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**ELECTROCHEMICAL HYDRIDE GENERATION
FOR ULTRATRACE ANALYSIS**

by

WENWU DING, B. Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirement of the degree of

Master of Science

Department of Chemistry

Carleton University

Ottawa, Ontario

August 11, 1995

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ELECTROCHEMICAL HYDRIDE GENERATION
FOR ULTRATRACE ANALYSIS

Submitted by WenWu Ding, B. Sc.

in partial fulfilment of the requirements for
the degree of Master of Science

Thesis Co-supervisor

Thesis Co-supervisor

Chair, Department of Chemistry

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September 11, 1995

ABSTRACT

An electrochemical hydride generation (EcHG) system was constructed consisting of a generation cell containing Pt anode and Pb cathode compartments separated by a cation-exchange membrane, a sampling valve, a gas-liquid separator and a detection system based on *in situ* trapping graphite furnace atomic absorption spectrometry. Efficiency of EcHG from 1 M HCl media averaged $94 \pm 3 \%$ and $86 \pm 4 \%$ for antimony and arsenic test elements, respectively. No significant influence from oxidation state was noted for either element. Estimated absolute limits of detection (LOD) of 45 pg Sb and 58 pg As were obtained corresponding to relative LODs of 180 pg/ml Sb and 232 pg/ml As, based on a 0.25 ml sample. The accuracy of the analytical approach was verified through analyses of National Research Council of Canada natural water reference materials SLRS-2 and SLRS-3 (river water) and NASS-4 (open ocean water). Severe interferences from Cu(II) and Ni(II) were noted for both elements when the former were present at concentrations below 15 $\mu\text{g/ml}$. A discussion is presented outlining the potential remedial action which can be undertaken to minimize or eliminate such interferences.

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1. INTRODUCTION

Hydride generation (HG) is a commonly used means of processing liquid samples for trace element analysis [1-3]. This technique makes use of a separation of the analyte elements from the matrix by conversion to their volatile hydrides. Separation offers a route to the analysis of several important elements which have specific problems when analysed by conventional methods. The hydrides of Group 14, 15 and 16 are of particular importance to analytical atomic spectrometry for the determination of As, Bi, Ge, Pb, Sb, Se, Sn, and Te. Holak [4] first reported the use of this technique for the analysis of arsenic in 1969. Since then, a tremendous interest in hydride generation has arisen, as evidenced by a flood of publications and several reviews [3, 5-10]. A comparison of detection limits for hydride generation and conventional sample introduction, i.e., pneumatic nebulization (PN), for atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES [3]) and ICP-mass spectrometry (ICP-MS [11]) is given in Table 1. It is clear, from a cursory examination of the data in this Table, why there is such a significant interest in HG. Limits of detection are readily improved by several orders of magnitude. Additionally, separation of the analyte from the matrix is achieved which invariably leads to improved accuracy and precision of determination, pre-concentration is easily implemented, chemical speciation may be discerned in many cases and the procedures are amenable to automation.

The analytical technique of HG comprises several distinct processes, namely: generation of the volatile analyte, its collection (optional) and transfer to the atomizer and,

Table 1. Comparison of detection limits ($\mu\text{g/l}$) for analytical atomic spectrometric techniques utilizing pneumatic nebulization (PN) and hydride generation (HG).

Element	AAS		ICP-AES		ICP-MS	
	PN	HG	PN	HG	PN	HG
As	630	0.8	40	0.02	1.0	0.05
Bi	44	0.2	50	0.3	0.3	0.02
Ge	20	3.8	150	0.2		
Pb	17	0.6	8	1		
Sb	60	0.5	200	0.08	0.5	0.04
Se	230	1.8	30	0.03	6.0	0.02
Sn	150	0.5	300	0.05		
Te	44	1.5	80	0.7	1.0	0.1

*Data compiled from Refs. 3 and 11.

lastly, decomposition to the gaseous metal atoms (and excitation). Many variations of each of these stages have been studied. A brief consideration of conventional hydride generation and atomization systems as well as their analytical performance follows. The limitations of the present systems for applications to ultratrace analysis of the hydride forming elements has recently fostered interest in the development of electrochemical hydride generation (EcHG). This is the subject of the present study.

1.1. Hydride Generation Techniques

Metal -acid reduction system:

This early technique is based on use of a metal-acid reduction system, such as the Zn-HCl reaction, as shown in the following equation:

where E is the analyte element and m may or may not equal n. This reduction system appears capable of generating AsH₃, SbH₃, and H₂Se. In this case, As(V), Sb(V), and Se(VI) need to first be reduced to As(III), Sb(III), and Se(IV), respectively, by addition of KI or Sn(II) chloride before the hydrides are evolved. A major drawback of the metal-acid reactions is that they are limited to use with arsenic, antimony, and selenium (occasionally bismuth and tellurium). As a result, this approach has not been used since the advent of the more efficient sodium tetrahydroborate (NaBH₄) - acid reduction system.

Sodium tetrahydroborate–acid reduction system:

The NaBH_4 –acid reduction system is now almost universally used for the production of the hydrides and is based on the generation of nascent hydrogen in the reaction of NaBH_4 with acid. Reduction is effected as shown in the following equation [1, 12]:

Arsenic, bismuth, germanium, lead, antimony, selenium, tin, and tellurium can all be reduced to their volatile hydrides using NaBH_4 . Braman et al. [12] first introduced this system into analytical chemistry and it is superior to the preceding metal–acid reduction system with respect to reaction yield and time, contamination from reagents and wider applicability. Thus, this system shows greater potential for multi-element determinations.

Electrochemical hydride generation:

Electrochemical hydride generation for analytical purposes is a novel technique which has not yet been fully established and is supported by only a few publications [13-17]. Rigin and co-workers utilized EcHG to reduce As [13] and Sn [14] to their hydrides in alkaline media followed by AAS detection for their determination in various samples.

Two principal steps may be involved in the electrochemical hydride generation reactions in acidic or neutral solutions [18-20]:

(1). Deposition of the analyte by electrochemical reduction on the surface of a cathode:

(2). Formation of the hydride from the deposited metal:

The sequential reactions 4(a-d) occur with copious co-evolution of hydrogen at the cathode. Here, E^{m+} is the analyte ion, EH_2 , EH_3 , and EH_4 are the forms of the different analyte hydrides of interest and $H\cdot$ represents a hydrogen atom from an unspecified source (discharged H_3O^+ , reduced water H_2O or an adsorbed H atom). Little data are available concerning which step is rate determining. For SbH_3 generation, when the concentration of the analyte is low, the reaction rate is controlled by step (1). When the concentration of Sb is high enough to cover the surface of the cathode, reactions in step (2) become rate controlling [19]. It appears that AsH_3 [13, 16, 17], GeH_4 [15], H_2Se [16, 17], SbH_3 [16] and SnH_2 [14] can all be produced by EchG.

1.2. Experimental Approaches to Hydride Generation

Batch operation:

In this simplest approach to hydride generation, the generated hydride and co-evolved hydrogen are immediately transported from the reaction cell to the detector, often with the aid of a carrier gas [21]. The sweep of the hydride from the reaction vessel is usually delayed for a few seconds to allow the generation reaction to proceed to completion. However, the inherent instability of the hydride must be taken into consideration when this technique is contemplated. Although significant improvements in sensitivity and detection limits over conventional AAS solution nebulization flame or electrothermal atomization techniques are realized with batch hydride generation [8, 22], the technique is not without problems, the principal one being that the dilution of hydrides by the co-evolved hydrogen and carrier gas decrease the sensitivity of the determination. A second, significant drawback is that atomization may not be complete and gas phase interferences often occur when using conventional heated tubes. Detection limits reported for direct transfer of the hydride to the atomizer are in the range of 0.2 - 4.0 $\mu\text{g/l}$ [3], often insufficient for the accurate determination of trace analytes in many samples. A low-temperature trapping device, such as a U-tube immersed in liquid nitrogen, can be used to concentrate the hydride so that it can be transported to the detector cell without dilution from co-generated hydrogen [15, 23-25]. Batch operation is of particular interest in applications with *in situ* concentration of hydrides in a graphite furnace [26, 27] or when a large sample volume is required for the analysis.

Continuous flow operation:

Flow systems utilizing peristaltic pumps for the continuous delivery of sample and reagent to a reaction manifold have been used for hydride generation both with and without air segmentation [28]. The hydride is separated from the carrier stream using a conventional gas-liquid separator [29] or by use of a membrane separator [30]. These systems have the advantage of intimate mixing of reagent with better pH control and they also appear to be much more tolerant of elements which normally interfere with the hydride generation reaction [28, 31-34]. However, they usually suffer from a higher detection limit compared to batch systems.

Flow injection:

Continuous reagent flow combined with continuous sample flow has the advantage that it provides a constant output signal as soon as a steady-state is reached. However, use of readily available flow injection equipment has produced methods in which discrete samples can be repeatedly introduced to yield a transient signal. Using this type of system, Petterson et al. [35] attained a limit of detection of $0.1 \mu\text{g/l}$ for selenium. However, copper was found to interfere if present at levels greater than about 1 mg/l . Pacey et al. [36] automated a flow injection system based on intermittent sample introduction into a continuous reagent flow, a microporous membrane separator with carrier gas on the outside of the membrane for hydride recovery, and the "Dédina" quartz flame-in-tube type atomizer [37] for the determination of arsenic. When determining As(V) with this system, introduction of potassium iodide into the manifold gave the same analytical signal as that of

an equivalent quantity of As(III) without potassium iodide. Others [29, 30] introduce the sample into a segmented reagent flow which is claimed to enhance sensitivity for arsenic by minimizing the broadening of the sample zone. With such a system, the carrier gas (argon) is introduced into the reaction mixture of the sample and reagent before separation in a PTFE tubular microporous membrane gas-liquid separator. Here, a short reaction time prior to the separation of the hydride favours better tolerance toward interfering elements such as copper(II) and nickel(II). Tesfalidet and Irgum [38] recently reported on a novel packed membrane diffusion cell which can be used for both hydride generation and separation of the gaseous hydrides. The reaction cell comprises a liquid channel packed with a polymer anion exchanger in tetrahydroborate form, a gas permeable membrane and a gas channel. The hydride is generated in a heterogeneous reaction between the bound tetrahydroborate ions on the polymer and the injected analyte, rapidly transferred, with the aid of the concomitantly generated hydrogen gas, to the gas phase and swept to the spectrometer. The presence of nickel, cobalt, copper, and iron at concentrations of up to 1,000 mg/l had no interference on response from 50 $\mu\text{g/l}$ As(III). This performance was attributed to the rapid transfer of the hydrides to the gas phase, kinetically discriminating the interfering reaction of the hydride with any metal borides and metal colloids which possibly formed. Flow injection may also offer advantages over the batch mode of operation and continuous flow operation when it is incorporated into an EcHG system [16, 17].

1.3. Atomization Techniques for Hydrides

Quartz tube atomizers:

Quartz tube atomizers are popularly used in two modes, externally heated and unheated. The externally unheated quartz tube atomizers were first described by Seimer and Hagemann [39]. They are often termed "flame-in-tube" atomizers, as they support a combustion flame in their interior. Excess hydrogen, generated in the reduction reaction, is used to carry the released hydride to a T-shaped quartz tube where it is mixed with a small amount of oxygen to support combustion and atomization of the hydride. The often used "Dédina" version of the flame-in-tube atomizer consists of two parts: an intake portion and a T-tube, both made of quartz, connected by a standard joint [8].

The earliest reported use of an electrically- or flame-heated quartz tube used for atomization of hydrides was by Chu et al. in 1972 [40]. Since then, externally heated quartz tubes have become the most commonly used atomizers [2, 3, 8]. Their design is very similar to the flame-in-tube atomizer and consists of a T-tube with a bar-tube aligned in the optical path and the central arm of the T-tube serving to deliver the hydrides carried by a flow of gas from a generator. The bar-tube is heated either by a chemical flame or, more often and more conveniently, electrically. This can be accomplished either by a resistance wire wound around the tube or by a tailored furnace. The two outlets of the bar tube are either open to the atmosphere or closed with optical windows [2, 41]. Atomization of the hydrides in a heated quartz tube is caused by reaction with free hydrogen radicals generated in the flame. If hydrogen is absent, the hydrides will not be atomized but thermally decomposed. Oxygen

or air is often introduced into the atomizer, mainly because of the supporting effect additional oxygen has on the atomization process. For optimum sensitivity, there is a need for a minimum oxygen concentration which depends on (in addition to the element hydride), temperature. The higher the temperature, the lower is the required oxygen concentration. At lower temperatures, oxygen present in the system as a contaminant may not be sufficient for optimum sensitivity and thus additional oxygen is often required [8].

There is a marked effect of the quality of the inner quartz tube surface on sensitivity [42], most often manifesting itself as a gradual deterioration of sensitivity and/or precision with continued operation. Optimum performance is most conveniently maintained by rinsing the tube in 40 % hydrofluoric acid. Grinding the inner atomizer surface with alumina has also been employed.

Compared with flame atomizers, externally heated quartz tubes have the following advantages: the flame background is virtually eliminated and better sensitivity is achieved owing to the longer residence time of the atom cloud in the optical path; the dilution is less pronounced and much lower noise levels are present.

Graphite furnace atomizers:

The first reported use of the graphite furnace (GF) atomizer for atomization of hydrides was by Knudson and Christian in 1974 [43]. Since then, use of the heated GF has been studied by several other workers. There are two approaches to using the GF: as a continuously heated atomizer (much like a heated quartz tube) and in combination with *in situ* trapping of the hydrides with subsequent atomization. These may be used on-line in

either a flow injection format, or with batch generation. In the simplest approach, direct transfer of the hydride from the generator to the GF is undertaken wherein the latter is preheated to a temperature usually over 2200°C [8, 44-48]. Although the continuous-flow generation of hydrides was recently shown to work in connection with GF atomization, batch or cold-trap collection methods have so far invariably been applied [8]. The generated hydrides are almost exclusively introduced *via* the internal gas line on commercial furnaces. This method is simple but the hydride can be captured on cooler metal or graphite components within the GF. A similar drawback, hydride capture in the connecting tube, can result from introduction of hydrides to the sampling port of the GF by use of a graphite transport tube [49]. A more viable approach for introducing hydrides into the GF is based on use of a quartz tube interfaced to the sampling hole. The latter does not retain hydrides and can withstand temperature above 2300°C for a reasonable time, if cooled by a gas flow. Naturally, the sensitivity for continuous atomization in the GF is generally worse than quartz tube atomizers as the small dimensions of commercial graphite furnaces and their high temperatures decrease the residence time of free analyte atoms and, subsequently, the sensitivity [8].

Improved detection limits with the GF may be realized by collection and concentration of the hydride prior to introduction into the atomization cell [50]. Such techniques have included cryogenic condensation in a U-tube immersed in liquid N₂ [4, 44], or trapping in solutions consisting of KI-I₂ [51], or pyridine-silver diethyldithiocarbamate [52]. Cryogenic condensation can improve the detection limits, but it is rather labourious and cumbersome for routine use. In addition, this collection method is not suitable for

unstable hydrides such as those of Bi, Pb, Sb, Sn, and Te [8, 53].

A considerably simpler and more elegant approach to this problem is the use of the graphite furnace as both the hydride trapping medium and atomization cell. Such an arrangement was proposed by Drasch et al. in 1980 [54] for the determination of As in biological samples. The setup was rather cumbersome and used a Perkin-Elmer HGA 72 furnace. No data were reported. Lee [55] utilized this technique to determine ultratrace levels of Bi in environmental samples. The hydride was generated in a reaction cell, stripped from solution in a He carrier gas and collected *in situ* in a modified carbon rod atomizer at 350°C. The collected Bi was subsequently atomized at 1880°C. This technique significantly enhances the sensitivity and effectively eliminates any vapour phase interference in the atomizer and any interferences due to variations in the rate of hydride generation from sample to sample. It appears to be a very promising method for the determination of the hydride-forming elements at trace or ultratrace levels. Hydrides of As [54, 56-58], Bi [55, 56], Sb [58, 59], Se [58, 60], Sn [58, 61], Te [62], and Pb [58] have been determined following trapping in a graphite tube. However, the effects of incomplete trapping and the influence of the graphite surface may reduce sensitivity and precision in some cases.

Recently, Zhang and Shan [63, 64] and Sturgeon et al. [65] reported that μg amounts of Pd can be used as an efficient low temperature adsorber for the hydrides of As, Bi, Ge, Sb, Se, Sn, and Te, significantly improving the sensitivity and precision of their collection in the GF. Satisfactory results have been obtained for the analysis of natural waters, urine and sediment reference materials [63, 64]. Doidge and Sturman [66] studied the effect of Pd pretreatment of the graphite tube on the trapping and atomization of germane. The general

applicability of the method to other hydride-forming elements was also reported. Sturgeon et al. [65] extensively studied the mechanisms of trapping and atomization of hydrides in the graphite furnace. Several platinum group metals were examined as collection substrates and it was determined that the catalytic reactivity of Pd promoted low temperature deposition of the hydrides by dissociative chemisorption. Matusiewicz et al. [67] determined As in seawater by coupling the *in situ* concentration technique with microwave-induced plasma emission spectrometry. It appears that a coating of palladium has to be achieved prior to every hydride trapping cycle [65, 68]. In the case of zirconium-coated tubes, one application permitted many subsequent determinations of the hydrides of lead [69] and tin [70]. Shuttler et al. [71] used a single manual application of a mixed trapping reagent consisting of 50 μg of palladium and 50 μg of iridium sufficient to activate the surface of the GF for up to 300 complete trapping and atomization cycles before re-coating was required. Precision of replicate measurement is better than 3 % RSD and efficiency of trapping is virtually 100 % for As, Bi, Se [71].

Inductively Coupled Plasmas:

Thompson first reported use of the hydride generation technique with ICP-AES for the determination of As, Bi, Sb, Se and Te [31, 32]. Two approaches to hydride manipulation were used to form and introduce the hydrides into the ICP. In the batch mode, the generated hydride is rapidly swept into the ICP along with other head space gases from the cell. In the more often used continuous approach, the analyte forms the hydride in a continuously flowing stream of reagents [31, 32, 72]. Concentration of the generated hydride in cold trap

is one method which has been adopted to avoid introduction of large volumes of hydrogen into the plasma and, although very time-consuming, it also provides a satisfactory method for increasing the sensitivity [24]. The initially attractive prospect of determining all of the volatile hydride-forming elements simultaneously using ICP-AES has not been fully realized because of the varied reaction media required for the reduction of the elements to their hydrides. For example, whereas As, Bi, Sb, Se, and Te can be reduced in moderately strong acid solutions (e.g., 5 M HCl), Ge and Sn are efficiently reduced only at much lower acidities, i.e., in 0.1 M HCl or in weak organic acids such as 1 % (m/v) tartaric acid [31,72].

1.4. Analytical Parameters

Influence of oxidation state:

The hydrides of As(III), Sb(III), Se(IV), and Te(IV) can be generated from HCl reaction media whereas their higher oxidation states—As(V), Sb(V), Se(VI), and Te(VI) do so with a lower efficiency. With practical analysis, therefore, pre-reduction procedures must be employed before hydride generation to ensure that these elements are in their lower oxidation states if determination of the total amount of these elements is required. In general, KI [29, 73, 74], NaI [75] and KBr [76, 77] are used as pre-reductants for As and Sb. The classical procedure to effect the reduction of Se(VI) to Se(IV) is by use of heating in 4 M HCl for one hour near 100 °C [78]. The boride ion in acid solution can perform the same reduction under more convenient conditions, i.e., 20 min. at 60°C [41, 76], and also reduce As(V) and Sb(V) to their trivalent oxidation states. Titanium(II) chloride solution can be

used for pre-reduction of Te(VI) to Te(IV) [79]. Halicz et al. [80] reduced Se(VI) to Se(IV) and Te(VI) to Te(IV) by heating with HCl prior to their simultaneous analysis (along with As and Sb) in silicate rocks. The difference in sensitivity obtained with hydride generation for the pentavalent and trivalent forms of Sb and As can be minimized under certain conditions [81]. With flow injection (FI) systems, the effect is more pronounced than in batch hydride generators for at least two reasons [82]: first, much lower sodium tetrahydroborate concentrations are typically used in FI-HG-AAS, and, second, because any hydride which is generated more slowly is pumped to waste, an effect occurs that is called kinetic discrimination [83]. On the other hand, because the difference in sensitivity between the two oxidation states is, at least in part, due to kinetically slower reduction of the pentavalent form, it can be reduced by increasing the residence time in the system using long reaction coils [82]. This approach, however, can not be generally recommended, as long reaction coils increase the total time of analysis and could result in increased interference. Potassium iodide alone [84, 85] or mixed with ascorbic acid [86] is most frequently used for reduction of Sb(V) to Sb(III). However, KI can only be used in strong acid media, typically in 5-6 M HCl. At acid concentrations less than 0.3 M, KI failed to completely reduce As(V) to As(III) [86, 87], and even at higher acid concentrations it could take a few hours to reduce As(V) at room temperature [86].

On-line pre-reduction of As(V) has been used for FI-HG-AAS [29, 88], but with an average consumption of 60 g/h of KI. Tyson et al. [89] improved the procedure by introducing stopped-flow pre-reduction, whereby the KI consumption was significantly reduced. However, a 30 % (m/v) KI solution and 12 M HCl was necessary. Such highly

corrosive solutions are not conveniently handled. In addition, blank values can increase with high reagent concentrations and affect detection limits. Potassium iodide solutions are not very stable and must be freshly prepared before each run. Chen et al. proposed use of L-cysteine instead of KI as an efficient pre-reducing agent for As(V) [90] and Sb(V) [91]. The low toxicity of the reagent and the low acid concentrations required for determination are particularly attractive for routine analysis. Chen et al. [92] have shown that L-cysteine can even be used for on-line reduction in a continuously pumped system and be used at sample throughput rates of 30 h^{-1} . Welz and Suchmanova [91] found that the reduction of Sb(V) to Sb(III) with 5% (m/v) L-cysteine solution was essentially instantaneous, whereas reduction of As(V) took about 30 min. at room temperature. If necessary, the reduction rate can be significantly increased by heating the solution [90], and this can even be achieved on-line [92].

It is considered very important for routine application that solutions of L-cysteine as well as L-cysteine containing standard and sample with low antimony and arsenic concentrations, are stable for at least one week, a significant advantage over the use of KI. More importantly, reduction of the acid concentration from 5 to 1 and 0.1 M HCl for Sb and As, respectively, as well as the low toxicity of L-cysteine compared to that of KI, are advantageous in that the waste created in the course of analysis is less problematic to dispose of. The reagents are much less corrosive and hence easier to handle by the operator and are more compatible with the instrument, and they are significantly less expensive.

The toxicity and function of a particular element depend critically on the chemical form [94]. It is well-known that arsenic, antimony, selenium and tellurium commonly exist

in solution in two oxidation states. Thus, hydride generation procedures can afford several methods for inorganic and/or organic speciation of some hydride-forming elements.

Aggett and Aspell [95] were the first to describe methods for the selective determination of As(III) and As(V) by making use of their difference in reduction rates. They noted that the reduction was pH dependent and obtained a quantitative yield of hydride from both As(III) and As(V) in 5 M HCl but hydride generation corresponding to only As(III) at pH 4.5 in an acetic acid/sodium acetate buffer. It must be noted that methyl-derivatives of arsenic such as monomethylarsonic acid and dimethylarsinic acid, if present (as they are likely to be in environmental samples), may also contribute to the apparent yield of hydride if the hydride generator is connected directly to the atomizer [96]. A comprehensive review of the speciation of derivatives of arsenic is given by Anderson et al. [34]. The determination of As(III), As(V), monomethylarsonic and dimethylarsinic acid using a continuous flow system permitted rigorous control over the reaction conditions. A time-consuming separation technique to differentiate between the generated hydrides of arsine, monomethylarsine and dimethylarsine was used. Holak and Specchio relied on use of chemical extraction for the separation of As(III) from As(V) prior to their quantitation by hydride generation [97]. Comber and Howard [98] refined an earlier system [99] which was based on the work of Andreae [100] and Braman et al. [101] and used it for the speciation of derivatives of arsenic in natural waters and in studies involving geological and biological processes. The hydrides were generated in a continuous flow system connected to a gas-liquid separator and collected in a U-tube packed with hydrofluoric acid-etched glass beads cooled in liquid nitrogen. The hydrides were sequentially released by selective volatilization

during warming of the trap and arsenic was determined by AAS following atomization in a heated quartz tube. This system yielded detection limits in the range 20 - 60 pg for arsenic derivatives and its performance was verified by the method of standard additions. Sturgeon et al. [102] identified a number of arsenic species in river water reference material SLRS-1 by combining hydride generation-AAS with chemical pre-separation techniques. A gas chromatography system [103] was used for the separation of the hydrides when determining arsenic derivatives in air-borne particulates collected on a quartz fibre filter with a high volume sample. The hydrides were trapped in a U-tube cooled in liquid nitrogen and then quickly transferred into a helium gas flow connected to a column of 5 % PEG-20M on Chromosorb 102. Hydrogen was added to the effluent gases from the gas chromatograph before determination by AAS based on atomization in a ceramic alumina tube at 900-1000°C. Detection limits were better than 100 pg for all arsenic derivatives.

Normally, the experimental conditions used for arsenic are appropriate for the determination of antimony, and this also applies to speciation of the inorganic forms of antimony. Campell and Howard [104] adapted a method previously applied to the determination of arsenic [99] for determination of antimony in estuarine and seawater. A quantitative yield of stibine from Sb(III) was obtained but no hydride was generated even from a 10-fold excess of Sb(V). The total antimony was determined following the reduction of Sb(V) to Sb(III) with KI. Although nitrite and metal interferences were overcome with the use of sulphanilamide, trapping was used to concentrate the hydride, yielding detection limits as high as 240 ng/l.

Selenide is readily reduced to hydrogen selenide in 4 M HCl acid but Se(VI) yields

H_2Se only from very strongly acidic solutions [105]. This distinction was successfully exploited by Cutter [106] who utilized the gas chromatographic system of Chan et al. [107]. With the flame-in-tube detection system used by Andreae [100], dimethylselenide and dimethyldiselenide as well as selenide and selenate were determined. For total selenium determinations, Se(VI) was reduced to Se(IV) by heating in 4 M HCl at just below the b.p. for several minutes.

Jin et al. [79] found that Te(IV) gave a quantitative yield of hydride on treatment with sodium tetrahydroborate in 3 M HCl but Te(VI) was unaffected even when present at a 2000-fold excess. They obtained hydride corresponding to the total tellurium following reduction of the tellurium(VI) with a 5 % titanium(II) chloride solution. A detection limit of 8 ng was reported. Heating with HCl has also been used to reduce Te(VI) to Te(IV) .

Interest in the biological activity of organotin derivatives has stimulated the development of analytical methods based on the production of its volatile hydrides with NaBH_4 for their determination at trace levels in sea and estuarine waters. Early analytical systems have been reviewed by Chamsaz et al. [108], who developed a method having detection limit of 0.4-1.5 ng for tin using a 0.5 l sample. Following the relatively slow addition of NaBH_4 to the sample acidified to pH 2 with HCl , the hydrides were collected in a liquid nitrogen cooled trap similar to that used by Valkirs et al. [109] and Donard et al. [110]. The efficiency of such a trap packed with a chromatographic grade stationary phase to facilitate good sequential volatilization of the various hydrides on warming had been earlier demonstrated. When analysing methyl derivatives, a dry ice/acetone cooled desiccant trap was used to protect the hydride trap from moisture. The butyl derivative, however, will

also condense at this temperature. Andreae and Byrd [47] have shown that it was not possible to distinguish between Sn(II) and Sn(IV) using hydride generation as both produce stannane under similar reaction conditions. Glass surfaces in contact with stannane and organic derivatives should be regularly treated with dimethyldichlorosilane to avoid loss of tin by adsorption [47, 111].

Effects of acidity of the reaction medium:

In the NaBH_4 -acid reduction system, HCl is almost exclusively the acid of choice, although H_2SO_4 [111, 112] and HNO_3 [113, 114] are equally suitable in some circumstances [115, 116]. Optimum acidity ranges appear dependent on both the elements of interest and types of hydride generators; for example, 1–9 M for As, Bi and Sb, 1–3 M for Ge, 0.1–0.2 M for Pb and Sn, 2–5 M for Se and 2.5–3.6 M for Te [3]. Thus, the prospect for simultaneous determination of all the elements with AES detection appears poor, even if a single sample preparation could be devised. Thompson et al. [31, 32] reported on the simultaneous determination of As, Sb, Bi, Se and Te, but found that for multielement work some compromises in operating conditions were necessary. Hydride generation from 5 M HCl was selected after a study involving a wide range of acids and conditions. However, Ge, Sn and Pb could not be included with the other five elements because of different acidity requirements. These authors also reported that, for Ge and Sn, the acid concentration for maximum hydride generation is very critical [72, 117], although detection limits near 0.2 $\mu\text{g/l}$ for these two elements could be obtained. In general, the acidities required for maximum hydride generation efficiency are high. This can introduce a high blank, as well

as elevate the cost per analysis. The different optimum acidity for the various hydride forming elements is inherent to the NaBH_4 -acid reduction system. It appears that no additional effort can be invested to improve this situation.

1.5. Interferences

Hydride generation-atomic spectrometry can be considered, at the present time, to be one of the most powerful analytical tools for the ultratrace determination of As, Sb, Bi, Se, Te, Ge, Sn, and Pb. The main limitation of the technique stems from interferences arising when some inorganic ions are present in the reaction media. Possible interferences have been classified according to whether they occur after (gas phase interferences) or before (oxidation state effects) and during the hydride generation stage (liquid phase interferences).

a. Gas phase interferences:

This type of interference includes spectral interferences, stable compound formation and hydride decomposition. As the analyte is separated from the sample matrix as its hydride, spectral interferences in the detection system should not occur. In the high temperature GF or ICP source, stable compound formation should not give rise to signal suppressions. Some hydrides, in particular those Pb, Sn and Te, tend to be unstable and therefore the analyte can deposit on the wall of the transfer tubing and the torch with subsequent risk of background instability and memory effects.

b. Liquid phase interferences:

This type of interference arises from acid effects, oxidation state effects, interelement interferences (mutual or with other elements) and the presence of organic material. As mentioned earlier, the efficiency of hydride generation depends critically on the acid concentration of the test solution and varies markedly among different acids. For As, Sb, Se, and Te, the lower oxidation state is more efficiently reduced to the hydride and, hence, has a higher sensitivity. Therefore, it is essential that samples and standards be matched for the oxidation state of the analyte.

Interferences from other chemical species can occur only at the reduction stage, as gas formation ensures a virtually complete separation from other solution constituents. Ions of the alkali and alkaline earth metals have negligible effect on the reduction efficiency. The effect of other elements has been detailed in the literature [32, 72]. The major interfering elements are transition metals such as Co, Cr, Cu, Fe, and Ni. In addition, mutual interelement effects of the hydride forming elements appear to be significant [3]. Organic materials in a sample can compete with the hydride-forming elements for reduction by NaBH_4 and give rise to a change in sensitivity.

Smith [118] studied interferences from 48 foreign elements on the response from As, Bi, Ge, Sb, Se, and Te. It was observed that many interferents form dispersed black precipitates following the addition of NaBH_4 to the solution. Reduction of the interfering ions to form metal-like precipitates can adsorb and decompose the analyte hydrides.

Kirkbright and Taddia [119] investigated interferences by Cu(II) , Ni(II) , Pt(IV) and Pd(II) on arsine generation. They observed the formation of a finely dispersed black

precipitate and proposed that the interference was caused by the reduction of the interfering ions to the metal by NaBH_4 . The finely dispersed metals were then thought to adsorb and decompose the arsine on their surface, as suggested by Smith [118]. In order to support this hypothesis, experiments were performed in which the addition of 500 mg Ni powder to the reaction solution in the presence of masking agent to complex the traces of metal eventually dissolved was found to completely suppress the arsine signal.

Welz and Melcher [21] proposed that metals in ionic form hardly contribute to the interference effects in the determination of Se. They bubbled hydrogen selenide, evolved from a batch system, through a wash bottle containing the metal ions Cu(II) , Ni(II) , Fe(II) , and Fe(III) , in acid solution and concluded that "...all the effects of copper, iron, and nickel observed in the determination of selenium can be explained by preferential reduction of the interferent to the metal, and capture and decomposition of the evolved hydride by the finely dispersed precipitated interfering metal". This was subsequently re-affirmed in another study [120]. The resulting measured interferences were several orders of magnitude lower than those observed when metal ions were directly present in the reaction vessel. This observation supported the interference mechanism proposed by Smith [118] and Kirkbright and Taddia [119].

Dittrich et al. [121] believed that formation of an insoluble compound between the analyte and the transition metal ions was the main cause of interference. However, subsequent experimental data [120] revealed that this mechanism was not entirely correct. It is impossible for Co_3As_2 , CoSe , NiAs_2 , and NiSe to dissolve in HCl solution, but an increase in the HCl concentration leads to a decrease in the degree of interference caused by

Ni(II), and Co(II) [120]. Meyer [42] proposed that Cu(II) can react with SeH_2 to form CuSe . This compound slightly dissolves in HCl solution, so, with increased HCl concentration, the extent of interference of Cu(II) on hydrogen selenide generation can be decreased. Each of the above explanations has been associated with qualitative observations on the formation of insoluble metal precipitates. However, there is some suggestion by others that the formation of precipitate does not always coincide with an interference. For example, Peacock and Singh [122] observed precipitate formation without interference in the presence of iron.

In an attempt to gain an insight into the mechanism of these interferences which might be caused by the formation of insoluble chemical species between analyte and interfering ions, Aggett and Hayashi [123] examined the interferences from 1 mg/l Cu(II), Co(II) and Ni(II) on arsine generation. The most noteworthy results of their experiments include the observation that, with the exception of Cu(II) at low HCl concentration (1 M), the use of smaller amounts of NaBH_4 does not greatly alter (less than 10 %) the extent of interference and that the two factors which have the greatest effect on interferences are the concentration of the interferent and the acidity of the solution from which arsine is generated. The data revealed no consistent evidence of a relationship between precipitation of the metal and interference on the arsenic signal. On the one hand, in the 1 mg/l Cu(II)-arsenic system, precipitation occurred without interference in 2 M HCl and, on the other hand, in the 1 mg/l nickel(II)-arsenic system, interference occurred without precipitation in 5 M HCl. They concluded that "... interference must probably occur through formation of a soluble, rather than an insoluble species, involving both arsenic and the interferent in lower than normal

oxidation states". Their explanation for this conclusion was that the interfering soluble species is probably stabilized in the presence of excess NaBH_4 and, on subsequent decomposition, the arsenic is converted to As(III) or some other form which converts to arsine at the same rate on the addition of NaBH_4 . If arsine is involved in the formation of the species responsible for the interference, it is not released, as such, on addition of thiourea. Aggett and Hayashi [123] disagree with Welz and Melcher [21] over the nature of the active interfering species, but they agree with each other that the rate of formation of the soluble or insoluble interfering species relative to that of arsine is important. This holds true for all the mechanisms proposed to date. Following a very detailed study of these interference effects for Cu(II) , Co(II) and Ni(II) , Bax et al. [124] concluded that a reaction between the transition metal ion and selenium hydride does not contribute (for cobalt or nickel) or hardly contributes (for copper) to the interference. The mechanism proposed by Mayer can only play a minor role in the case of copper interference, but none at all in the interference from other metals such as Ni(II) and Co(II) .

Brown et al. [125] proposed that the precipitates that formed could be borides rather than reduced metals. Bye [126] further investigated the cause of interference by the divalent cations Sn(II) , Ni(II) , Cd(II) , Fe(II) and Zn(II) on the determination of selenium by HG-AAS. It was suggested that these ions react with NaBH_4 to produce the metal borides and not, as generally supposed, the elemental metals. The metal borides are known to be highly reactive and could cause decomposition of the selenium hydride. There are two noteworthy results of these experiments: the precipitate from a nickel solution was found to be amorphous and a qualitative test revealed the presence of boron; no precipitate was formed

in a solution of Zn(II) following the addition of NaBH_4 , whereas a large amount of iron precipitate was formed. If the precipitate formed in iron solution is metallic iron, then zinc metal should also be formed from the zinc solution. It is more likely that the precipitate formed in the iron solution is iron boride. Bye [126] concluded that the interference on SeH_2 caused by certain metal ions, at least, Ni(II) and Fe(II), was due to its capture and decomposition by the metal boride precipitate formed on the addition of NaBH_4 . Zhang et al. [127] determined the composition of precipitates of Ni(II), Co(II) Fe(II), and Cu(II) formed in the presence of KBH_4 and found Ni_3B , Co_3B and Fe_6B . The precipitate from Ni(II) or Fe(II) was actually a mixture of metals and borides; that from Cu(II) was CuCl , whereas the composition of the Co(II) precipitate could not be determined by X-ray diffraction.

c. Minimizing interferences:

Many workers have tried to eliminate or minimize interferences by using a variety of approaches. These are summarized as follows:

(i). Increases in the acidity of the reaction solution and/or decrease the concentration of the reducing agent [42, 104, 128-130];

(ii). Addition of masking agents, including EDTA [45, 131, 132], KI [75, 132-135], thiourea [123, 125, 126, 136-139], KCN [125, 140], ascorbic acid [141], citric acid [142], malic acid [143], oxalic acid [144], tartaric acid [72], 1.10-phenanthroline [48, 114, 119] and thiosemicarbazide [119];

(iii). The use of L-cysteine as an interference releaser [90-92, 145, 146];

(iv). Separation of the analyte from the matrix by liquid-liquid extraction [147], co-precipitation [62, 73, 80], colloid floatation [71], chelating resins such as Chelex-100, poly(acrylamidoxime) and poly(dithiocarbamate) [46, 49, 148];

(v). Addition of "interference-releasing" elements such as iron [149, 150], copper [151], tellurium [152], mercury [139] to minimize interferences from some metal ions.

The use of L-cysteine is perhaps the most universal approach that can be utilized. This reagent has been found to be extremely useful in the analyses of complex samples. The mechanism proposed by Brindle and I.e [153] suggests that the thiol group from L-cysteine (HS-R) and the BH_4^- anion form an intermediate species ($\text{BH}_3\text{-S-R}^-$) which is more selective in achieving reduction of the hydride analytes in preference to interfering transition metal ions.

Although there have been successful minimizations or eliminations of interferences as described above, the use of standard addition techniques for analysis is essential in many instances [2, 137, 138]. However, this cannot be recommended as a general means of overcoming interference as it is both a time-consuming and sample-consuming approach.

1.6. SUMMARY

The most commonly used hydride generation technique, reduction of analyte in a NaBH_4 -acid system, offers more efficient sample introduction than conventional pneumatic nebulization, permits pre-concentration, chemical separation of the analyte from possible matrix interferences and yields high powers of detection when coupled with atomic

spectrometric instrumentation. However, this system is prone to interferences by concomitants, oxidation state of the analyte of interest is critical, and pH, as well as reagent concentration of generation solutions, for some elements, must be closely controlled. Sodium tetrahydroborate is susceptible to introducing contamination and in solution form it is unstable. Since these disadvantages are inherent to the system itself, it is useful to examine alternative hydride generation techniques, such as EcHG.

The reducing power of NaBH_4 has been proven so effective that the latter system has drawn little attention. However, as early as 1977, Rigin and co-workers [13, 14] reported their work on an EcHG technique. In their system, a thin platinum plate was used as cathode, and a 5 % (m/v) KOH solution was used as electrolyte. The batch-type cell was constructed of PTFE. A 0.4 A/cm^2 current density was used to generate SnH_2 from natural water media [14]. A nickel cathode, $0.1\text{-}1 \text{ A/cm}^2$ current density and $0.1\text{-}10 \text{ M}$ alkaline electrolyte were also used to generate GeH_4 [15]. Because the rate of GeH_4 generation was low, the hydride was collected before the determination to yield a detection limit of 0.3 ng/l . The electrolytic cell was cooled by circulating water. It appears that the idea of more widely utilizing EcHG did not become clear until two recent papers were published. Lin et al. [16] showed that 100 mg/l Co(II) and Ni(II) and 5 mg/l Cu(II) caused 10 % suppression in the signal from $100 \mu\text{g/l Se(IV)}$ when using a vitreous carbon cathode, whereas 20 mg/l Co(II) , Ni(II) and Cu(II) caused at least 8 % suppression on the signal from $100 \mu\text{g/l As(III)}$. When using a platinum cathode, Co(II) and Ni(II) present in concentrations of 100 mg/ml had no interference on arsine generation. Arsine generation is subject to more interferences with the vitreous carbon cathode. Brockmann et al. [17] showed that Co(II) and Ni(II) in

concentrations up to 10,000 mg/l had no interference on either 50 $\mu\text{g/l}$ As(III) and Se(IV) when using a platinum cathode. The goals of these two studies were to overcome the disadvantages, while maintaining the advantages, of the conventional NaBH_4 -acid reduction system. Whereas the interferences arising from use of different cathode materials reported in these two studies are very different, results of analytical applications appeared to be satisfactory compared with those obtained using the NaBH_4 -acid reduction system.

It is the objective of this study to more closely examine the analytical potential of FCHG and to couple it with flow injection techniques for sample processing and *in situ* trapping in the GF to enhance detection power. Use of flow injection for sample handling is the best approach in regard to economy of sample, analysis throughput and the ability of the system to tolerate interferences. Similarly, *in situ* trapping of analyte hydrides in the GF eliminates potential gas-phase interferences and the effects of varying rates of generation of the hydrides. Additionally, dilution of hydrides by the co-evolved hydrogen and carrier gas is avoided thereby permitting substantial pre-concentration of the analyte by prior to analysis.

2. EXPERIMENTAL

2.1. Apparatus

Atomic absorption measurements were made using a Perkin-Elmer Model 5000 spectrometer fitted with a Model HGA-500 graphite furnace and Zeeman effect background correction. In-house software was used to permit the visualization of the transient signals in real time and the evaluation of peak-height and integrated absorbance. An antimony hollow cathode lamp (Cathodeon) was run at 8 mA with the spectral bandpass of the spectrometer set at 0.7 nm and centered at the 217.6 nm resonance line. An arsenic electrodeless discharge lamp (Perkin-Elmer) was run at 8 watts with the spectral bandpass of the spectrometer set at 0.7 nm and centered at 193.7 nm resonance line. Standard Perkin-Elmer pyrolytic graphite coated tubes were used throughout. A Gilson Minipuls-2 and a Cole-Parmer Ismatec peristaltic pump were used to deliver samples and anolyte solutions, respectively, to the electrochemical cell.

The electrochemical hydride generation system is schematically illustrated in the block diagram of Figure 1. Figure 2 shows an exploded cross-sectional view of the electrolytic cell. The plexiglass body of the cell consists of the upper (cathode) and lower (anode) blocks (external dimensions: anode block - 13 x 3 x 1.5 cm machined to contain a central channel of 9.5 x 1.0 x 0.4 cm; cathode block - 13 x 3 x 0.6 cm), each with tubular inlets and outlets (1 mm id) for solutions, as illustrated. A platinum anode (9.5 x 0.95 cm) is fixed onto the bottom of the anode cell channel. A silicone gasket (0.08 cm thick) is

placed under the cathode block and is used to prevent leakage of solution. A second silicone gasket, containing a central slot with dimensions 10×1 cm, serves as the cathode channel. The cathode electrode is placed between these two silicone gaskets. A cation ion-exchange membrane, used to physically isolate the cells, is layered between two such slotted gaskets next to the anode block. The blocks, gaskets, electrode and membrane are held together with several C-clamps. This system provides a large ratio of cathode surface area to cathode cell volume, no leakage of electrolyte, even electrolysis, a long operation time, and ease with which the surface area of the cathode can be adjusted and the cathode material changed.

The cell was powered by a PAR (EG & G) Model 371 potentiostat-galvanostat and normally operated in the constant current mode. For some experiments, a saturated calomel electrode (S.C.E.) was installed in the system in the sample delivery line, approximately 4 cm from the working electrode.

The gas liquid separator, shown in some detail in Figure 1, consists of two plexiglass blocks with appropriate inlets and outlets for the gas and liquid phases. In operation, the cell is positioned vertically, as illustrated. One of the blocks is imbedded with a $10 \times 1 \times 0.1$ cm channel used for introduction of the liquid phase. The other contains a $10 \times 1 \times 0.2$ cm channel used for the gas phase portion of the cell. A sheet of $1.2 \mu\text{m}$ porosity Versapor-1200R (Gelman Sciences) gas-liquid separation membrane is placed between the two blocks. To separate the hydrides from the liquid phase and direct them to the furnace, an auxiliary Ar carrier gas (50 ml/min) is introduced into the liquid phase through a glass frit set in the bottom of the back wall over which the liquid phase flows prior to exiting as waste at the bottom of the liquid cell. The separated hydrides and excess hydrogen are introduced into

the furnace by inserting a quartz capillary tipped Teflon® transfer line through the sample introduction port so as to rest on the interior back wall of the graphite tube.

2.2. Reagents and materials

Stock solutions (1000 mg/l) of Sb(III) and As(III) were obtained from Seignior Chemical Products Ltd. (Montreal, Can.). The elemental contents were verified against in-house standards. A solution of 500 mg/l Sb(V) in 4 M HCl was prepared by adding 1 ml 0.0025 M KIO₃ solution and 4 ml 10 M HCl to 5 ml 1000 µg/l Sb(III) solution and allowing the mixture to stand for 10 min. A 1000 mg/l As(V) stock solution was prepared from As₂O₅ (Baker Chemical Co.). A 7.7 % (m/v) thiourea solution was obtained by dissolving reagent grade thiourea (Aldrich Chemical Co) in deionized, distilled water (DDW) which was obtained from a Barnsted NanoPure system. A 10 g/l stock solution of Pd(II) was prepared by dissolution of high-purity metal (Johnson Matthey, Ward Hill, MA) from which a working standard of 200 mg/l was obtained through dilution with DDW. High-purity sub-boiling distilled HCl (prepared in-house) was used for all analyses. A mixture of 0.05 % (m/v) Pd and 0.05 % (m/v) Ir in 2 % HCl (v/v) was prepared by dilution of 10 g/l stock solutions of the high-purity metals (Johnson Matthey). A 5 % (m/v) solution of reagent grade L-cysteine was obtained by dissolution in 0.5 M high-purity HCl. A 1 mg/l Ni(II) stock solution was prepared by dissolving 0.5098 g reagent grade Ni(NO₃)₂ 6H₂O in DDW. A 3 mg/l Cu(II) solution was obtained by dissolving reagent grade CuCl₂ (Fisher Scientific) in DDW in 0.5 M HCl. Reagent grade hydroxylamine hydrochloride and sulfuric acid were

Figure 1. Schematic diagram of the instrumental set-up.

Figure 2. Exploded view of ECHG cell.

also obtained from Fisher Scientific. Neosepta® (CM-1), Raipore® 1010 and Nafion® (112 and 417) cation exchange membranes were obtained from the Electrosynthesis Company (Lancaster, N.Y.). High-purity lead (99.99+ % purity, 1 mm thick), obtained from Goodfellow metals (Berwyn, PA), Pt (0.025 mm thick, 99.9 % purity) obtained from Johnson Matthey, as well as solid pyrolytic graphite obtained from Ringsdorff-Werke (Bonn, Germany) were examined as cathode materials. National Research Council of Canada certified river water reference materials SLRS-2 and SLRS-3 and open ocean seawater NASS-4 were analysed to verify the accuracy of all procedures.

2.3. Procedure

All sample and analytical manipulations were conducted in a routine laboratory environment. The catholyte, including blank, standard and sample, was continuously pumped through the cathode cell at a flow rate of 0.5 ml/min for Sb determination and 0.6 ml/min for As determination. The stibine (or arsine), excess hydrogen and the liquid waste were subsequently delivered to the gas-liquid membrane separator from which the gases were directed to the graphite furnace by an auxiliary Ar carrier stream at a flow rate of 50 ml/min. The anolyte solution was continuously recirculated at a flow rate of 7.5 ml/min and was kept cool by passing it through a cold water-jacketed glass cell. The furnace program and the procedures for stibine collection and atomization of antimony and arsenic are summarized in Table 2. Hydride trapping conditions reported for stibine in a previous publication [65] and those used by Shuttler et al. [71] for arsine were adopted and no

additional optimization was undertaken. The preparation of the Ir-Pd coated graphite tube for trapping arsine was as described by Shuttler et al. [71]. For the optimization of antimony response, 4 $\mu\text{g/l}$ Sb(III) in 1 M HCl and a lead cathode were used, if not otherwise stated. For the optimization of arsenic response, 4 $\mu\text{g/l}$ As(III) in 0.36 M H_2SO_4 and a lead cathode were used, if not otherwise stated. The sequence of operations for antimony determination was as follows: before each hydride collection cycle, 50 μl of 200 mg/l Pd solution was manually injected into the graphite furnace using a Gilson microlitre pipet fitted with a disposable polypropylene tip, whereupon it was dried, reduced at 600 $^\circ\text{C}$ and cooled to the deposition temperature of 350 $^\circ\text{C}$. The quartz tube transfer line was then manually inserted into the graphite furnace for the collection of the hydride. Following completion of the hydride generation/collection cycle, the transfer line was removed and furnace program "3" was initiated to complete the analysis cycle. Quantitation was achieved by generating a standard calibration curve using standards processed through the electrochemical cell. Integrated absorbance measurements were used throughout. During non-working hours, the anode cell is left empty and the cathode cell is filled with DDW. The cell could be run at least one month without changing either the electrolytic membrane or cleaning the surface of the cathode.

Table 2. Furnace program.

Program	Step	Temp. (°C)	Ramp (s)	Hold (s)	Internal purge (ml/min)	Comments
1	1	120	5	15	300	inject Pd solution and dry
	2	600	5	5	300	reduce Pd deposit
2	1	350	10	*	0	insertion of quartz transfer tube and collection of hydride
3	1	200	5	5	300	moisture removal
	2	2400	0	3	0	atomization of analyte
	3	2500	1	1	300	clean tube
4	1	120	5	15	300	dry aqueous standard
	2	200	5	5	300	atomization of analyte
	3	2400	0	3	0	tube clean

30 s for the optimization of signal, 250 s for sample analysis

3. RESULTS AND DISCUSSION

3.1. Optimization of signal generation

The optimization of the EcHG cell was primarily accomplished by in-depth study of the effect of experimental variables on the analytical response from solutions of Sb(III).

Cathode material:

Lead, solid pyrolytic graphite and platinum were evaluated as materials for use as cathodes for the production of stibine. The efficiencies for stibine generation obtained with these three electrodes operating under the same experimental conditions are $90 \pm 5\%$, $\sim 45\%$ and zero %, respectively. In the context of this study, efficiency is defined as the ratio of the response obtained for the atomization of a given mass of antimony which has been processed as a hydride and collected in the furnace to that of the same mass of antimony directly introduced as an aqueous solution and subjected to an identical atomization program. It is thus a measure of the overall efficiency of generation of the hydride, its separation from the liquid phase as well as transport to, and deposition in, the furnace. As noted earlier, electrochemical hydride generation consists of at least three sequential events: reduction and deposition of the aqueous Sb(III) onto the surface of the cathode (or at specific active surface sites); stepwise reaction of the deposited antimony with nascent hydrogen ($H\cdot$) generated on the surface of the cathode; and subsequent desorption of the SbH_3 . It was found that the lead cathode yields the highest sensitivity and best reproducibility of the three electrode materials

examined. High generation efficiency for stibine on lead cathodes has been noted earlier [19, 154]. This suggests that either the deposition step, the hydride formation step, or both, on the lead cathode are more favourable than on graphite or platinum. The sensitivity obtained with pyrolytic graphite was approximately half that with lead. When an efficiency of 40 % HG with the graphite cathode was attained, it was found that 25 % of the antimony had been irreversibly deposited on the surface without conversion to stibine. Addition of 1.6 $\mu\text{g/ml}$ Pb(II) to the antimony solution increased the efficiency of generation of stibine from the graphite cathode by nearly 2-fold. No such effect could be achieved with the Pt cathode. If the pyrolytic graphite cathode was pre-treated by application of 0.5 ml conc. H_2SO_4 on its surface for 3 min. followed by rinsing in DDW and a further 3 min. application of concentrated HNO_3 , the efficiency for HG increased to 70 ± 6 %. Efficiency for stibine production is clearly the highest on lead and least on Pt cathodes. This parallels the hydrogen overvoltage on these materials. Softer metals, such as lead (and particularly mercury) are more useful in this respect because their high hydrogen overvoltages permit the analytically useful reactions to proceed with higher current efficiency. When 2 M H_2SO_4 is used in the anolyte solution, in conjunction with the Nafion[®] 417 membrane and a platinum cathode, no signal could be obtained with 4 $\mu\text{g/l}$ Sb(III) in 1 M HCl, 1 M HNO_3 or 0.5 M H_2SO_4 solution. Figure 3 illustrates typical results for the operation of the cell with a Pt cathode. For the first few runs, no signal can be obtained. As more of the 1 mg/l Sb(III) solution is pumped through the cell, the HG efficiency gradually increases, attaining a steady-state 4.5 % after about 10 runs. A possible explanation for this effect is that the Pt surface becomes coated with Sb, thereby increasing efficiency. This suggests that the system

described by Brockmann et al. [17] could not be used to determine antimony at very low concentrations under the conditions of their experiments.

The efficiencies for generation of arsine from the three electrodes operating under the same experimental conditions are $86 \pm 6 \%$, $< 40 \%$ and $< 7 \%$, respectively. The sensitivity obtained with pyrolytic graphite was less than half that with lead. Addition of $1.6 \mu\text{g/ml}$ Pb(II) to the arsenic solution increased the efficiency of generation of arsine from the graphite cathode by nearly 2-fold. The platinum cathode results in the lowest efficiency and the poorest reproducibility. When $2 \text{ M H}_2\text{SO}_4$ is used in the anolyte solution, in conjunction with the Nafion® 417 membrane and a platinum cathode, no signal could be obtained with $4 \mu\text{g/l As(III)}$ in 1 M HCl , HNO_3 or $0.5 \text{ M H}_2\text{SO}_4$. This suggests that the system used by Brockmann et al. [17] could not be used to determine arsenic at very low concentrations under the conditions of their experiments.

Electrolytic membrane:

Nafion® 112, Nafion® 417, Raipore® 1010 and the CM-1 grade NEOSEPTA® ion exchange membranes were examined as electrolysis membranes. Raipore® 1010 and the CM-1 grade NEOSEPTA® membranes exhibited the same performance. The efficiency of stibine generation with Nafion® 417 membrane was only $60 \pm 15 \%$ of that obtained using the CM-1 grade NEOSEPTA® membrane. The difference in performance between Nafion® 112 and Raipore® 1010 membranes is illustrated by the data in Figure 4. Whereas the Nafion® 112 membrane was apparently unstable in $2 \text{ M H}_2\text{SO}_4$, the performance of the Raipore® 1010 was satisfactory. The CM-1 grade NEOSEPTA® ion-exchange membrane

Figure 3. Typical results for stibine generation with a Pt cathode and a 1 mg/l Sb(III) solution.

and Raipore® 1010 were used for antimony and arsenic, respectively, in all subsequent experiments. It was observed that when chlorine could be visibly detected in the anolyte solution, the signal for both arsenic and antimony would drop dramatically. In the case of arsenic, the degree of suppression was the most pronounced. If hydroxylamine hydrochloride is added to the anolyte at this time to reduce the chlorine, the signals could often be recovered.

The reason for this appears to be that the free chlorine in the anolyte can diffuse through the membrane into the cathode compartment of the hydride generation cell and severely interfere with both stibine and arsine formation. No other experimental parameter can be altered so as to alleviate the interferences caused by interfering species generated in the anolyte, and the signal can be totally suppressed if the membrane permits such interferences to transfer from the anode cell to the cathode cell. This suggests that low diffusion coefficient membranes should be used.

Anolyte solution:

When 1 M H_2SO_4 is used in the anolyte solution in conjunction with Nafion® 112 membranes, signals could initially be generated, but the system would not perform for more than several runs before the signal would drop to zero. Changing the anolyte to a 20 % (m/v) solution of hydroxylamine hydrochloride in 2 M HCl caused the signal to recover in some cases, as illustrated by the data in Figure 4. As a result, this latter anolyte solution was selected for all further studies and, with the present arrangement, only required changing after 6 hours of electrolysis. Remarkable differences were found between 1 M H_2SO_4 and

Figure 4. Effect of anolyte composition and membrane type on analytical response from stibine using 4 $\mu\text{g/l}$ Sb(III).

- ◻ Raipore[®]1010 membrane with 1 M H₂SO₄ anolyte solution;
- Nafion[®] 112 membrane with 1 M H₂SO₄ anolyte solution;
- ◊ Nafion[®] 112 membrane with 20 % (m/v) NH₂OH · HCl in 2 M HCl anolyte solution.

a 20 % (m/v) hydroxylamine in 2 M HCl anolyte solution for arsine generation, as illustrated by the data in Figure 5. Following about 10 runs of the hydride collection cycle using the former anolyte, the signal decreased dramatically. Only by changing the anolyte back to the hydroxylamine hydrochloride could significant recovery of the signal be instantly obtained. Therefore, the latter anolyte solution was selected for all further studies for arsine production.

Electrolytic current density:

Tomlinson [19] has shown that the electrochemical rate of formation of stibine on a lead cathode is independent of the current density in the cell but strongly dependent on the total current flow through the cell. In addition, the increase of current density may result in an increase of hydrogen overvoltage which may be a factor permitting more efficient hydride generation. As expected [19], absorbance signals increase with increasing current (density), as shown by the data in Figure 6. It was found sufficient to use 150 mA/cm² to obtain maximum signal under the optimized conditions. Possibly, mass transfer effects become rate limiting as the current density is increased beyond this value. If the efficiency was significantly below 90 %, increases in current density were not effective in improving the sensitivity due to other factors limiting the efficiency of the ECHG process. The limiting current density recommended [155] for use with CM-1 ion-exchange membranes is < 200 mA/cm².

Absorbance signals for arsine production also increase with increasing current (density), as shown by the data in Figure 7. Maximum response was obtained at 170 mA/cm².

Figure 5. Effect of anolyte composition on analytical response from arsine using $4 \mu\text{g/l As(III)}$. From run number 1-11, $1 \text{ M H}_2\text{SO}_4$ used as anolyte; from run number 12-15, $20 \% \text{ NH}_2\text{OH} \cdot \text{HCl}$ in 2 M HCl used as anolyte.

Figure 6. Effect of EcHG cell current density on analytical response from stibine using 4 $\mu\text{g/l}$ Sb(III).

Figure 7. Effect of EcHG cell current density on analytical response from arsine using 4 $\mu\text{g/l}$ As(III).

Sample flow rate:

The effect of sample flow rate on stibine production is illustrated by the data in Figure 8. Over the range 0.5 - 1.5 ml/min, the efficiency decreases by 30 %. In the case that sample volume may be limited, it is preferable to use a flow rate less than 0.5 ml/min to maintain maximum sensitivity. The effect of sample flow rate on arsine production is illustrated by the data in Figure 9. Over the range 0.6 - 2.0 ml/min, efficiency decreases by 46 %. A flow rate of 0.6 ml/min was selected as a working compromise between an optimal efficiency and reasonable sample throughput. Where sample volume is not limited, flow rates may be increased, collection time minimized and optimal signal-to-blank attained for analysis. Using a higher flow rate is desirable to maximize throughput and is also practical with this system. It is likely that the rate controlling step for the hydride generation is the reduction of antimony or arsenic onto the surface of the cathode when the concentration of either analyte is very low, consequently, as the sample flow rate is increased, more analyte will go to waste before the hydrides can be formed.

Acidity and acid of sample solution:

With the conventional NaBH_4 -acid reduction system, HCl is generally used for stibine and arsine production in the concentration range of 1-9 M [3]. Results presented in Figure 10 show that the acidity of the sample solution is not critical for FeHCl of stibine and both H_2SO_4 and HCl may be used. The % RSD of replicate signals is less than 4.4 % over the range of 0.3 to 2.4 M HCl and over the range 0.09 to 0.54 M for H_2SO_4 . Higher concentrations of H_2SO_4 are not permitted because of severe attack of the lead cathode,

Figure 8. Effect of sample flow rate on efficiency of EcHG of stibine using $4\mu\text{g/l}$ Sb(III).

Figure 9. Effect of sample flow rate on efficiency of EcHG of arsine using $4 \mu\text{g/l}$ As(III).

whereas the CM-1 membrane is resistant to attack by even 40 % H_2SO_4 [154]. As the samples to be analysed contain 0.15 % (v/v) HNO_3 , the effect of the presence of HNO_3 was examined; results are presented in Figure 11. Suppression of stibine production occurs at levels as low as 0.04 M HNO_3 in 1 M HCl . This may be caused by the presence of NO_3^- or reduced nitrogen oxide species such as NO_2^- or chlorine formed by oxidation of Cl^- . It has been shown that oxidizing media also reduce the efficiency of the BH_4^- - acid reduction system [125].

The results illustrated by the data in Figure 12 show that both H_2SO_4 and HCl may be used as sample media for arsine production by EcGH. The overall RSD of replicate signals is less than 10 % over the range of 0.3 to 2.4 M HCl and over the range 0.18 M to 1.44 M for H_2SO_4 . With 0.36 M H_2SO_4 , anolyte medium, the cell could be operated for one month without fouling of the electrode surface leading to reduced arsine generation efficiency. However, lower efficiency of arsine production resulted after ten runs of a sample in 1.44 M H_2SO_4 due to its severe attack of the cathode. The RSD of replicate signals ($n=4$) using H_2SO_4 media is better than 10 %. No significant difference in the analytical performance was obtained using either HCl or H_2SO_4 . The presence of 0.15 % (v/v) HNO_3 in 0.36 M H_2SO_4 or 1 M HCl had no effect on arsine generation.

Effect of oxidation state:

One of the major drawbacks present in the NaBH_4 -acid reduction system is the need for a pre-reduction step to reduce Sb(V) to Sb(III) for determination of total antimony [59,99]. It is also well documented in the literature [84] that, in batch systems, pentavalent

Figure 10. Effect of sample acidity on analytical response from stibine using 4 $\mu\text{g/l}$ Sb(III).

□ HCl □ H₂SO₄

Figure 11. Effect of HNO_3 concentration on analytical response from stibine using $4 \mu\text{g/l}$ Sb(III) .

Figure 12. Effect of sample acidity on analytical response from arsine using 4 $\mu\text{g/l}$ As(III).

⊙ HCl □ H₂SO₄

arsenic is 25-30 % less sensitive with peak absorbance measurements than its trivalent form. In FI systems [82], it is also advisable to reduce arsenic to its trivalent state prior to its determination by HG-AAS. L-cysteine has been shown to be very effective and less time-consuming than KI for the reduction of both Sb(V) to Sb(III) and As(V) to As(III) [91, 92, 145]. However, use of pre-reduction reagent will always increase the time for analysis, elevate the cost and labour per analysis and may introduce contamination from the reagents. In this study, production of stibine from either Sb(III) or Sb(V) by electrochemical means resulted in no significant difference in efficiency of generation. Production of arsine from either As(III) or As(V) in 0.1-1 M HCl and 0.36 - 1.07 M H₂SO₄ media by EcHG produces no significant difference in sensitivity.

The efficiency of EcGH for the generation of volatile forms of arsenic when present as monomethylarsenic acid (MMA), dimethylarsonic acid (DMA) and arsenobetaine (AsB) are $100 \pm 8 \%$, $65 \pm 12 \%$, and zero, respectively (n=3).

3.2. Analytical results

Results for the analysis of NRCC river water reference materials SLRS-2 and SLRS-3 for antimony are presented in Table 3. Good agreement with certified values is evident. A simple aqueous standard of 1 $\mu\text{g/l}$ Sb(III) was used for calibration with signal integration. Results for the analyses of NCC seawater reference material NASS-4 are given in Table 4. A simple aqueous standard of 0.2 $\mu\text{g/l}$ Sb(III) could be used for calibration with results indistinguishable from those generated by use of the method of additions. Unfortunately,

this material is not certified for Sb content but the concentration of this analyte is likely not significantly different from that of NASS-1, i.e., 0.21 ± 0.00 $\mu\text{g/l}$ [59]. It is evident that pre-reduction of Sb(V) to Sb(III) is not necessary for the analysis of total antimony using EcHG whereas it is required with the BH_4^- chemical generation system [59, 99].

An attempt was made to analyse river water reference material SLRS-2 for arsenic content. Both simple calibration curve (using As(III) and As(V) standards) as well as the method of additions were utilized. Identical response was obtained from standards prepared from either As(III) or As(V) in $0.72\% \text{H}_2\text{SO}_4$. Analysis of SLRS-2 by calibration against a standard curve (using either As(III) or As(V) produced low results [i.e., 0.54 ± 0.02 $\mu\text{g/l}$ ($n=7$)]. Similarly, results from the method of additions were biased low compared to the certified value, i.e., 0.66 ± 0.03 ($n=5$) vs 0.77 ± 0.09 $\mu\text{g/l}$, respectively. It is evident that there is an interference with the determination of arsenic in this sample but it is unclear what this effect is. The possibility of organic material influencing the results cannot be discounted.

Figures of merit:

The sensitivities of the method, as determined from the slopes of calibration curves, are 0.0623 ± 0.0022 absorbance·s/ng, (71 ± 3 pg/0.0044 absorbance·s) for antimony and 0.0732 ± 0.0030 absorbance·s/ng (60 ± 2 pg/0.0044 absorbance·s) for arsenic. These are in reasonable agreement with values obtained for the atomization of aqueous solutions, i.e., 65 ± 3 pg/0.0044 absorbance·s for Sb and 52 ± 4 pg/0.0044 absorbance·s for As using the same furnace thermal program. Thus, the signal obtained by atomization of trapped stibine and

Table 3. Analysis of NRCC river water reference material for: antimony

Run	Concentration, $\mu\text{g/l}$	
	SLRS-2	SLRS-3
1	0.268	0.100
2	0.231	0.107
3	0.247	0.107
4	0.253	0.114
5	0.232	0.100
6	0.267	
7	0.262	
8	0.266	
9	0.266	
10	0.238	
11	0.253	
12	0.242	
mean	0.252 ± 0.014	0.106 ± 0.006
certified value	0.26 ± 0.05	0.12 ± 0.01

Table 4. Analysis of NRCC seawater reference material for antimony

Concentration, $\mu\text{g/l}$		
Run	Std curve	Std additions
1	0.23	0.20
2	0.20	0.23
3	0.22	0.20
4	0.23	0.24
5	0.22	
mean	0.22 ± 0.01	0.22 ± 0.02

arsine generated from a sample solution are $92 \pm 4 \%$ and $86 \pm 4 \%$ of the response obtained by atomization using an identical thermal program of an equivalent amount of Sb and As introduced into the furnace in a $10 \mu\text{l}$ volume of aqueous sample, respectively. Estimated detection limits, based on the variability of the blank ($3\sigma_b$) and the variability of the sample ($3\sigma_s$), are 23 pg/ml and 37 pg/ml , respectively, using a 2 ml sample volume for Sb and 114 pg/ml and 64 pg/ml , respectively, using a 0.5 ml sample volume for As. The precision of determination, expressed as a % RSD, is approximately 6% and 18% at 0.5 ng and 0.08 ng mass, respectively for Sb and 4% and 9% at 1 ng and 0.02 ng mass, respectively, for As. The absolute blanks for Sb and As are $79 \pm 15 \text{ pg}$ and $21 \pm 18 \text{ pg}$, respectively. Dynamic range for Sb and As extends to 3.2 ng and 4 ng , respectively.

The major source of the blank for Sb determination appears to arise from use of the lead cathode. Although high-purity ($99.99+ \%$) material was utilized, initial runs following installation revealed considerable surface impurity which decreased with continued usage. Only minor impurities are present in the support electrolyte (1 M HCl) as the blank does not increase in proportion to the volume of blank solution electrolysed. An increase from 0.4 to 2 ml gave rise to only a 60% increase in the total blank. The use of reduced Pd as a sequestering agent for stibine contributes negligibly to the blank. The instrument measurement "blank" arising from the heating of a dry tube contributes $45 \pm 17 \%$ to the measured total. These figures of merit compare favourably with those reported earlier from our laboratory characterizing the BH_4^- generation of stibine with *in situ* pre-concentration in the graphite furnace [59, 65].

The major source of the blank for As determination appears to arise from instrument

noise. The instrument measurement "blank" arising from heating of a dry tube contributes 72 ± 25 % to the measured total. An increase of sample volume from 0.5 to 1.5 ml produced no increase in the total blank. The use of a mixture of reduced Ir and Pd as sequestering agent for trapping arsine contributes negligibly to the blank.

3.3. Interferences

Influence of copper or nickel on stibine generation:

To date, only one report addressing applications of EcHG for the determination of antimony has appeared in the literature and it presents no data concerning potential interferences from concomitant elements [16]. The effects of copper and nickel on the EcHG of SbH_3 using lead and pyrolytic graphite cathode materials were briefly examined in this study. The degree of interference can be expressed as a percentage "recovery" of the signal from the interferent-free solution. As copper and nickel are well-recognized as producing the most severe interference effects in the borohydride - acid reduction system, they were selected for investigation. The effect of various concentrations of copper on the recovery of the signal on the first run of a $4 \mu\text{g/l}$ solution of Sb(III) is illustrated by the data in Figure 13. A flow injection sampling format was used wherein the sample solution containing the analyte and copper was valved into the carrier line using a $500 \mu\text{l}$ sample loop. It is clear that the presence of as little as $7.5 \mu\text{g/ml}$ copper severely interferes with stibine generation, resulting in a 50 % suppression of the signal compared with that from an interferent-free solution. Furthermore, severe memory interference immediately occurs in that attempts to

run a subsequent solution containing only Sb(III) through the cell continues to result in a suppressed response relative to that obtained in a cell which was never exposed to the presence of a copper solution. If an argon flow of 50 ml/min was permitted to pass through the cathode compartment, it was often found that no interferences and no memory effects resulted from even 15 $\mu\text{g/ml}$ copper, at least for the first few runs of the solution containing interferent. Severe memory interference, resulting in more than 50 % suppression, often occurs in the very next run with the interferent-free solution if the argon purge is not used. An argon flow may facilitate the desorption of stibine off the surface of the cathode and the rapid separation of stibine from the liquid phase. With the electrolysis process stopped, 2 M HNO_3 can be pumped through the cell for 5 minutes to clean the cathode surface. This was found effective in decreasing the memory interference from copper.

Nickel, at a concentration of 10 $\mu\text{g/ml}$, caused more severe interference and more severe memory effects than that of copper. Any reduced nickel present in the cathode compartment depresses the signal for the next determination even in the absence of interfering ions in the solution. Interferences by copper and nickel on pyrolytic graphite cathodes are very similar to those on lead. The presence of 15 $\mu\text{g/ml}$ copper resulted in a 50 % suppression of the stibine signal, whereas 10 $\mu\text{g/ml}$ nickel produced an 80 % signal suppression. No study was made of the platinum cathode system because the efficiency of stibine generation from this material is less than 1 % at analytically significant levels of Sb(III).

Figure 13. Influence of Cu(II) on EcHG of stibine using 4 µg/l Sb(III).

Influence of copper and nickel on arsine generation:

The effect of copper and nickel on arsine generation using lead and platinum cathodes was briefly examined. Significantly greater interference was noted when using the lead cathode. The presence of 120 $\mu\text{g/ml}$ Cu(II) resulted in a 30 % recovery of the AsH_3 signal and 20 $\mu\text{g/ml}$ nickel produced a 20 % signal recovery. In contrast to this, 600 $\mu\text{g/ml}$ nickel exhibited no effect when a platinum cathode was used, despite the observation that after about a dozen runs at this concentration a loose black deposit was visible on the surface of the cathode. Both Lin et al. [16] and Brockmann et al. [17] reported on the interference from nickel using a platinum cathode and concluded that there was no effect from the presence of 100 and 10,000 $\mu\text{g/ml}$, respectively. However, it should be noted that the efficiency of arsine production on platinum is less than 8 %, which is not considered analytically useful for ultratrace applications. Since no discussion concerning memory interference or fouling of the cathode surface was given by either of these authors, these data cannot be considered convincing.

It is well-known that copper, nickel and cobalt are amongst the elements which interfere the most severely with the conventional NaBH_4 -acid reduction system [3]. As noted earlier, one of the mechanisms proposed to account for this effect is that interfering metal ions are reduced to finely dispersed metallic particles which remain in the solution or become deposited within the system and subsequently decompose or capture hydrides, thereby causing immediate and/or memory-like interferences [118, 119, 123]. It is likely that this interference mechanism may also apply to EchHG.

Under the conditions used for this interference study, the cathode potential was

measured to be approximately - 1 V relative to the S.C.E. At this cathode potential, nickel and copper are reduced to the metal. The half-cell reduction potentials for the Ni^{2+}/Ni , Cu^{2+}/Cu , As/AsH_3 and Sb/SbH_3 systems are - 0.47 V, 0.10 V, - 0.78 V and - 0.75 V, respectively, relative to the S.C.E.. As long as the hydrides are electrochemically formed, the interfering metal ions would be reduced to metal on the surface of the cathode with the possibility that they are also subsequently dispersed as fine metal particles within the cathode compartment. Such a deposit of metal would change the physico-chemical surface characteristics of the lead cathode and, consequently, destroy the favourable nature of lead for electrochemical hydride generation and lower the efficiency of hydride production. Additionally, the dispersed metal phase in the solution may also scavenge the generated hydrides and reduce response. Indeed, the interference noted by the presence of $7.5 \mu\text{g/ml}$ copper on antimony is consistent with the above. The lead cathode was immediately fouled and the highly favourable characteristics for hydride generation on this material were lost. The amount of copper present in solution to cause this effect is, to a first approximation, sufficient to form a monolayer coverage over the entire geometric area of the cathode surface. It is also possible that the entire surface of the cathode does not serve to generate hydrides but that the reaction proceeds predominantly at active sites. These are the first to be fouled by the concomitant elements. Once blocked, there is a memory effect in the system until the deposited metal is physically or chemically removed. A comprehensive explanation of the influence of these metals on the surface activity of the cathodes and the nature of their deposits is beyond the scope of this study.

Effects of acid or acidity of catholyte and sample flow rate:

As noted by Welz and Schubert-Jacobs [120], an increase in the concentration of HCl is effective in decreasing the interference caused by copper or nickel in the NaBH_4 -acid reduction system. With EcHG, an increase from 1.2 to 7 M HCl had no effect in alleviating interference from copper. Additionally, there was no difference between using 0.54 M H_2SO_4 or 1.2 M HCl. An increase in sample flow rate through the cell from 0.5 ml/min to 3.75 ml/min also resulted in no diminution in the degree of interference. All of these observations are consistent with the fouling of the cathode surface by a deposit of the interfering metal.

Effects of L-cysteine and thiourea:

The effects of copper on the determination of antimony using the NaBH_4 -acid reduction system are less than those arising from other elements such as nickel [145]. The best reported tolerance limit for copper in a flow injection system is 200-250 $\mu\text{g/ml}$ [145]. If L-cysteine is used, this value is increased to 1000 $\mu\text{g/ml}$ [145]. Brindle and Le [153] as well as Bye [126] have commented on the utility of L-cysteine and thiourea as reagents for the minimization of interferences from transition metal ions on the generation of volatile hydrides with the NaBH_4 - acid reduction system. In the present case, addition of 5 % (m/v) L-cysteine in 1 M HCl to the analyte solution was found ineffective in alleviating interference caused by the presence of 100 $\mu\text{g/ml}$ copper. Furthermore, L-cysteine itself caused a 19 % suppression of the response from Sb(III) as compared to an L-cysteine-free solution. No attempt was made to test the effect of L-cysteine in 0.1 M HCl media, which

was the optimum medium reported for use of this reagent in the NaBH_4 -acid reduction system. Use of a 1 % (m/v) solution of thiourea in 1 M HCl caused neither interference on SbH_3 production nor beneficial effect from the presence of 100 $\mu\text{g/ml}$ copper interference.

As noted earlier, recent investigations by Brindle and Le [153] into the mode of action of L-cysteine in the NaBH_4 - acid system suggest that this reagent complexes with BH_4^- to prevent or minimize the concomitant reduction of matrix transition metal ion interferences. As a consequence, it is clear that these reagents would be completely ineffective in the EcHG system, as noted experimentally.

Effect of added lead(II):

As the EcHG efficiency was found to be greatest on a lead cathode, it was reasoned that the introduction of Pb(II) into the system along with the analyte and the interferent may have a beneficial effect. Deposition of a "soft" metal onto a host cathode material may serve to increase the hydrogen overpotential and, as noted earlier, analyte hydride formation may proceed at a higher current efficiency. Electrodeposition of lead onto the cathode surface may provide a means of continuously regenerating the active surface. In accordance with this, addition of 1.6 $\mu\text{g/ml}$ lead to the 4 $\mu\text{g/l}$ Sb(III) solution enhanced stibine production by 50 % on a pyrolytic graphite cathode. The usefulness of Pb(II) in reducing interference by copper on stibine production with the lead cathode was also examined. In the presence of 1000 $\mu\text{g/ml}$ Pb(II) , interference from 100 $\mu\text{g/ml}$ Cu(II) was reduced to approximately 15 % suppression. These studies support the idea that specific active sites on the surface may be operative in the EcHG system but, unfortunately, provide an impractical alternative to

interference reduction because the methodological blank is enhanced by more than 50 - fold above usual (due to contamination) and, at best, 120 $\mu\text{g/ml}$ Cu(II) can be tolerated. An attempt was made to intermittently electrochemically generate Pb(II) direct from the surface of the lead cathode which could then be subsequently redeposited. In order to implement this, the lead electrode polarity was momentarily reversed and held at a potential of 0.7 V vs. the S.C.E. for a period of 1 s, after which a second polarity reversal was made and the cell operated galvanostatically at a current of 1.5 A for 4 s to generate stibine. Unfortunately, severe interference by 15 $\mu\text{g/ml}$ Cu(II) on 4 $\mu\text{g/l}$ Sb(III) persisted.

Remedial actions:

Interference mechanisms proposed for the NaBH_4 -acid reduction system have been related to the catalytic effect of metal ions on the decomposition of BH_4^- and reaction of BH_4^- with metal ions to form borides and finely dispersed reduced metal [124]. Presumably, the interference mechanism is much simpler in the EcHG system. If deposition of interfering metal ions during the hydride generation process can be avoided, analytical methodology applicable to real samples can be developed.

As stated earlier, the process of hydride formation using EcHG involves at least two steps: reduction of the aqueous analyte ion with its deposition onto the surface of the cathode, and stepwise reaction of the deposited element with nascent hydrogen generated on the surface of the cathode to produce the hydride [18 - 20]. Examination of the standard half-cell reduction potentials for metal ions [156] suggests that one may take advantage of their differences to effect a preliminary separation of the analyte element of interest from the

interferent through control of the cathode potential. As an example, the standard half-cell reduction potentials for Cu(II) and Ni(II) are 0.10 and -0.47 V, respectively (vs. the S.C.E.). Standard half-cell reduction potentials for Sb(III), As(III) and Se(IV) are -0.03, 0.006 and 0.49 V, respectively. In principle, therefore, controlled potential deposition should permit the accumulation of antimony on the cathode while Ni(II) flows unimpeded through the EcGH cell. Conversely, with a pre-cell arrangement, it should be possible to electrochemically remove Cu(II) from the analytical solution and subsequently deposit only the antimony from the flowing stream as it passes through the analytical EcGH cell. In the case of Se(IV), deposition of this element could be achieved before either copper or nickel. In both cases, such pre-treatment would be followed by the galvanostatic generation of the analyte hydride in an interference-free medium. The Nernst equation can be used to calculate the voltage necessary to reduce the concentration of the interfering element to an acceptable level in the system. As an example, in 1 M HCl, if the level of Sb(III) is to be reduced to the limit of detection in the system (i.e., 0.02 µg/l or 1.6×10^{-10} M), the following relationship can be used to calculate the resulting half-cell potential:

$$E_{\text{SbO}^+/\text{Sb}} = E_{\text{SbO}^+/\text{Sb}}^0 + (0.0592 / 3) \log [\text{SbO}^+] [\text{H}^+]^2 \quad (5)$$

yielding a result of -0.22 V vs S.C.E. under the above conditions. If Ni(II) is present in the analyte solution at a concentration of 1000 µg/ml (0.016 M), the half-cell potential can be calculated from the following relationship:

$$E_{Ni^{2+}/Ni} = E^{\circ}_{Ni^{2+}/Ni} + (0.0592 / 2) \log [Ni^{2+}] \quad (6)$$

yielding - 0.52 V vs S.C.E.. Thus, the difference in potential between Ni(II), or any other interfering species with a half-cell potential less than that of nickel, and Sb(III) is 0.27 V under the prescribed composition of the final solution. In principle, this will permit the separation of Sb(III) from Ni(II) by electrodeposition of antimony onto the cathode, allowing interference-free generation of stibine. It must be noted that the above calculations are based on ideal systems in which there are no kinetic barriers to the deposition processes and the activities of the condensed phases have been assumed to be unity.

Similar calculations can be made if the matrix element of interest is copper, in which case if it is assumed that a final concentration of 0.1 $\mu\text{g/ml}$ Cu(II) is acceptable, this element, or any other interfering metal ion with a reduction potential higher than that of copper, can be removed from the analyte solution by deposition in a pre-cell, permitting interference-free generation of stibine in a second cell. In theory, the procedure applying to the separation of Sb(III) from the matrix would also apply to that of As(III).

The half-cell reduction potential for the $\text{H}_2\text{SeO}_3/\text{Se}$ system is 0.74 V, significantly higher than those of copper, nickel and cobalt. The reduction potential difference between 0.001 $\mu\text{g/ml}$ Se(IV) and 1000 $\mu\text{g/ml}$ Cu(II) in 1 M HCl media would theoretically exceed 0.29 V. Therefore, it should be feasible to first deposit Se(IV) while interfering metal ions remain in the solution and are pumped to waste. This can be followed by generation of selenium hydride. Bye and Lund [157] successfully demonstrated the electrochemical separation and concentration of Se(IV) at a concentration of 5 $\mu\text{g/l}$ Se in a sample solution

of digested biological material.

One potential problem with the implementation of the above procedures is the formation of lead chloride at the cathode during the deposition of the interfering matrix ion. This may lead to electrode fouling and loss of efficiency. However, as was briefly mentioned earlier, pyrolytic graphite treated with concentrated H_2SO_4 and HNO_3 yields a 70 % stibine generation efficiency with satisfactory precision (although exhaustive studies were not undertaken to determine the lifetime of such a treated cathode). This material would be inert under the potential used to deal with interference problems described above and electrode fouling would not be of concern. This cathode material is a likely choice for EcHG, especially when matrix isolation is attempted by electrochemical means.

Although very useful for extending the range of tolerable concentrations from interfering ions, such reagents as L-cysteine and thiourea are still limited to relatively low tolerance limits of interfering metals in the NaBH_4 -acid reduction system [158]. As a consequence, additional means of achieving matrix separation should be sought. These may include the use of immobilized chelates packed into convenient columns that can be incorporated into flow injection systems, such as recently outlined by Offley et al. [158] and Fang et al. [159]. In such case, the matrix ions may be removed from solution first, to permit the interference-free generation of the analyte hydride, or the analyte may be removed, the solution pumped to waste and then the analyte released in a suitable medium and passed to the EcHG cell for hydride generation.

4. CONCLUSIONS

Electrochemical hydride generation techniques provide a potentially much cleaner hydride generation system as well as ease of operation as compared to the NaBH_4 - acid reduction system. With lead as the cathode material, the high sensitivity of the latter system can be attained with much less critical requirements on the experimental conditions. EcHG permits direct analysis of antimony and arsenic without the need of a pre-reduction step to reduce Sb(V) to Sb(III) . Unfortunately, severe interference from Cu(II) or Ni(II) on Sb(III/V) or As(III/V) production exists with EcHG.

In combination with FI techniques, considerable advantages may accrue, including improved precision, increased sample throughput, reduced blank and higher power of detection. In combination with an Ir-coated tube, unattended operation becomes feasible.

Future work in this area should be concentrated on investigation of remedial methods to eliminate potential interferences. Matrix separation using immobilized chelates may be a method of choice to deal with interferences. The matrix ions may be removed from solution first to permit the interference-free generation of the analyte hydride, or the analyte may be removed, the solution pumped to waste and then the analyte released into a suitable medium and passed to the EcHG cell for hydride generation. Matrix separation by electrochemical means appears to be, in principal, more interesting and promising. Matrix ions such as Cu(II) may be removed from solution first by deposition of Cu onto a pre-cell cathode to permit the interference-free generation of the analyte hydride in a following EcHG cell, or the analyte may be removed by deposition of analyte, i.e., Sb(III) , as Sb on the

cathode surface, the solution containing interfering ions such as Ni(II) pumped to waste followed by generation of stibine.

Lead cannot be used as a cathode material when matrix isolation is attempted by electrochemical means since chloride will be formed on the surface under the required cathode potential. Graphite, after suitable treatment with concentrated H_2SO_4 and/or HNO_3 , is likely the cathode material of choice. This material would be inert under all EcHG working conditions. In particular, reticulated vitreous carbon is especially attractive due to its large surface area and porosity. Finally, it remains to extend the EcHG technique to additional analytes such as tin and selenium.

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