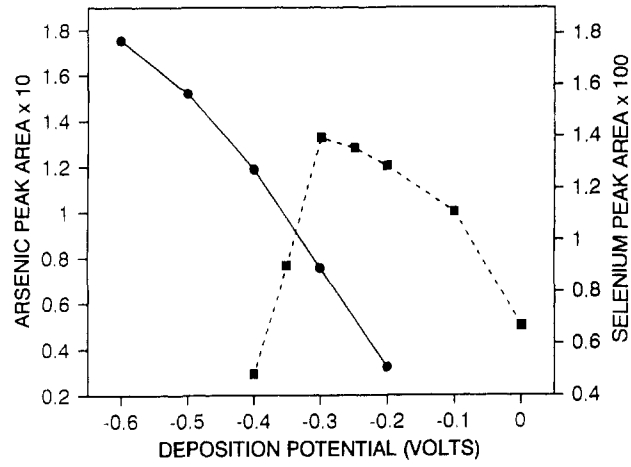

Figure 1. Deposition potential versus ICP-AES peak area for As(III) and Se(IV). Samples, 10 μg/mL As(III) or Se(IV) in 0.1 mol/L HNO_3 electrolyte. Peak area units are arbitrary; different scales reflect relative intensities of analyte signals in ICP-AES. Solid line, As(III); dashed line, Se(IV).

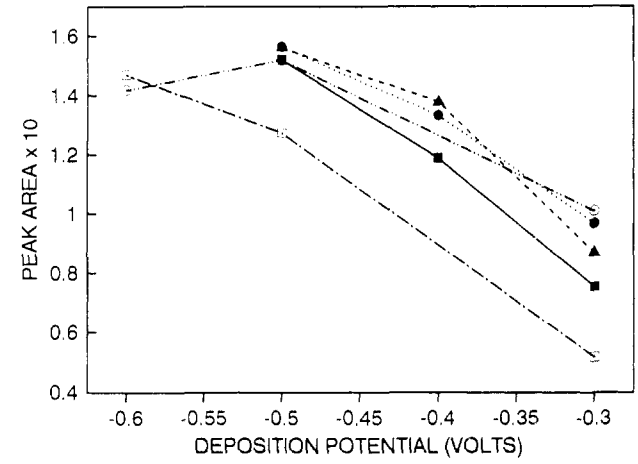

Figure 2. Deposition potential versus ICP-AES peak area for 10 μg/mL As(III), using various concentrations of HNO_3 and HCl as sample electrolyte. ASV cell supply electrolyte is 0.1 mol/L HNO_3 for all. Peak area units are arbitrary. Solid square 0.1 mol/L HNO_3; solid triangle 0.5 mol/L HNO_3; solid circle 1.0 mol/L HNO_3; open square 0.1 mol/L HCl.

flow of dilute HNO_3 to the ICP continued[18]). To avoid distorting the current peaks in the voltammograms, 50 mV/s was selected as the maximum scan rate.

Arsenic deposition on gold was reported to become more efficient at higher acid levels.[20] Figure 2 illustrates the effect of sample acid concentration on analytical sensitivity as observed by ICP-AES detection of the ASV cell output. At lower deposition potentials, use of higher levels of nitric acid slightly enhanced the arsenic peak signals, but at −0.5 V all levels that were tested yielded virtually the same result. Similar tests were briefly run using 0.1 and 1 mol/L hydrochloric acid as sample media (ASV cell supply electrolyte was not altered). Neither improved the sensitivity (Figure 2), and 0.1 mol/L nitric acid was used as the sample electrolyte in all remaining work with arsenic.

The effect of sample delivery flow rate was examined with the intention of minimizing the time required to run larger volumes of sample. Times allowed for deposition of arsenic from 1-mL samples were modified in accordance with the flow rate, and the same rate was always used for cell washout and delivery to ICP. Minor drops in deposition efficiency inevitably occurred at faster flow rates, but increasing the rate by more than 4 times only moderately reduced the size of ICP-AES arsenic peak signals (Table II).

(28) Bodewig, F. W.; Valenta, P.; Nurnberg, H. W. *Fresenuis' Z. Anal. Chem.* **1982**, *311*, 187.
(29) McLaughlin, K.; Boyd, D.; Hua, C.; Smyth, M. R. *Electroanalysis* **1992**, *4*, 689.
(30) Johnson, D. C.; LaCourse, W. R. *Anal. Chem.* **1990**, *62*, 589A.

Table II. Selected Results for Arsenic(III) Using Gold-Plated Electrode with ICP-AES Detection[a]

	height	area
Effect of Flow Rate of Sample[b] to ASV Cell on As Response (n = 2)		
0.48 mL/min	5.96×10^{-3}	1.67×10^{-1}
1.02 mL/min	5.58×10^{-3}	1.60×10^{-1}
1.59 mL/min	5.23×10^{-3}	1.54×10^{-1}
2.15 mL/min	4.55×10^{-3}	1.43×10^{-1}
max decr vs signal for 0.48 mL/min (%)	23.7	14.4
Demonstration of Specificity for As(III) (n = 4)		
1 μg/mL As(III)	2.12×10^{-3} (1%)	2.77×10^{-2} (5%)
1 μg/mL As(III)/10 μg/mL As(V)	2.19×10^{-3} (3%)	2.87×10^{-2} (3%)
incr for mixture (%)	3.3	3.5
Response for 1 μg/mL As(III) in Chloride Matrices (n = 4)		
electrolyte only	2.12×10^{-3} (1%)	2.77×10^{-2} (5%)
+ 1000 μg/mL Cl	2.06×10^{-3} (3%)	2.92×10^{-2} (1%)
+ 10 000 μg/mL Cl	1.71×10^{-3} (2%)	2.46×10^{-2} (2%)
decr for As in 10 000 μg/mL Cl vs As in electrolyte only (%)	15.7	17.0

[a] Abscissa has no units in ICP-AES signal display; all units for peaks are arbitrary. RSD values in parentheses. [b] Samples were 10 μg/mL As(III).

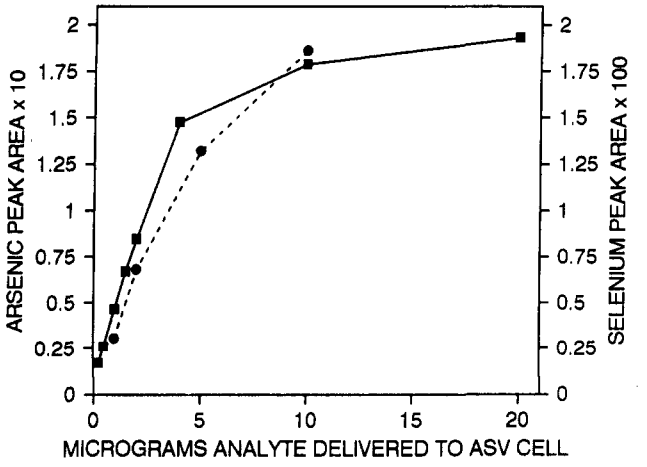

Figure 3. Plots of ICP-AES peak response versus mass of As(III) or Se(IV) delivered to ASV cell. Peak area units are arbitrary; different scales reflect relative intensities of analyte signals in ICP-AES. Solid line, As(III); dashed line, Se(IV).

To demonstrate that detection was specific for trivalent arsenic, results were obtained for 1 μg/mL As(III) with and without 10 μg/mL As(V) also present in the sample. Peak heights and areas observed for the mixture and for As(III) alone are listed in Table II. Mean values for the respective peak areas did not differ significantly (t = 1.28, t_c = 2.45, p = 0.05).

Elemental arsenic is not electrically conductive, and once deposited at an active electrode site, it passivates the location to further deposition of electroactive species,[13,20,28] including more arsenic. Deviations from linearity have been noted in ASV analysis of As(III).[13,20] It was thus necessary to determine the maximum mass of arsenic that could be introduced into the ASV cell before electrode saturation occurred. Figure 3 plots ICP-AES peak response for 0.25–20 μg As(III). The plot levels off above 4 μg, suggesting formation of an arsenic monolayer at this point. The RVC electrode disk used here was ~4 mm thick; it may be expected that changing the electrode size (and the plating efficiency) would alter the linear response range accordingly.

With the range of linearity established, analysis was performed on noncertified urine which was diluted 10-fold with 0.1 mol/L nitric acid and spiked with 1.25 μg/mL As(III). The sample was diluted to minimize possible electrode fouling and to reduce viscosity. Calibration plots covering up to 2 μg/mL were generated using two sets of standards one prepared in supporting electrolyte only, the other prepared in urine diluted 10-fold with electrolyte. Both sets of standards were found to have the same pH. Runs of the electrolyte yielded no detectable arsenic peaks in ICP-AES, but unspiked dilute urine produced a measurable peak, and appropriate corrections were made on sample and standard data.

Calibration plots for both sets of standards were linear, but the slopes of plots generated with standards in electrolyte only were ~36% higher than those generated with matrix-matched standards. By peak height or area, the As(III) recovery was only 0.95 μg/mL (76%) versus electrolyte standards and 1.3 μg/mL (103%) versus matrix-matched standards. Voltammograms showed that the stripping current peaks for replicate runs were very reproducible. Current peaks for the spiked sample were in correct proportion to peaks for matrix-matched standards, but were disproportionately small relative to current peaks for standards in electrolyte only, as observed for the ICP-AES signals. Arsenic deposition efficiency had apparently been altered by the dilute urine matrix. Although the mechanism is not yet understood, comparison with other recovery results (below) suggest that use of an electrode that had been gold-plated a few days prior to experiment may have been a factor.

Determination of Arsenic(III) in ASV–ICPMS. The ASV flow system with ICPMS detection was used to determine arsenic in NIST SRM 2670 (Normal and Elevated Trace metals in Urine), a certified reference material which had responded well in earlier trace metal studies using ASV–ICPMS.[18] No speciation information was provided. Arsenic is generally methylated prior to excretion in human urine,[15] while the state of the arsenic standard added to produce NIST 2670 Elevated Urine was unknown. Pretreatment methods for decomposition of organoarsenic species and reduction of As(V) to As(III) were explored, but the results obtained for synthetic test samples in preliminary ASV tests were inconclusive. Recovery values for As(III) spikes therefore became the primary measure of analytical system performance. Spiked sample data were also used to generate standard addition plots, providing a check on quantitation of any As(III) which might be found in the unspiked urines.

A new RVC electrode disk was plated and conditioned immediately before work began. Urine samples were diluted 10-fold with 0.1 mol/L HNO_3 electrolyte as before. For 1-mL samples, 2 min was allowed for analyte deposition and clearance from the ASV cell, and the cell was flushed with electrolyte for 2 min prior to stripping the deposited arsenic.

Table III. Determination of Arsenic(III) in Tenfold-Diluted NIST SRM 2670 Urine Using ASV-ICPMS[a]

samples	true (ng/mL)	exp (ng/mL)	%
normal urine calib plot		0.7 ± 0.5	
normal urine std addn		0.5 ± 0.1	
normal urine spiked soln 1		4.0 ± 0.6	
spike 1 only	3.6	3.4 ± 0.8	94 ± 22
normal urine spiked soln 2		9.9 ± 0.5	
spike 2 only	9.0	9.2 ± 0.8	102 ± 8.8
elevated urine cal plot		1.4 ± 0.6	
elevated urine std addn		1.4 ± 0.6	
elevated urine spiked soln 1		23.1 ± 0.5	
spike 1 only	19.2	21.7 ± 0.8	113 ± 4.0
elevated urine spiked soln 2		57.8 ± 0.5	
spike 2 only	51.9	56.4 ± 0.8	109 ± 2.2

[a] Most of the arsenic in the urine is present in states other than inorganic As(III) and therefore does not respond; spike recoveries indicate system performance and total certified arsenic values are not listed. Experimental values reported to ±1 standard deviation. $n = 4$ for normal urine, $n = 3$ for all other samples.

A calibration plot was generated with standards ranging up to 100 ng/mL. Runs of the electrolyte gave very small peak signals (RSD 15%). The detection limit, calculated as three times the standard deviation of electrolyte blank peak area divided by plot slope, was 130 pg of As(III) (130 pg/mL for a 1-mL sample). Plot parameters were as follows: calibration plot (m = 14 571 area counts·mL/(s·ng), b = −2257 area counts/s, Se_y = 9949 area counts/s); standard addition for NIST 2670 Normal Urine, same units (m = 14842, b = 7023, Se_y = 2288), standard addition for NIST Elevated Urine, same units (m = 15820, b = 21737, Se_y = 10067).

In Table III, true values are listed only for spikes of As(III), since the uniformly low results for unspiked samples indicated that most of the analyte in NIST urine was not present as As(III) and was therefore unresponsive in ASV. Spike recoveries ranged from 93.6 to 113%. For spikes in normal urine the recoveries were both well within one standard deviation of the true values (Table III). Both spikes in NIST 2670 Elevated Urine gave recovery values above 100%, and the slope of the corresponding standard additions plot was higher than that of the calibration plot. This does not appear to have been due to interference by $ArCl^+$ at m/z = 75, since tests using elevated urine spiked sample 2 later the same day would demonstrate that the ASV flow system provided total elimination of matrix chloride (below). It appears that the deposition efficiency of arsenic at the electrode increased slightly during urine sample analysis.

Results for Selenium in ASV-ICP-AES. All references located for ASV of selenium involved hydrochloric or perchloric acid media. Although no precedent existed in the available literature, all work with selenium was done using a sample medium of 0.1 mol/L nitric acid, as had been done for arsenic. It was presumed that no significant loss in analytical sensitivity resulted in this way.

Gold-plated electrodes in 0.1 M nitric acid exhibited oxidative current at potentials greater than +1.0 V, and the oxide film was reduced on the negative scan at about +0.8 V.[3] Selenium deposits at gold electrodes have been shown to exist as "adsorbed" selenium up to one monolayer coverage, with further deposition yielding a "bulk" selenium layer.[3] Both states have characteristic anodic stripping peaks, with that of adsorbed selenium located at +0.8 to +0.9 V.[3,24] Complete stripping thus required scanning to potentials where gold oxides could be generated. Such oxidation would have to be fully reversed during the negative potential scan which preceded each run of standard or sample, or changes in the extent of electrode passivation could degrade precision. To promote reproducible electrode behavior, each step of the ASV cycle was carefully timed; exactly 2 min was allowed for stripping deposited selenium, and when the potential was returned to the deposition value, 1 min was allowed for reduction of surface oxides prior to injection of the next sample.

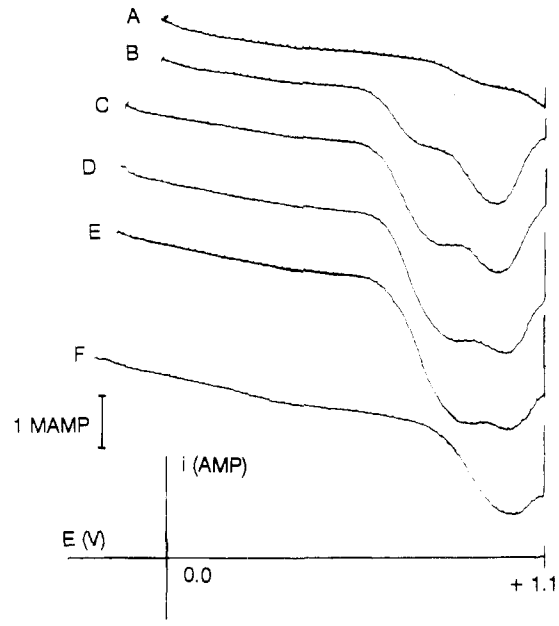

Figure 4. Voltammograms obtained for (A) electrolyte blank at deposition potential 0.0 V and for 10 μg/mL Se(IV) at deposition potentials (B) 0.0, (C) −0.1, (D) −0.2, (E) −0.3, and (F) −0.4 V.

Because selenium exhibits relatively poor sensitivity in ICP-AES, 10 μg/mL Se(IV) was used in the initial tests (stripping scan rate 50 mV/s). A plot of peak response in ICP-AES as a function of potential indicated that deposition efficiency was maximized over a narrow range (Figure 1). Deposition at −0.5 V, the optimal value for arsenic, was substantially less than maximum. In corresponding voltammograms, a shoulder present on one side of the main stripping current peak became more pronounced as deposition efficiency was maximized and then faded as deposition potentials less than −0.30 V were used (Figure 4). This shoulder had a broad maximum at about +0.7 V and was assumed to correspond to stripping of bulk selenium as improved deposition led to saturation of the electrode surface. A final scan potential of +1.1 V proved necessary for efficient stripping of deposited selenium from the electrode. Eight replicates of 10 μg/mL Se(IV) gave RSDs of 1 and 4% for ICP-AES peak height and area, respectively. Voltammograms for replicate runs of 10 μg/mL selenium were equally reproducible.

Calibration plots in ASV deviate from linearity when more than one monolayer equivalent of selenium is deposited.[23,24] This was also evident for the plot of ICP-AES peak response versus mass of Se(IV) delivered to the ASV cell (Figure 3). The deviation was less severe than that found for As(III), possibly because selenium has more metallic character than arsenic, and passivation will be less severe even when active sites on the electrode are saturated.

Noncertified urine was diluted 10-fold in 0.1 mol/L nitric acid, spiked with 5.0 μg/mL Se(IV), and analyzed by ASV-ICP-AES using an electrode which was gold-plated a few days prior to the experiment. A calibration plot was generated using standards of 2 and 5 μg/mL Se(IV) in electrolyte (the blank gave no measurable peak in ICP-AES and was taken as zero). Unspiked urine yielded no signal peak. Spike recovery as determined by peak height or area was 91%. In the corresponding voltammograms, the portion of the stripping current peak attributed to bulk selenium was notably

Table IV. Determination of Se(IV) in Elevenfold-Diluted NIST SRM 2670 Elevated Urine Using ASV–ICPMS with Monitoring at m/z = 82[a]

samples	true (ng/mL)	exp (ng/mL)	%
elevated urine calib plot	41.4 ± 2.7	42.5 ● 2	103 ± 2.2
elevated urine std addn	41.4 ± 2.7	41.8 ± 2	101 ± 5.5
elevated urine spiked soln 1	51.4 ± 2.7	51.7 ± 2	101 ± 4.2
spike 1 only	10.0	9.2 ± 3	92 ± 30
elevated urine spiked soln 2	66.4 ± 2.7	67.6 ± 2	102 ● 3.6
spike 2 only	25.0	25.1 ± 3	100 ± 13

[a] True values reported as ± 95% confidence interval. Experimental values reported to ±1 standard deviation. n = 3 for all samples.

more pronounced for the 5 μg/mL standard than for the 5 μg/mL sample spike, while the portion attributed to adsorbed selenium was about the same size for both. This would suggest that the nonquantitative selenium spike recovery was due to the dilute urine matrix affecting analyte deposition efficiency.

Quantitation of Selenium in ASV–ICPMS. The ASV flow system was also used to determine selenium in NIST SRM 2670 urine with ICPMS detection. Comparison of peak signals for Se(IV) standards at m/z = 77 and 82 indicated that the latter provided higher sensitivity and less baseline noise (an attempt to determine Se(IV) in dilute NIST 2670 urine using m/z = 77 has been discussed elsewhere[27]). A newly plated and conditioned electrode was used. Runs of the electrolyte yielded very small peaks (RSD 10%) and standards ranging up to 100 ng/mL produced a linear calibration plot (m = 1211 area counts·mL/(s·ng), b = −2195 area counts/s, Se_y = 3454 area counts/s). The detection limit was calculated (as described for arsenic) at 1.0 ng/mL.

NIST 2670 Elevated Urine was diluted in the proportion of 2.25 mL of urine in 25 mL total, or ~11-fold (the available supply was not quite sufficient for 10-fold dilution). The NIST 2670 Normal Urine supply had been depleted prior to experiment. No pretreatments were applied to the samples. Results for elevated urine are listed in Table IV. Recoveries were excellent for total selenium and spikes (except spike 1, for which recovery was within one standard deviation of 100%). The result obtained using the standard additions plot (m = 1221 area counts·mL/(s·ng), b = 51052 area counts/s, Se_y = 910 area counts/s) also matched the certified value very well (Table IV).

Generally, analyte recoveries in diluted urine which were determined against calibration standards that were not matrix-matched showed some dependence on the age of electrode plating. ASV–ICP-AES work, performed with electrodes plated a few days prior to experiment, gave nonquantitative recoveries, while ASV–ICPMS work performed with newly plated electrodes gave far better recoveries, especially for selenium. Use of matrix-matched standards with an older electrode did give quantitative arsenic recovery in ICP-AES. In the ASV–ICPMS determination of Se(IV) at m/z = 77,[27] the ASV system had been idle for three days prior to experiment, and analyte recoveries were again very erratic. The use of newly plated electrodes appears to provide better tolerance to sample matrix effects as well as higher sensitivity. However, results for elevated urine in ASV–ICPMS also suggest that newly plated electrodes may exhibit short-term instability. This may indicate that changes at the gold surface in the course of use have their most pronounced effect when electrode response is at its highest overall; when some of the active surface area has been lost through aging, short-term effects are less pronounced.

Signal Enhancement for As(III) in ICP-AES. The relative insensitivity of arsenic in ICP-AES prompted a study

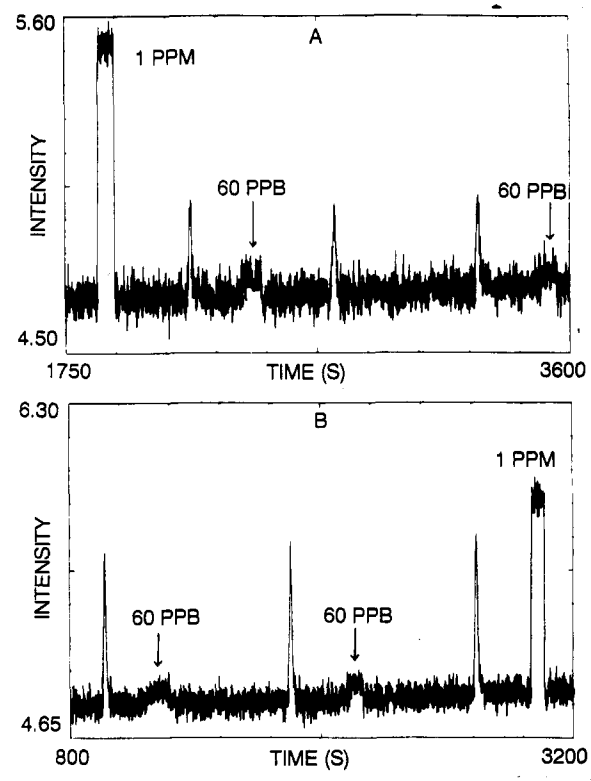

Figure 5. Enhancement of signal for As(III) in ICP-AES. Peak signals from (A) 2 and (B) 5 mL of 60 ng/mL As(III) using ASV flow system. Continuous nebulization signals for 60 ng/mL and 1 μg/mL arsenic are also shown. Display is not smoothed.

of signal enhancement using the ASV flow system. The most sensitive emission wavelength for arsenic that could be observed with the available photomultiplier tube was 228.81 nm. The standard deviation of the baseline (σ_b) was determined from the recorded values for 20 or more successive data points, and a value for sensitivity was estimated as the height of the continuous nebulization signal for 1 μg/mL arsenic. Detection limit in the absence of signal enhancement was then calculated as $3\sigma_b$ divided by the estimated sensitivity. The mean result for two separate files of data was 106 ng/mL without smoothing and 50 ng/mL after smoothing with a nine-point Savitsky–Golay program. The former compared well with a reference value of 83 ng/mL.[5]

For signal enhancement, 2- and 5-mL samples of 60 and 125 ng/mL As(III) were delivered to the ASV cell at a flow rate of 1.02 mL/min. A 2-min deposition time was allowed per milliliter of sample (to compensate for broadening as the sample moved through the system manifold) followed by 2 min of flushing with supply electrolyte at 1.70 mL/min regardless of sample size. The 2-mL volumes thus required 6 min from sample injection to stripping of deposited arsenic, while 5-mL samples took 12 min; 2 and 5 mL of electrolyte produced no detectable signal peaks in ICP-AES.

Peaks obtained with the ASV cell for 2 mL of 60 ng/mL As(III) were visible above baseline without smoothing (Figure 5A). Precision (area RSD 6%, n = 3) was acceptable, given that baseline noise can influence the integration of small peaks. Peaks from 5-mL samples of 60 ng/mL As showed better precision (area RSD 2%, n = 3) and were nearly as high as continuous nebulization signals for 1 μg/mL As (Figure 5B). Peaks obtained with 2 and 5 mL of 125 ng/mL As(III) showed similar enhancements (area RSD, respectively, 2 and 1%, n = 3).

The enhancement factor for any sample volume may be defined here as the ratio of the ICP peak signal height obtained by preconcentration of that volume (using the ASV flow cell) and the ICP continuous nebulization signal height for the

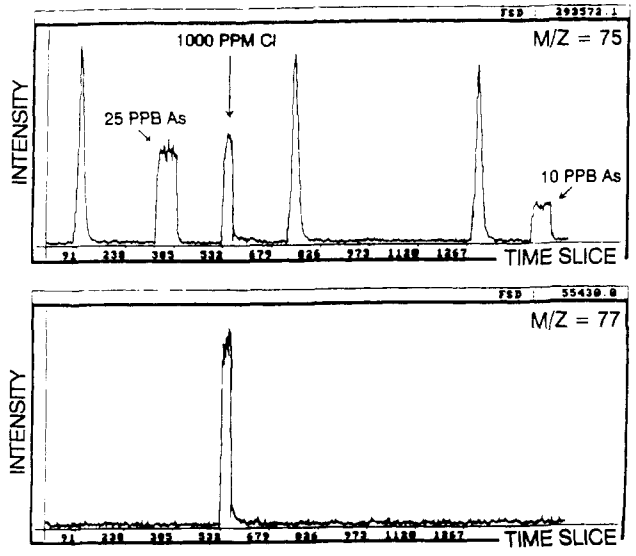

Figure 6. Matrix elimination in ASV–ICPMS for 1:10 diluted NIST SRM 2670 Elevated Urine, spiked solution 2. Simultaneous monitoring at m/z = 75 and 77 using time resolved acquisition software; one time slice unit equals 0.75 s. Scale is not same for both displays. Peak signals for urine sample were obtained using ASV flow cell; continuous nebulization signals as indicated.

level of analyte in the sample. Since 60 ng/mL arsenic was below the calculated detection limit, its continuous nebulization signal height was not read directly but was estimated against that of the 1 μg/mL standard. The mean enhancement factors were 4 for 2-mL samples and 10 for 5-mL samples. Detection limits obtained using the ASV flow cell for preconcentration of a 5-mL arsenic sample can then be estimated as one-tenth of those found in continuous nebulization, or 10 ng/mL without smoothing and 5 ng/mL after smoothing. Use of larger sample volumes would decrease detection limits accordingly, as observed for signal enhancement of other analytes using ASV–ICP-AES.[19]

Elimination of Chloride Matrices. (1) ASV–ICP-AES of As(III) in Synthetic Samples. The effects of high chloride levels on arsenic deposition were initially tested in ASV–ICP-AES. 1 μg/mL As(III) was prepared in (1) electrolyte only, (2) electrolyte and 1000 μg/mL chloride, and (3) electrolyte and 10 000 μg/mL chloride (1% by mass). The reagent was ammonium chloride, which did not alter the sample pH. Due to the high levels of matrix involved, 4 min was allowed for cell washout prior to stripping the deposited analyte. ICP-AES signals for arsenic in 1000 μg/mL chloride did not differ significantly from those found for matrix-free analyte ($t < t_c$, $p = 0.05$), but signals for arsenic in 10 000 μg/mL chloride did show significant decrease (Table II). Continuous nebulization signals for matrix-free 1 μg/mL arsenic (run both before and after the ASV-ICP data were obtained) demonstrated that the efficiency of the ICP nebulizer had not changed. Precision was not degraded by the presence of the matrices (Table II).

Assuming that the matrix reagent contained no significant electroactive impurities, it is not known why 10 000 μg/mL chloride moderately suppressed the arsenic signal. It will be remembered that use of even 1.0 mol/L HCl (~3.5% chloride by mass) as an electrolyte did not depress arsenic deposition efficiency (Figure 2), so the 1% matrix level alone is not likely to be responsible. Acidic chloride media can promote oxidation of gold into complex chlorides at positive potentials.[31] Since chloride could not be monitored in ICP-AES, it had to be assumed that matrix elimination was complete

(31) Wang, J. *Stripping Analysis: Principles, Instrumentation and Applications*; VCH Publishers: Deerfield Beach, FL, 1984.

Table V. Determination of As(III) in Synthetic Samples with High Levels of Chloride Matrix Using TRA Software[a]

sample	area counts/s m/z = 75	area counts/s m/z = 77
electrolyte blank	9286 (7%)	2577 (8%)
50 ng/mL As(III) in electrolyte only	28324 (5%)	3339 (4%)
50 ng/mL As(III) corrected	19038 (8%)	762 (33%)
1000 μg/mL chloride in electrolyte	10028 (4%)	2764 (4%)
50 ng/mL As(III) in 1000 μg/mL chloride and electrolyte	27010 (5%)	4314 (5%)
50 ng/mL As(III) corrected	16982 (8%)	1550 (16%)

[a] RSD values in parentheses. n = 3 for all samples.

before arsenic was stripped, so that suppression was not due to dissolved solids affecting the ICP nebulizer efficiency or to electrode degradation during successive potential scans.

(2) Elimination of $ArCl^+$ Interference in Dilute Urine. Arsenic is monoisotopic at m/z = 75, while chloride isotopes yield signals for $ArCl^+$ at m/z = 75 and 77,[8,32] in a ratio of ~3:1. Comparison of ion signals at both m/z values can thus indicate whether a signal at m/z = 75 includes a contribution from the interferant or is solely due to arsenic. Time-resolved acquisition (TRA) software was used to simultaneously observe m/z values 74–78. Data were obtained immediately after completion of the ASV–ICPMS arsenic determination study, and the electrode plating was only a few hours old. The test sample was NIST 2670 Elevated Urine spiked solution 2, which had been found to contain 57.8 ng/mL As(III) in the determination study (a fairly high level was required since TRA is less sensitive than single-ion monitoring). The diluted urine contained 440 μg/mL chloride. Two minutes was allowed for arsenic deposition from 1 mL of sample, followed by 2 min of flushing with supply electrolyte prior to stripping the deposited analyte.

Three replicates of the dilute urine sample yielded sharp peaks at m/z = 75 (RSD 5%), and no detectable peak signals appeared at the corresponding points on the time axis at m/z = 77, indicating effectively complete elimination of $ArCl^+$ due to chloride in the sample (Figure 6). Continuous nebulization signals for arsenic standards (25 and 10 ng/mL) and for 1000 μg/mL chloride also illustrate how the ion signal contributions of the elements differ at the two m/z values. If not eliminated, 1000 μg/mL chloride would produce $ArCl^+$ ion signal at m/z = 75 equivalent to the signal for ~30 ng/mL arsenic (Figure 6). While the chloride level in the diluted urine sample was not especially high, it was eliminated completely with only a brief cell washout time.

(3) Elimination of $ArCl^+$ Interference in Synthetic Samples. The efficiency of the ASV flow system for eliminating $ArCl^+$ was later examined more extensively, again using TRA monitoring. Samples were 50 ng/mL As(III) in electrolyte with and without 1000 μg/mL chloride. Sodium chloride was used since the available supply was of higher purity than the ammonium chloride used in ASV–ICP-AES work. The matrix reagent did not alter sample pH. The electrode was freshly plated with gold and conditioned just before the tests began. Because of the higher chloride level involved, the time for flushing the ASV cell with electrolyte before stripping deposited arsenic was extended to 4 min. This had given complete elimination of high matrix levels in earlier ASV–ICPMS studies.[18]

Table V lists the mean integrated area counts for electrolyte blank, 1000 μg/mL chloride in electrolyte, 50 ng/mL arsenic

(32) Mulligan, K. J.; Davidson, T. M.; Caruso, J. A. *J. Anal. At. Spectrom.* **1990**, *5*, 301.

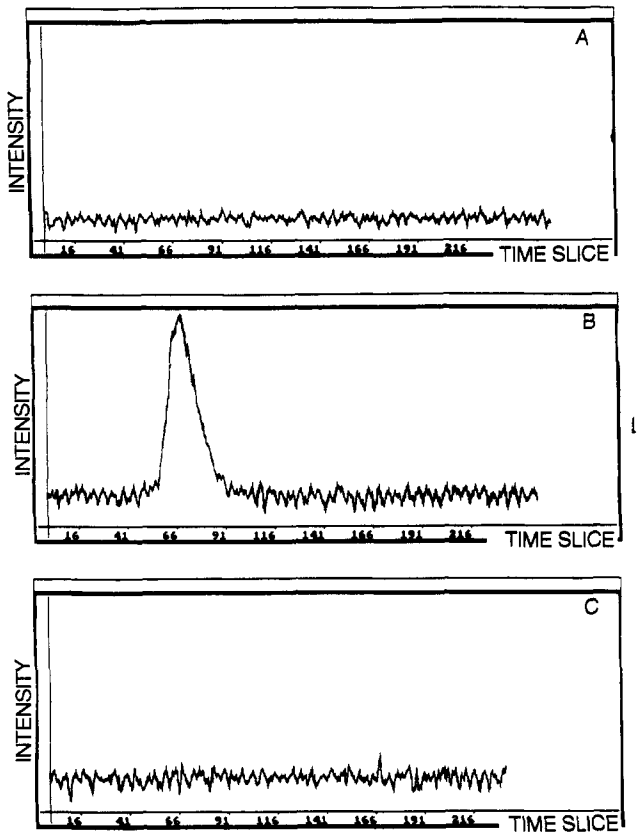

Figure 7. ICPMS signal at m/z = 75 during release of ASV cell contents to plasma, demonstrating elimination of $ArCl^+$ signal due to chloride matrix. Samples are (A) electrolyte blank, (B) 50 ng/mL As-(III) in electrolyte blank, and (C) 1000 μg/mL chloride with electrolyte. Scale is same for all displays. Slight rise in baseline height discussed in text. Obtained using time resolved acquisition software; one time slice unit equals 0.75 s.

in both matrices, and the corrected counts for arsenic (subtracting the mean area counts of the appropriate matrix). Counts for 1000 μg/mL chloride at m/z = 75 and 77 were slightly higher than corresponding counts for the electrolyte blank, but may be shown not to differ significantly (t = 1.75 and 1.40, t_c = 2.78, p = 0.05). The ion signals observed by TRA also indicate that the small increase for 1000 μg/mL chloride was not due to incomplete matrix elimination; no peak signal due to $ArCl^+$ appeared at m/z = 75 and 77 when the contents of the ASV cell were directed to the ICPMS unit or at any other time during the scans (Figure 7C). It was observed that the level of background ion signal was increasing in the course of the experiment, and this resulted in a higher total of integrated area counts for 1000 μg/mL chloride. The source of this gradual rise in background signal is presently unknown.

Mean corrected counts for arsenic at m/z = 75 indicate an 11% suppression when the 1000 μg/mL chloride matrix is present; it may however be shown that the two values did not differ significantly (t = 1.84, t_c = 2.78, p = 0.05). Since the matrix is efficiently eliminated, the standards addition method could be used to compensate for the apparent suppression should this be desired.

ACKNOWLEDGMENT

Our gratitude to William Brauntz, Arthur Case, and Douglas Hurd of the Department of Chemistry Machine Shop for fabricating the components of the ASV flow cell, Robert Voorheis and Paul MacKensie of the Electronics Shop for their contributions, and Lisa K. Olson for technical assistance with the ICPMS unit during portions of this work. National Institute of Environmental Health Service research grants ES03221 and ES04908 provided support for portions of the research. The potentiostat and x–y recorder were loaned for our use by the National Forensic Chemistry Center of the U.S. FDA. The VG Plasma Quad was provided through the NIH Shared Instrument Grant Program (Grant S10 RR-02714). Portions of this paper were presented at the 1990 FACSS Conference, Cleveland, OH, October 1990.

RECEIVED for review February 8, 1993. Accepted September 2, 1993.®

® Abstract published in *Advance ACS Abstracts*, October 15, 1993.