ELECTROCHEMICAL HYDRIDE GENERATION AND ATOM TRAPPING ATOMIC ABSORPTION SPECTROMETRY FOR DETERMINATION OF ANTIMONY

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ABSTRACT

ELECTROCHEMICAL HYDRIDE GENERATION AND ATOM TRAPPING ATOMIC ABSORPTION SPECTROMETRY FOR DETERMINATION OF ANTIMONY

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Electrochemical hydride generation is a suitable alternative to common hydride generation by $NaBH_4$ which is widely used for the detection of volatile elements such as As, Se, Sb, Sn, Bi, Ge, Te and Pb. In this study, a thin-layer flow through electrochemical cell was designed. Lead and platinum foils were employed as cathode and anode materials, respectively, for the generation of antimony hydride. Argon was used as the carrier gas. The inlet arm of the conventional quartz tube atomizer was used for on-line preconcentration of generated hydrides. A portion of the inlet arm was heated externally to the collection temperature for trapping the analyte species which were generated electrochemically. For the revolatilization of the trapped species, the trap was further heated to the revolatilization temperature and hydrogen gas was introduced into the system 10 seconds afterwards. The experimental operation conditions for electrochemical hydride generation which include the acidities and flow rates of catholyte and anolyte solutions, carrier gas flow rate and the applied electric current, were optimized. For trapping, collection and revolatilization temperatures and hydrogen flow rates were optimized. Analyses of standard reference materials were performed to check the accuracy of the proposed method. 3σ limit of detections were found as 1.03 ng ml^{-1} and 0.053 ng ml^{-1} with and without employing the trap, respectively. The trap has provided 20 fold sensitivity improvement.

Keywords: Electrochemical Hydride Generation, Preconcentration, Atomic Absorption Spectrometry, Quartz Trap, Sb

ÖZ

ELEKTROKİMYASAL HİDRÜR OLUŞTURMALI VE ATOM TUZAKLI ATOMİK ABSORPSİYON SPEKTROMETRİ KULLANILARAK ANTİMON TAYİNİ

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Elektrokimyasal hidrür oluşturma As, Se, Sb, Sn, Bi, Ge, Te ve Pb gibi uçucu elementlerin tayininde yaygın olarak kullanılan $NaBH_4$ ile hidrür oluşturma tekniğine bir seçenek olarak sunulmuştur. Bu çalışmada ince tabakalı, akış sistemli elektrokimyasal hücre tasarlanmıştır. Antimon hidrür oluşturmak için, katot ve anot maddeleri olarak sırasıyla kurşun ve platin folyolar kullanılmıştır. Taşıyıcı gaz olarak sisteme argon gönderilmiştir. Hat üzerinde önzenginleştirme için kuvars atomlaştırıcının giriş kolu kullanılmıştır. Elektrokimyasal olarak oluşturulan analit türlerinin tutulması için kuvars atomlaştırıcının giriş kolu dışarıdan ısıtılmıştır. Tutulan türleri yeniden buharlaştırmak için tuzak daha yüksek bir sıcaklık olan geri buharlaştırma sıcaklığına ısıtılmakta ve sisteme ısıtmanın başlangıcından 10 saniye sonra hidrojen akışı verilmektedir. Elektrokimyasal hidrür oluşturma parametereleri olan katolit ve anolit çözeltilerinin asitliği ve akış hızları, taşıyıcı gaz akış hızı ve uygulanan elektrik akımı optimize edilmiştir. Tuzak için ise, toplama ve geri buharlaştırma sıcaklıkları ve hidrojen akış hızı optimize edilmiştir. Önerilen metodun doğruluğunu ölçmek için standart referans maddelerin analizi yapılmıştır. 3σ tayin limiti tuzaksız ve tuzaklı olarak sırasıyla 1.03 ng ml^{-1} ve 0.053 ng ml^{-1} olarak bulunmuştur. Tuzak kullanılarak duyarlılıkta 20 kat artış elde edilmiştir.

Anahtar Kelimeler: Elektrokimyasal Hidrür Oluşturma, Önzenginleştirme, Atomik Absorpsiyon Spektrometri, Kuvars Tuzak, Sb

To my family,

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INTRODUCTION

1.1 Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is based on the absorption of electromagnetic radiation by neutral, ground state atoms produced by an atomizer. This technique has become the most widely used single-element technique for the determination of metals [1]. In 1955, Walsh [2] introduced hollow cathode light sources, flame atomizers and a modulated system and showed that the system works as a quantitative analytical tool. Flame AAS was accepted as an analytical technique in 1960s after the introduction of the first commercial flame atomic absorption spectrophotometer in 1959. Since then, the technique has been widely used as it provides high sensitivity, accuracy and precision.

1.1.1 Flame Atomic Absorption Spectrometry

In flame AAS, a solution of the sample is nebulized by a flow of gaseous oxidant, mixed with a gaseous fuel, and carried into a flame where atomization occurs [3]. The analyte atoms pass rapidly and continuously through the measurement zone while the solution is being aspirated and only the equilibrium concentration of the atoms are measured; the residence time of the analyte atoms in the optical path is around 0.1 ms which limits the sensitivity of flame AAS. Sensitivity of the system also depends on the nebulization efficiency which is the ratio of the sample reaching the flame to the amount of sample introduced to nebulizer [4].

Several techniques have been reported to improve the sensitivity of flame atom cells. These techniques involve two mechanisms. In the first one, employing long-tube absorption cells, a Delves' cup [5] or a slotted-tube atom trap, the time spent by ground-state atoms in the optical path of the spectrophotometer is increased. In the other technique, the analyte is preconcentrated and then released for atomization in a more concentrated form, which produces a transient signal (in-situ atom trapping) [6, 7, 8].

1.2 Atom Traps for Flame Atomic Absorption Spectrometry

In the atom traps for flame AAS, the primary concept is in situ preconcentration of analyte atoms in the body of the flame; by this way higher population of the analytes would be available for atomic absorption measurements and preconcentration could be achieved without the usage of additional chemicals. Several traps have been developed to provide this.

1.2.1 Slotted Quartz Tube

The slotted quartz tube was first utilized by Watling [9] who has placed a heated slotted quartz tube with two slots at 120^0 to each other on the conventional flame. The sensitivities of the elements Ag, As, Bi, Cd, Sb, Se, Sn and Pb were increased by 2-5 fold. It is thought that the increased sensitivity is due to the reduced flame speed, longer optical path and the increased lifetime of free analyte atoms in the flame [10]. In addition to obtaining an increase in sensitivity, the precision is also increased.

1.2.2 Water-Cooled Silica Trap

This technique was developed by Lau et al. [11] by placing a water cooled silica tube with 4 mm o.d. and 3 mm i.d. on an air-acetylene flame. A sample solution is aspirated for a measured time interval and after the aspiration is stopped, water flow through the tube is replaced by air. Rapid heating of the silica tube is achieved and the trapped analyte species are released into the beam of the hollow cathode lamp. Consequently, a peak shaped analyte signal is obtained. This type of trap increased the sensitivity of the determination of volatile elements by 8-40 times [12].

Coating of the silica surface with aluminum or vanadium oxides improved the reproducibility in the determination of As, Cd, Pb, Se and Zn and also increased the lifetime of the silica trap tube [13].

1.2.3 Water-Cooled Silica Trap Combined with Slotted Quartz Tube

Ertaş [14] introduced the trap system which is a combination of a water-cooled trapping system and the slotted quartz tube. The sensitivities for Pb and Cd were increased 50-200 times by positioning a slotted quartz tube and double slotted quartz tubes on the water-cooled atom trap. This increase is attributed to the increase in the residence time of the analyte atoms in the optical path.

Another trap designed by Matusiewicz [15] is composed of a slotted tube atom trap with a water-cooled silica tube trap passing through it. In this study, determination of Ag, Cd, Cu, Fe, In, Pb, Tl and Zn in beer was performed.

1.2.4 Slotted Quartz Tube as an Atom Trap

Huang et al. [16] utilized the slotted quartz tube for preconcentration of the analyte atoms. The slotted quartz tube is placed directly above the flame with the narrower slot at the bottom. At a fixed collection time the sample solution is aspirated and preconcentration is achieved. Flame conditions are altered to atomize the preconcentrated atoms. 70-270 fold increase compared to conventional flame AAS was achieved for volatile elements.

Ertaş et al. [7] investigated the analytical performance of three trap systems for determination of Cd and Pb in water samples. Water-cooled U-shaped silica trap, water-cooled U-shaped silica trap combined with a slotted silica tube and the slotted silica tube trap were investigated in the study. In the first trap design, the water-cooled U-shaped silica tube is centered on the flame and the sample solution is aspirated for a deliberate time interval to trap the analyte species. Analyte aspiration is stopped; the silica tube is allowed to heat up by removing the cooling water by a blast of air and consequently the trapped species were released into the optical path of the spectrometer and the signal is measured. In the second trap design which is the combination of water-cooled U-shaped silica trap and slotted silica tube, the analyte atoms are preconcentrated on the water-cooled U-shaped silica tube surface and the trapped species are atomized by changing the flame conditions. During this procedure, water passes through the tube continuously. In slotted tube trap, the sample solution is aspirated for a measured time interval and the analytes are collected on the inner surface of the slotted silica tube. Flame conditions are changed and the atomization of the trapped species is provided. Investigation of these trap systems have shown that the slotted silica tube trap which provided 137 and 90 fold increase in the sensitivities of Cd and Pb respectively is the most sensitive, effective and simplest device among these three traps.

1.3 Hydride Generation

Hydride generation (HG) is the most widely used gas phase sample introduction technique in atomic spectroscopy for the determination of the analytes with ions that can readily be converted into stable hydride derivatives and transferred into an excitation source in that form. The technique is limited to a small number of elements, which include arsenic, antimony, bismuth, germanium, lead, selenium, tellurium and tin. These elements can form their covalent hydrides (AsH_3, SbH_3, BiH_3, GeH_4, PbH_4, H_2Se, H_2Te and SnH_4) in the reaction performed in acidic media and in the presence of a reducing agent. Although the number of the elements is limited, HG is a valuable technique for the determination of very low levels of these elements.

Hydride generation was first used as sample introduction technique in atomic spectrometry in 1969 by Holak [17] to determine arsenic. Braman et al. [18] used sodium tetrahydroborate ($NaBH_4$) as the reducing agent in the reaction of arsine generation in 1972. In 1978, Thompson and co-workers used ICP-AES for determination of arsenic, antimony, bismuth, selenium and tellurium, with their hydrides being generated in the reaction with $NaBH_4$ in a continuous flow-reaction system. Since 1978, HG has been studied extensively. Different aspects of the analytical capabilities of the HG reaction with respect to speciation analysis and multielement determinations are being investigated and also procedures for eliminating the interferences are being developed. Nowadays, HG is conveniently used for introducing As, Bi, Sb, Pb, Se, Te or Sn into different atomizers of atomic absorption spectrometry (AAS) and into excitation sources of atomic emission spectrometry (AES) [19].

There are two main reactions for hydride generation. The earlier technique used a metal / acid reduction system to produce nascent hydrogen to reduce the analyte to hydride:

$$Zn + 2H^+ \rightarrow Zn^{2+} + 2H \qquad (1)$$

$$A^{m+} + (m+n)\ H \rightarrow AH_n + m\ H^+ \qquad (2)$$

where *m* is the valency of the analyte A in the sample solution and *n* is the valency of analyte A in hydride.

The other technique for hydride formation is BH_4^- / acid reaction:

$$BH_4^- + 3H_2O + H^+ \rightarrow H_3BO_3 + 8H \qquad (3)$$

The resulted nascent hydrogen in reaction (3) reduces analyte to hydride according to reaction (2). In hydride generation technique, sodium or potassium salt of tetrahydroborate is used for hydride formation. Water solution of $NaBH_4$ stabilized by 0,05 - 2 % (w/v) NaOH or KOH is the most convenient and widely used reduction agent.

The BH_4^- / acid system is superior to the metal / acid reduction system in terms of the reduction yield, reaction time, contamination of the blank and applicability to the elements concerned.

There are two basic modes of hydride generation: direct transfer mode and collection mode [20]. In the direct transfer mode hydride released from a sample solution is directly transported to an atomizer. There are three commonly used direct transfer modes: continuous flow (CF), flow injection (FI) and batch. Continuous flow hydride generation is the most popular mode of hydride generation. In this mode, a sample solution and a tetrahydroborate solution at constant flows are mixed; a purge gas is introduced into this mixture. Then, the liquid and the gas are separated in the gas-liquid separator. There are two outlets of the gas-liquid separator; one of these is for the gaseous hydride with hydrogen and purge gas flow to the atomizer and the other one is for the liquid effluent drained. In the flow injection mode the experimental arrangement is similar to CF mode, the main difference is that instead of the sample flow as in the continuous flow a constant flow of carrier acid is used. A certain volume of the sample is injected and subsequently dispersed into the carrier stream. In the batch mode, first a batch of acidified sample solution and then the reducing agent (mostly tetrahydroborate solution) are placed inside a batch generator which is a vessel made of glass or plastic serving both as the reactor and the gas-liquid separator. After this, the purge gas flow is introduced to improve stripping the hydride out of the reaction mixture. Released hydride and the hydrogen formed from the decomposition of the reducing agent are supported by the purge gas flow to the atomizer. The batch mode has lost its popularity with the development of CF and FI modes.

In the collection mode, the hydride is trapped in a collection device until the generation is completed and then transported to an atomizer at once. In this mode, after the hydride evolution has been finished the collected hydride can be atomized by two different ways. In the first one, the collected hydride is released from the collection device and transported to the atomizer on line, and in the second way it can be stored and atomized off line. There are also two ways of hydride collection. In the first way the released hydride is bubbled from the reaction mixture into an absorbing solution and in the second way it is collected in a closed vessel under pressure or in a cold trap [20].

The principal advantages of the hydride generation technique include; providing chemical preseparation of the analyte from possible matrix interferents, being a more efficient sample introduction system than conventional pneumatic nebulization, obtaining low limit of detections and applicability to inorganic and/or organic speciation (As, Ge, Sb, Se, Sn and Te). On the other hand, it is prone to interferences by concomitants which reduce the efficiency of the technique, and the rate of hydride generation can be kinetically controlled and slowed in cases which necessitate collection apparatus prior to introduction of the hydrides to the source or atom cell and also in this technique the oxidation state of the analyte of interest may be critical as in the case of Sb (III) and Sb (V) [21].

1.3.1 Hydride Generation and Atom Traps

The trapping of volatile analyte species on heated surfaces is well known and is one of the most popular techniques in atomic spectrometry. The hydride forming elements can be trapped in graphite tubes or on platforms, which are coated with modifiers or uncoated, on silica surfaces and tungsten coils or tubes.

A novel silica trap for lead determination by hydride generation atomic absorption spectrometry was proposed by Korkmaz [6], who has used externally heated silica tubing as the trapping medium. The Pb species were trapped at 500 ^{0}C and released at 750 ^{0}C. For a trapping period of 60 seconds, the limit of detection was found as 19 ng ml^{-1}.

Guo and Guo [22] collected SeH_2 on gold wire that was heated to 200 ^{0}C and released the trapped species by heating the trap to 600 ^{0}C. The gold wire was placed in the inlet arm of the quartz tube atomizer. The use of tungsten coil for on-line preconcentration of bismuthine formed by $NaBH_4$ reduction was studied by Cankur [23]. The hydrides were trapped on a tungsten coil previously heated to 270 ^{0}C and revolatilized by increasing the coil temperature to 1200 ^{0}C and by using a mixture of argon and hydrogen the revolatilized species were transported to the quartz T-tube. Employing this trap, a limit of detection of 0.0027 ng ml^{-1} was obtained with 18 ml of sample volume.

In another study by Korkmaz [8] a quartz tube was proposed for collecting SbH_3. A 0.8 mm Ni-Cr wire with a resistance of 1 Ω was coiled around a 40 mm quartz tube and that tube was connected to the inlet arm of the atomizer by Tygon® tubing. Voltage was applied to heat the wire and subsequently the quartz tube. The analyte species were collected at the collection temperature and then revolatilized at the revolatilization temperature by introducing hydrogen gas flow into the tube. Using this trap, a detection limit of 3.9 pg ml^{-1} was obtained for a collection time of 120 seconds (8 ml sample).

1.4 Electrochemical Hydride Generation

Generation of the volatile hydrides of As, Se, Sb, Sn, Ge, Pb, Bi and Te electrochemically is an example of electrolytic sample pre-treatment in trace element analysis. It has the advantage of nearly 100% sample introduction compared to solution nebulization which is 5-10%. Further advantages of the technique include having increased sensitivity following removal of interfering elements of the sample matrix and collecting the hydrides to achieve even a higher sensitivity [24].

Electrochemical hydride generation (ECHG) was introduced to atomic spectroscopy in the batch arrangement by Rigin [25] to reduce As and Sn to the hydrides in alkaline media for detection by atomic absorption and atomic fluorescence. In their study, a discontinuous electrolytic hydride generation system (batch generator) with platinum or lead spiral cathode was used. Chen and Han [24] used a simple batch generator with a platinum cathode and observed the influence of the acidity of the electrolyte, the current and the carrier gas flow on the absorbance signal. The first thin-layer flow through electrochemical cells were developed by Brockman [26,27] et al. and Lin and co-workers [28, 29, 30] to combine the advantages of flow injection analysis and the electrochemical hydride generation technique. In the flow injection arrangement, catholyte and anolyte solutions are pumped at continuous flows through cathode and anode channels of an electrolytic flow cell respectively. The sample is injected into the catholyte stream which is used as a carrier. In the continuous flow mode, the sample is in the catholyte solution and it flows through the cathode channel continuously. In both of these modes the hydrides and hydrogen, formed at the cathode compartment are separated from the waste solution in a subsequent gas-liquid separator using a purge gas flow [20].

Electrochemical hydride generation technique was developed as an alternative to the original chemical generation technique because it has several advantages compared to the chemical approach.

1.4.1 Advantages and Disadvantages of ECHG

Electrochemical hydride generation relieves the use of sodium tetrahydroborate in acidic media as the reduction system that is commonly used in chemical hydride generation. This technique can also be performed in alkaline media. $NaBH_4$ is an expensive reagent which is considered as a potential source of contamination and also unstable in solution form and has to be freshly prepared each working day. Using ECHG technique with a flow injection hydride generator, low consumption of expensive, high purity acids and sample as well as a high sample throughput and automation can be achieved. It does not depend on the oxidation state of the analyte when using cathode materials with high hydrogen overvoltage like Pb or amalgamated Ag. The interferences in the solution phase by matrix elements, like Fe, Cu, Ni, Co etc., and in the gas phase by other hydride forming elements can be reduced (dependent on the cathode material used) compared to chemical hydride generation. This technique is appropriate to speciation analyses such as the speciation of inorganic arsenic and selenium or the determination of arsenic in different oxidation states. Speciation can be done by choosing the cathode material according to its influence on the analyte oxidation state. For example, for the speciation of Sb (V) and Sb (III) glassy carbon or fibrous carbon electrodes can be employed as both of these electrodes are selective to Sb (III) but not to Sb (V). On the other hand, there are some problems in ECHG. Solid electrode surface must be reproducible therefore the cathode surface should be conditioned daily, before changing the sample type or when the signal does not return to baseline. Dependent on the cathode material and operating parameters, the formation of hydrides can be negatively or positively affected; transition metal ions which are reduced and deposited on the cathode surface interfere with the hydride formation. The deposition of these metals alters the cathode surface physico-chemically and changes the hydrogen overvoltage and consequently a depression of the analytical signal can be observed [24].

1.4.2 Electrode Materials

The electrodes used in ECHG should not become involved in chemical or electrochemical reactions that take place at their surfaces. Generally employed cathode materials include Pd wire, Pt foils (0.025mm thick) or Pt sheets, Pt wire, Pt covered Ag wool, Ag foil, Ag wool, Ag wire, amalgamated Ag foil, Cu cuttings, Cu powder, polished vitreous carbon, reticulated and crushed vitreous carbon, fibrous carbon, pyrolytic graphite, Pb covered fibrous carbon, Pb sheet (1mm thick), Pb wire, Mo sheet, Cd sheet. Because of their inertness to the sample matrix, the most useful cathode materials are carbon in its different forms and Pb. The only disadvantage for Pb cathode is its being susceptible to interferences by some matrix elements at higher concentrations and the carbon cathode needs a pre-reduction step. As an anode material generally platinum foils are used because of their inertness against the permanent formation of oxygen in the anodic half cell [24].

1.4.2.1 Reactions on the Cathode Surface

Generation of hydrides on the surface of the cathode is a three step reaction: deposition of the hydride forming elements on to the surface of the cathode and their reduction; formation of the hydrides; desorption of the hydrides. Before hydrogenation can take place, the hydride forming element has to be deposited on the cathode surface. The deposition is connected with the reduction of analyte in the acidified solution which is a charge transfer reaction [24].

The processes involved in electrochemical hydride generation can be summarized by the following overall reactions:

$$\mathrm{Me} + \mathrm{X} + n\,\mathrm{e}^- \rightarrow \mathrm{Me\text{-}X} \qquad (4)$$

$$\text{Me-X} + m\,e^- + m\,H_3O^+ \rightarrow \text{Me-XH}_m + H_2O \quad (5)$$

$$\text{Me-XH}_m \rightarrow \text{Me} + \text{XH}_m \uparrow \quad (6)$$

where Me is the cathode surface, X the hydride forming element and the source of hydrogen can be the hydronium ion or water [31].

Simultaneously, water is reduced to hydrogen on the cathode whereas it is oxidized in the separated anodic chamber and oxygen is formed [21].

1.4.2.2 Pre-treatment of the Cathode Surface

Pre-treatment of the cathode surface should be done to enhance repeatability. Two procedures are given in the literature; chemical one using chromic-sulfuric acid or hot nitric acid and the electrochemical one by anodic polarization. The most simple and useful procedure to clean the surfaces of Pb and Cd cathodes is treating them with semi-concentrated hot nitric acid for a few seconds and subsequent rinsing [24].

1.4.3 Electrochemical Hydride Generators

The electrochemical hydride generators are generally composed of three components: a flow system, the electrochemical cell and a gas-liquid separator.

The flow system is employed for the transport of the electrolyte and the sample solutions. The electrochemical cell is the primary part of the electrochemical hydride generators. It is also composed of three parts: anode chamber, cathode chamber and an ion-exchange membrane. The hydrides are produced in the cathode chamber on the surface of the cathode. The ion-exchange membrane separates the anode and cathode chambers physically and prevents the diffusion of anode products into the cathode chamber. The hydrides and the excess of hydrogen are rinsed out of the electrochemical cell with the catholyte and separated from the aqueous solution in the gas-liquid separator and swept into the atomizer with an auxiliary carrier gas stream [24].

1.4 Interferences

In atomic absorption spectrometry two types of interferences are observed; spectral and nonspectral. Spectral interferences are observed due to radiation absorbed by species other than free atoms of the analyte and nonspectral interferences are due to the influence of sample constituents on the analyte signal.

Hydride generation atomic absorption spectrometry is less prone to spectral interferences than conventional liquid sampling atomic absorption spectrometry as the analyte is separated from the matrix [20].

1.4.1 Interferences in Chemical Hydride Generation

The main limitation of the chemical generation of volatile hydrides with tetrahydroborate is the interferent effects of inorganic compounds. Inorganic interferents are divided into three groups: i) strong oxidants; İİ) ions of transition and noble metals; and iii) other species including ions of other hydride forming elements. Three mechanisms have been suggested to explain the effects of these elements: tetrahydroborate depletion; formation of insoluble species between the interferent ion and the analyte after the hydride has formed; and decomposition of hydrides on metal borides, or on colloidal metals formed by the reduction of the interferent ion [32]. The tetrahydroborate depletion mechanism is based on the competition between interferent ions and the analyte for reduction by tetrahydroborate and it was first suggested by Pierce et al. [33]. Meyer et al. [34] suggested the formation of insoluble species between the interferent ion and the hydride. Welz and Melcher [35] first supported the idea for this mechanism but later on they proposed that this mechanism was overwhelmed by the decomposition of hydrides on colloidal metals and this decomposition was effective at lower interferent ion concentrations [36]. Smith [37] proposed that the interferences in chemical hydride generation were based on the reduction of the interferent ion to its metallic form and the co-precipitation of the analyte or adsorption and decomposition of the hydride formed. Kirkbright et al. [38] attributed the interferences to the adsorption and decomposition of the hydride by the dispersed elemental forms of the interfering ions.

1.4.2 Interferences in Electrochemical Hydride Generation

Electrochemical hydride generation suffers from the same kinds of interferences as chemical generation. The tolerance limits are different than those of chemical hydride generation and are dependent on the cathode material employed in the electrochemical cell. As the reactions take place on the cathode surface in electrochemical hydride generation, the interferent effects from concomitant species are related with the available surface of the cathode, the residence time of the reducible species in the cathode compartment and the concentration of the concomitant species. Reducible species on the cathode include: the analyte; protons from the acid; and interferents. When the reduction products of the interferent are gases or soluble species, the nature of the cathode surface is not modified and the interference mechanism is the competition of the interferents and the analyte species for available reduction sites on the cathode. If reduction products are solid species, such as transition metals, they can be deposited on the cathode surface, modify its nature, and/or pass to the catholyte and act as liquid phase interferences. The interferences from different elements are related to their standard potentials [$E_0(M^{n+}/M^0)$]. Therefore, the elements with positive standard potentials, such as copper and platinum can be easily reduced in an acidic medium to their metallic forms, whereas those with negative potentials, such as zinc, cannot be reduced.

The interferences in electrochemical hydride generation can be controlled by selecting the cathode material and the generation conditions. For example, lead and reticulated vitreous carbon electrodes show different performance and behavior with respect to interferences. Under the hydride generation conditions used, interfering ions reduced to metals are deposited on the lead surface; on the other hand, the surface of the reticulated vitreous carbon electrode surface does not change [32].

The effect of interfering species for the determination of arsenic by electrochemical hydride generation was first studied by Sand and Hackford [39], they observed that the presence of Cu (II), Fe (II), Sn (IV), Hg (II) and Ni (II) decreased the electrode efficiency and there were no interferences from organic substances. Using a batch electrolytic hydride generator Rigin et al. [25, 40, 41] observed that the presence of Cu (II) and Au (III) had a negligible effect on arsine signal using NaOH as the electrolyte and related this observation with the immediate precipitation of the metal ions as insoluble hydroxides in the cell. Employing platinum cathode in flow injection mode, Lin et al. [28] investigated the effects of several interferent species for the determination of hydrogen selenide and concluded that interferences were significant for Cu (II), Ag (I), Sb (III) and Bi (III). Brockmann [27] investigated the influence of Ni (II) and

Co (II) on hydrogen selenide and arsine generation with a platinum cathode in flow injection mode and observed no interferent effect. Hueber and Winefordner [49] observed a large interference effect of Cu (II), Pt (II) and Au (III) on arsine and hydrogen selenide generation. They also investigated the effect of Sb (III) and observed that Sb (III) showed an interfering effect on the generation of both hydrides. Schaumlöffel and Neidhart [42] observed that Cr (III), Co (II), Ni (II) and Cu (II) led to a depression of the absorbance signal in arsine generation in flow injection mode with a fibrous carbon cathode. The interference of copper and nickel on electrochemical generation of arsine, stibine and hydrogen selenide using lead, pyrolytic graphite, vitreous carbon and platinum as cathode materials was studied by Ding and Sturgeon [43]. With the stibine generation they observed 50% and 80% signal suppressions in the presence of 7.5 mg l^{-1} copper and 10 mg l^{-1} nickel respectively. Bolea et al. [32] studied the interferences of Cu (II), Zn (II), Pt (IV) and nitrate on electrochemical hydride generation of hydrogen selenide with lead and reticulated vitreous carbon electrodes. They observed signal suppression up to 60 and 75% for lead and reticulated vitreous carbon electrodes respectively, at Se/NO_3^- ratios 1:1000. No interference of Zn (II) up to Se/Zn ratios 1:1000 was observed. Copper and platinum showed suppression levels up to 50% for Se/interferent 1:100. Using reticulated vitreous carbon electrodes total signal suppression was observed in the presence of Se/Cu ratios 1:100.

1.5 Determination of Antimony

Antimony is a silvery-white metal that makes up about $2/10^7$ of the earth's crust. It is sometimes found free in nature but mainly occurs as Sb_2S_3 (stibnite, antimonite) and Sb_2O_3 (valentinite). These two compounds are found in ores of silver, copper and lead.

Antimony has been known since ancient times. Its property of dissolving metals such as gold was used for purifying gold from copper and silver until the 18th century. The presence of antimony increases the hardness and mechanical strength of lead. Batteries, antifriction alloys, type metal, cable sheathing and minor products use about half the metal produced. The other half are found as the oxides, sulfides, and sodium antimonite and antimony trichloride. Antimony trioxide, Sb_2O_3, is used in manufacturing flame-proofing compounds, paints, ceramic enamels, glass and pottery. Antimony tetroxide, Sb_4O_8, is mainly used as an oxidation catalyst [44].

Antimony is an accumulative toxic element that is released to the environment from natural sources and from industry. It has been detected in natural waters at ultratrace levels. U.S. Environmental Protection Agency (EPA) considers it a priority pollutant and allows 0.006 parts of antimony per millions of drinking water (0.006 ppm). In polluted waters concentrations are in the ng l^{-1} range. Two inorganic forms, Sb (III) and Sb (V), and two organic species, methylstibonic acid $[(CH_3)SbO(OH)_2]$ and dimethylstibinic acid $[(CH_3)_2SbO(OH)]$, have been detected in natural water sources. The toxicity and biological behavior of the element depends on its oxidation state; Sb (III) is 10 times more toxic than Sb (V), which is why the determination of antimony species is essential for environmental studies [45].

Hydride generation-atomic absorption spectrometry has been the most widely used technique to determine antimony species, especially inorganic ones. The first work on the determination of antimony in aqueous solution by stibine generation using $NaBH_4$ as a reducing agent was presented by Braman et al. [18]. Fernandez [46] coupled hydride generation technique with atomic absorption spectrometry and this method has been applied for the determination of total antimony and also to differentiate between Sb(III) and Sb (V). Nakashima et al. [47] presented selective determination of Sb (III) and Sb (V) by pH-control at the ng/L level in water samples. Andreae et al. [48] observed that in the pH range 1 to 7, Sb (III) is reduced at constant yield and no Sb (V) reduction took place at pH 6-7. Using this fact, he made the selective determination of Sb (III) at near-neutral pH.

Electrochemical hydride generation is another technique which is also commonly used for the determination of inorganic antimony species. Hueber and Winefordner [49] constructed a flowing electrolytic hydride generator for sample introduction in atomic spectrometry and investigated the effect of cathode material form on electrochemical hydride generation for As, Se and Sb. Their electrochemical cell consisted of a cathode flow cell immersed in an electrolytic solution. A cylindrical container which also contains the anode, held the cathode flow cell and the electrolytic solution. A platinum mesh with a surface area of 18 cm^2 was used as the anode material and coils of silver, platinum, lead and palladium wires were investigated as cathode materials. For the generation of SbH_3, lead cathode gave the largest signal. They have obtained a sensitivity increase of 11-18 times over pneumatic nebulization. Ding and Sturgeon [50] developed a continuous flow electrochemical hydride generation system for the determination of total antimony in river water and sea water by electrothermal atomic absorption spectrometry. Their cell had a plexiglas body which consisted of cathode and anode blocks. Silicone gaskets were placed between the two blocks to prevent leakage and an ion exchange membrane was used to isolate the cells physically. Lead and platinum were used as cathode and anode materials respectively. The generated hydride was trapped in a Pd-coated graphite furnace and by using 2 ml sample volumes an absolute limit of detection of 45 pg and a concentration limit of detection of 0.02 $\mu g\ l^{-1}$ was obtained. In another study by Laborda [51] a tubular electrolytic-flow through cell where the cathode and anode spaces have a concentric configuration was employed. It consisted of a central cathode made of reticulated vitreous carbon inside a porous ceramic tube and an anode made of a coil of platinum wire. The limit of detection for antimony in aqueous solution was 1.4 ng ml^{-1} using a flame heated quartz tube. Electrochemical hydride generation of stibine by using flow injection method was employed by Bings [52] by coupling the system with an inductively coupled plasma time of flight mass spectrometer. A low volume electrolysis cell designed for flow injection analysis was used. The cathode and anode employed were fibrous carbon and platinum respectively.

1.6 Aim of the Study

Generation of SbH_3 using electrochemical hydride generation technique and preconcentration of the generated hydrides in the inlet arm of the quartz tube atomizer is the main purpose of the study. To achieve this purpose, a thin-layer electrochemical flow through cell was constructed. The experimental operation conditions for hydride generation and collection and revolatilization conditions for the generated hydrides in the inlet arm of the quartz tube atomizer will be optimized. Interferences of copper, nickel, iron, cobalt, arsenic, selenium, lead and tin on electrochemical hydride generation of antimony using lead cathode are to be examined. Finally in order to check the accuracy of the system, analysis of standard reference materials will be performed.

CHAPTER II

EXPERIMENTAL

2.1 Chemicals and Reagents

All reagents used were of analytical grade. Standard solutions which were used as the catholyte solutions were prepared by appropriate dilution of the 1000 mg l^{-1} Sb stock solution (Ultra Scientific) with 1.0 mol l^{-1} HCl (Merck). The anolyte solution was 2.0 mol l^{-1} H_2SO_4 (Carlo Erba) and as blank 1.0 mol l^{-1} HCl was used. For the interference studies, standard solutions of Ni, Co, Cu, Fe, As, Se, Sn and Pb were prepared in 1 mol l^{-1} HCl from the 1000 mg l^{-1} stock solutions (Aldrich) of the corresponding element. Deionized water from Milli-Q Water Purification System and Elga Deionized Water System was used throughout the experiments.

2.2 Apparatus and Materials

The electrodes used were lead (99.9995%, Aldrich) and platinum (99.9995%, Altın Yıldız İthalat-İmalat, Kapalıçarşı, İstanbul) as cathode and anode materials respectively. As an ion exchange membrane Nafion 117 (Aldrich) was employed.

100 mL, 50 mL and 25 mL Dupont polyethylene containers were used to store and prepare the solutions. Adjustable micropipettes (Transferpipette, 5-50 µL, 50-250 µL and 100-1000 µL) with polyethylene tips were used to distribute the reagents. Gilson Minipuls 3 peristaltic pumps with Tygon® tubing were used to transfer the catholyte and anolyte solutions into the electrochemical cell and to remove the waste from the gas-liquid separator.

Quartz tubes with various diameters were supplied from Quartz Scientific Inc., Fairport Hairbour Ohio. The quartz T-tubes used throughout this study were made in the glass shop of our Chemistry department. Two different types of quartz T-tubes were used; one for the electrochemical hydride generation procedure and the other for the trapping procedure. Both of these T-tubes had an optical arm length of 117 mm and an inlet arm length of 95 mm and the inner and outer diameters of the optical arm were 8 mm and 10 mm, respectively. The inlet arm of the quartz T-tube used for electrochemical hydride generation had an inner diameter of 4 mm and an outer diameter of 6 mm. The inner and outer diameters of the inlet arm of the t-tube used for trapping were 3 mm and 4 mm, respectively.

2.3 Atomic Absorption Spectrometer

A Pye Unicam PU 9200 atomic absorption spectrometer with electrochemical hydride generation system was used throughout the study. The results were printed with an Epson FX-850 printer connected to the spectrometer. Photron Sb hollow cathode lamp with an operating current of 9 mA was used as the radiation source. The analyses were done at a wavelength of 217.6 nm and 0.2 nm slit width. Background correction was not employed. Air-acetylene flame with a 50 mm burner slot was used for atomization and argon was used as the carrier gas.

2.4 Electrochemical Cell

A thin-layer electrochemical flow through cell similar to the one described in ref. [53] was used throughout the study (Figure 2.1). The cell had a Plexiglas body. It was made up of two blocks which have cathode and anode chambers on them. Both of the chambers had dimensions of 100 mm x 3 mm x 3 mm and inner volume of 900 µL. Nafion 117® was placed between the two blocks as the ion exchange membrane. A lead foil, 1 mm thick, 100 mm long, 3 mm wide and a platinum foil, 0.2 mm thick, 100 mm long, 3 mm wide were placed inside the cathode and anode chambers respectively. Eight screws were used to screw down the two blocks.

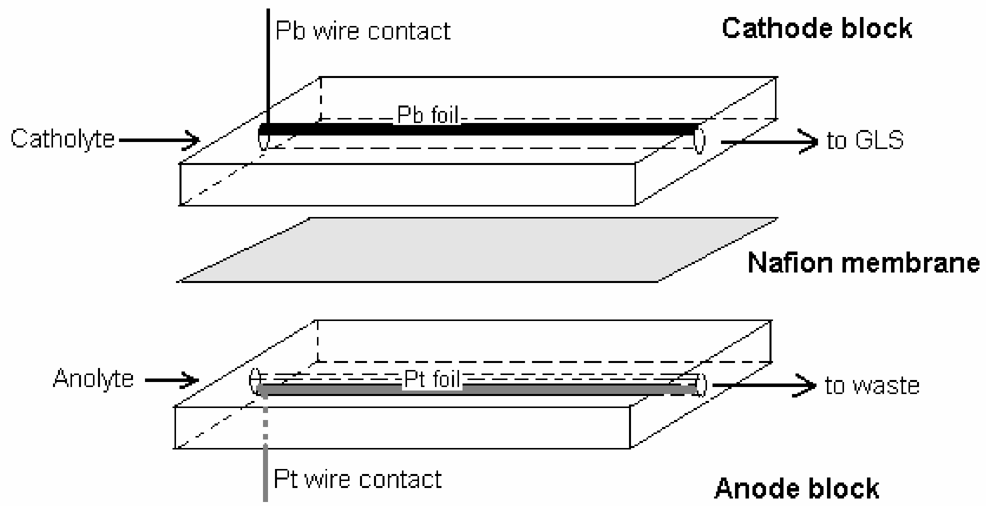

Figure 2.1 Scheme of the electrochemical flow through cell

PTFE (polytetrafluoroethylene) tubings with 0.8 mm inner diameter were connected to the inlets and outlets of cathode and anode chambers with 1/16” tubing fittings. The same kinds of tubings and fittings were employed in the whole experimental set-up.

An in house made power supply with I_{max}= 2.5A and U_{max}= 100V was used to provide constant current to the electrochemical cell. The electric contact was provided by lead and platinum wires which were pressed into the two electrodes respectively.

When the sensitivity of the experiments decreased by 20%, the cell was disassembled and the cathode surface was cleaned initially by wiping with a filter paper, by fine sand paper then by rinsing the surface using deionized water. If this cleaning process did not result in a visually clean surface, the electrode was treated by 2 ml of 1 mol l^{-1} HNO_3 and subsequent rinsing with deionized water.

2.5 Electrochemical Hydride Generation System

The main part of the electrochemical hydride generation system (Figure 2.2) is the electrochemical cell. The catholyte and anolyte solutions were pumped through the cathode and anode chambers respectively with the peristaltic pump. The catholyte was either blank or the analyte in a dilute acid solution and the anolyte was diluted acid. The electrochemical cell was connected to the power supply and by applying current to the electrodes hydrides were generated. The outlet of the cathode chamber was connected to a T-piece (PEEK- polyether ether ketone) by which argon was introduced to the system as the carrier gas. The outlet of the T-piece was connected to the gas-liquid separator with 100 mm PTFE tubing. The gas-liquid separator was made up of a standard 10/19 joint.

Two tubings were inserted into a rubber septum that was placed at the bottom of the gas-liquid separator. One of these tubings was for introducing the generated hydrides and the excess hydrogen to the gas-liquid separator and the other tubing was for pumping the liquid waste away. The gas outlet of the gas-liquid separator was connected to the quartz T-tube atomizer with 100 mm tubing.

The flow rates of catholyte and anolyte solutions were 3.0 ml min^{-1} and 4.0 ml min^{-1} respectively. The anolyte solution that has passed from the anode chamber was sent to waste. The flow rate of argon introduced into the system was controlled by using a Cole-Parmer gas flow meter.

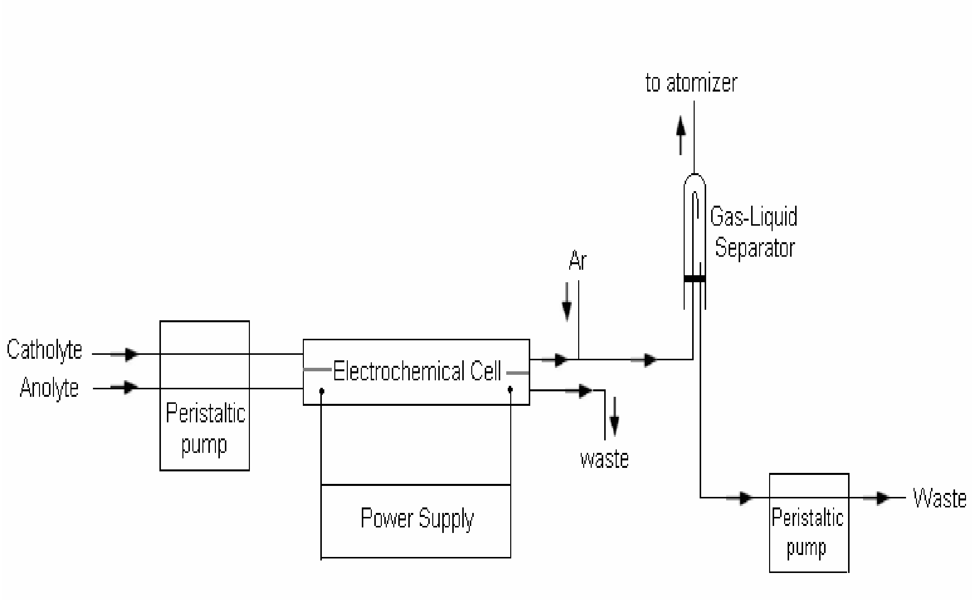

Figure 2.2 Scheme of the electrochemical hydride generation system

2.6 Trap System

The inlet arm of the quartz tube atomizer (i.d. 3 mm, o.d. 4 mm) was used as the trapping medium during the trap experiments. The hydrides were generated as explained in section 2.5 and trapped in the inlet arm. The trap was prepared by coiling 360 mm long Ni-Cr wire with 0.8 mm diameter and 1Ω resistance around the inlet arm of the quartz T-tube, 3 cm away from the junction point of inlet and optical arms (Figure 2.3). The two ends of the wire were attached to an autotransformer which is connected to the mains electricity.

The generated hydrides and the excess of hydrogen were swept out of the gas-liquid separator with PTFE tubing that was connected to its outlet. Hydrogen gas was introduced into the tubing with a T-piece and the outlet of the T-piece was connected to 100 mm long tubing which was inserted into the inlet arm of the quartz T-tube atomizer. The tip of tubing was 0.5 cm near the trapping zone.

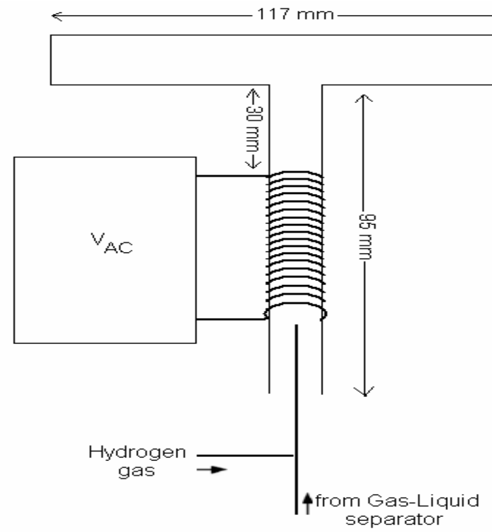

Figure 2.3 Scheme of the quartz t-tube used as trap

When voltage was applied to Ni-Cr wire, the part of the inlet arm that was covered by coil heated up. The temperature inside the trap was measured with a thermocouple. Table 2.1 shows the correlation between the voltage applied to the wire and the temperature inside the trap.

Table 2.1 The relation between the applied voltage and the trap temperature

Voltage, V	Temperature, °C
0	27
1.1	170
2.2	400
3.3	610
4.4	800
5.5	940
6.6	1030

The temperature data given in Table 2.1 was taken by placing the thermocouple in the middle part of the trap under a total gas flow rate of 145 ml min^{-1} (45 ml min^{-1} argon flow and 100 ml min^{-1} hydrogen flow). When voltage applied to the wire was increased the temperature of the trap did not increase immediately, it took some time for its temperature to become stable. Figure 2.4 illustrates the change of temperature inside the trap after increasing the voltage from 2.2 V (400 ^{o}C) to 6.6 V (1030 ^{o}C).

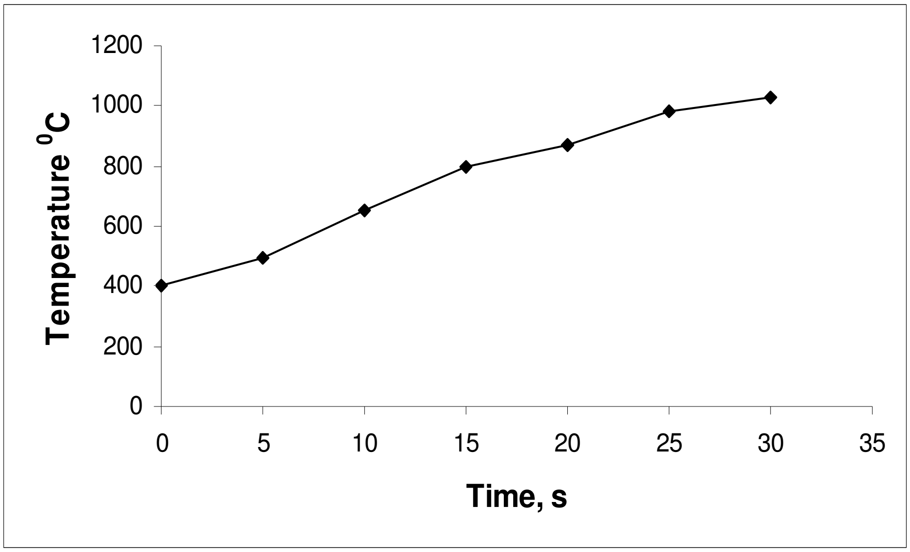

Figure 2.4 Temperature inside the trap after increasing the trap voltage from 2.2 V (400 ^oC) to 6.6 V (1030 ^oC)

When the sensitivity of the experiments decreased, the trap was cleaned by leaching the t-tube in a mixture of 7/3 concentrated HNO_3-HF mixture for 15 minutes and then it was washed with distilled water.

2.7 Experimental Procedure

First, the optimizations of experimental parameters for electrochemical hydride generation were performed. To generate the hydrides electrochemically, the catholyte solution was either the sample in 1 mol l^{-1} HCl or the blank which was 1 mol l^{-1} HCl; this solution was pumped through the cathode chamber at a flow rate of 3 ml min^{-1} and the anolyte solution that was 2 mol l^{-1} H_2SO_4 was pumped through the anode chamber at a flow rate of 4 ml min^{-1}. After the flows of these solutions were provided, electric current was applied to the electrodes and the hydrides were generated on the cathode surface. Argon flow of 45 ml min^{-1} was introduced into the upstream of cathode products and has led these products into the gas-liquid separator where the generated hydrides and the liquid were separated. Finally the hydrides were sent to the quartz tube atomizer, atomized there and the absorbance signals were obtained.

After optimizing the electrochemical hydride generation conditions, calibration plot was obtained and the limit of detection (LOD) was calculated. To investigate the difference between chemical and electrochemical hydride generation techniques; calibration plot was obtained and the limit of detection was calculated for the chemical hydride generation technique as well.

In the second part of the experiments, trapping of the generated stibine was performed. The trap experiments were composed of two steps: collection and volatilization. First, in order to investigate whether the generated SbH_3 can be trapped on quartz surface or not, the trap was heated to different collection temperatures and the analyte signal was obtained. Figure 2.5 shows that the absorbance values decrease when the trap temperature is increased; this indicates that the generated hydrides can be trapped on the surface of the inlet arm of the quartz tube atomizer.

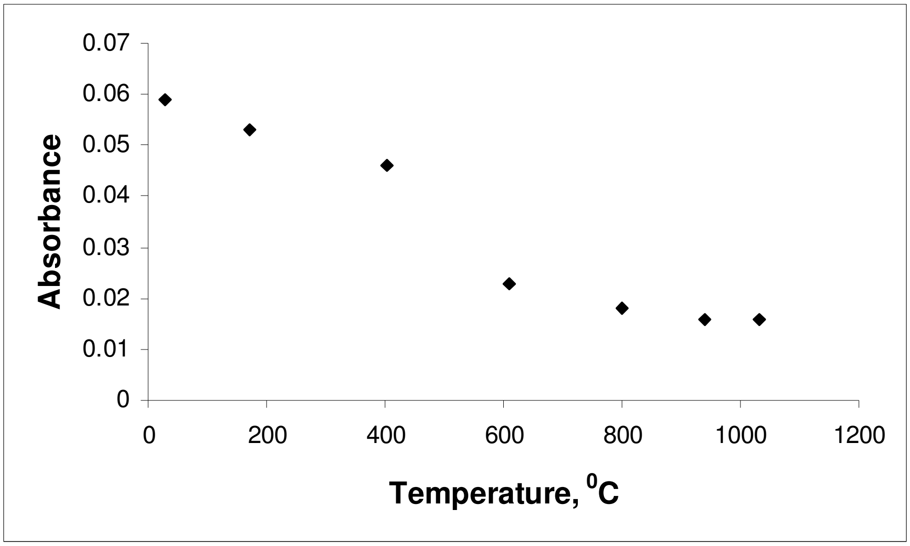

Figure 2.5 Collecting SbH_3 in silica trap

In the collection step the voltage applied to the wire was adjusted to the collection level which was 2.2 V corresponding to 400 ^oC. Electrochemical hydride generation was started by providing the flows of anolyte and catholyte solutions through the anode and cathode compartments respectively by switching on the peristaltic pump and also by applying current to the cell by switching on the power supply. During the collection step the argon flow rate into the system was 45 ml min^{-1} and the flow rates of the catholyte which was the sample solution and the anolyte were 3 ml min^{-1} and 4 ml min^{-1} respectively. The collection time was 30 seconds during optimization of the parameters and 120 seconds for obtaining the calibration plot and the analysis of standard reference materials.

At the end of the collection period, the collection was stopped by switching off the peristaltic pump and the power supply and simultaneously the trap temperature was increased to the volatilization temperature which was 1030 ^0C that corresponded to 6.6 V (Table 2.1).

The trap was allowed to heat up for 10 seconds and hydrogen gas at a flow of 100 ml min^{-1} was introduced into the trap. The volatilization of the collected analytes took place and the absorbance signal was obtained. After obtaining the signal, the hydrogen gas flow into the trap was switched off, the voltage applied to the trap was decreased to 2.2 V and trap was allowed to cool down to the collection temperature for 45 seconds and the experiments were carried on with the next collection step. Flow chart for the trapping process is given in figure 2.6.

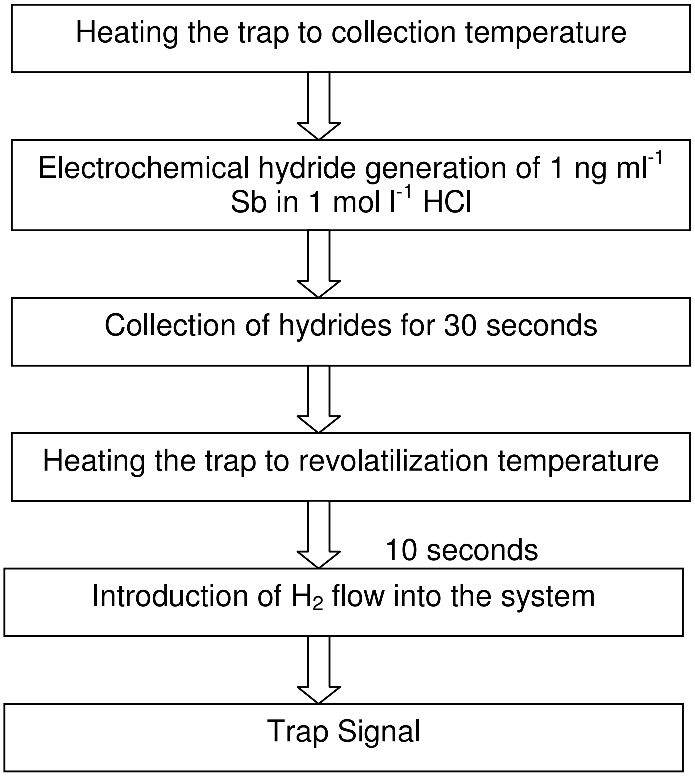

Figure 2.6 Flow chart for the trapping process

The interference effects of cobalt, copper, nickel and iron among the transition metals and arsenic, selenium, tin and lead among the hydride forming elements on electrochemical stibine generation were investigated. The interference studies were performed with and without trapping of the generated hydrides. The effect of every interferent ion was investigated by preparing standards with Sb / interference ratios of 1:10, 1:100 and 1:1000. The Sb concentration was 50 ng ml^{-1} for the experiments performed without the trap and 1 ng ml^{-1} for the experiments performed with the trap. The hydrides were generated and the influences of every interferent on the absorbance signal at the three concentrations were investigated.

2.8 Accuracy Check

Two standard reference materials (SRM); Trace Metals in Drinking Water, Cat # CRM-TMDW (High Purity Standards) and Metals on Soil / Sediment #4, IRM-008 (Ultra Scientific) were used for the validation of the proposed method.

The Trace Metals in Drinking Water SRM was diluted 10 times with 1 mol l^{-1} HCl and analyzed. 0.100 g of Metals on Soil / Sediment SRM in 5 ml of HNO_3 was decomposed with a Milestone Ethos Plus microwave oven and diluted to 100 ml. This solution was further diluted 25 times with 1 mol l^{-1} HCl and analyzed.

CHAPTER III

RESULTS AND DISCUSSION

Two sets of experimental operation conditions were optimized: electrochemical hydride generation and atom trapping conditions. In the first part catholyte composition, anolyte composition, catholyte flow rate, anolyte flow rate, carrier gas flow rate and electric current applied to the electrochemical cell were optimized. The calibration plot for the generation was obtained and the limit of detection was calculated. Electrochemical and chemical hydride generation techniques were compared in terms of their linear range and limits of detection. In the second part, optimizations of collection temperature, revolatilization temperature, the time passed after increasing the temperature to revolatilization temperature and the hydrogen gas flow rate were performed. The effect of collection time on the sample and blank signals were investigated. The calibration plot for the technique with the trap was obtained and the limit of detection was calculated. The effects of the concomitant ions were also investigated without and with trap. Finally, analyses of standard reference materials were performed for accuracy check.

3.1 Optimization of Experimental Operation Conditions in ECHG

Sb at a concentration of 50 ng ml^{-1} in 1 mol l^{-1} HCl was used and the signals were obtained at continuous flow mode.

3.1.1 Optimization of Anolyte Acidity

The electrochemical generation of antimony hydride is highly dependent on the anolyte composition. As anolyte solution, seven different H_2SO_4 and HCl concentrations in the range 0.25 – 3.0 mol l^{-1} were tested. Using H_2SO_4 higher absorbance signals were obtained than those obtained for HCl. 2 mol l^{-1} H_2SO_4 was chosen as the optimum anolyte concentration (Figure 3.1).

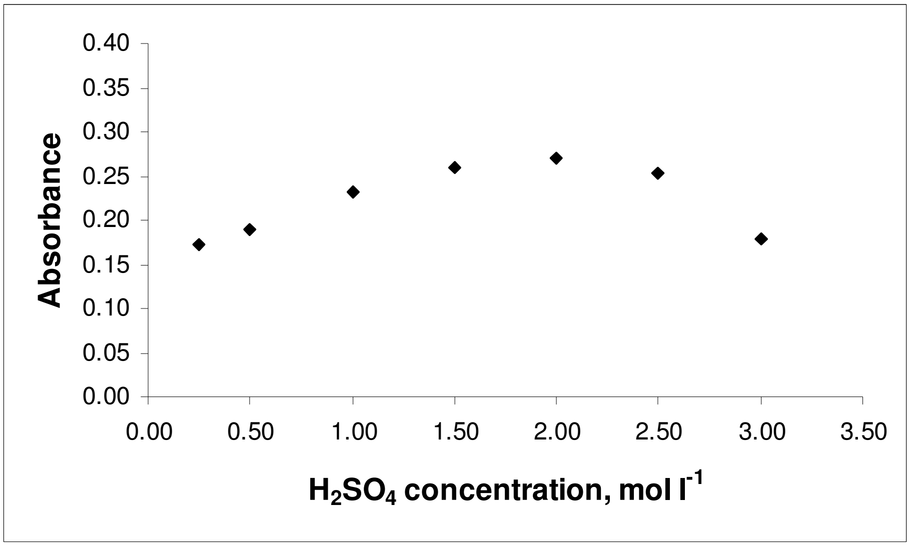

Figure 3.1 Optimization of anolyte acidity

Catholyte: 50 ng ml^{-1} Sb in 1 mol l^{-1} HCl, Ar flow: 45 ml min^{-1}, Current: 1200mA, Catholyte and Anolyte Flow: 4ml min^{-1}

3.1.2 Optimization of Catholyte Acidity

Ten different HCl concentrations in 0.5 – 5 mol l^{-1} range containing 50 ng ml^{-1} Sb were tested as catholyte solution. The use of catholyte solutions at concentrations lower than 0.5 mol l^{-1} was not suitable as the conductance of the solutions decreased. The highest absorbance values were obtained with 1 mol l^{-1} HCl and the reproducibility of the signals were better than 4% at this acid concentration, so the optimum acid concentration was selected as 1 mol l^{-1} (Figure 3.2).

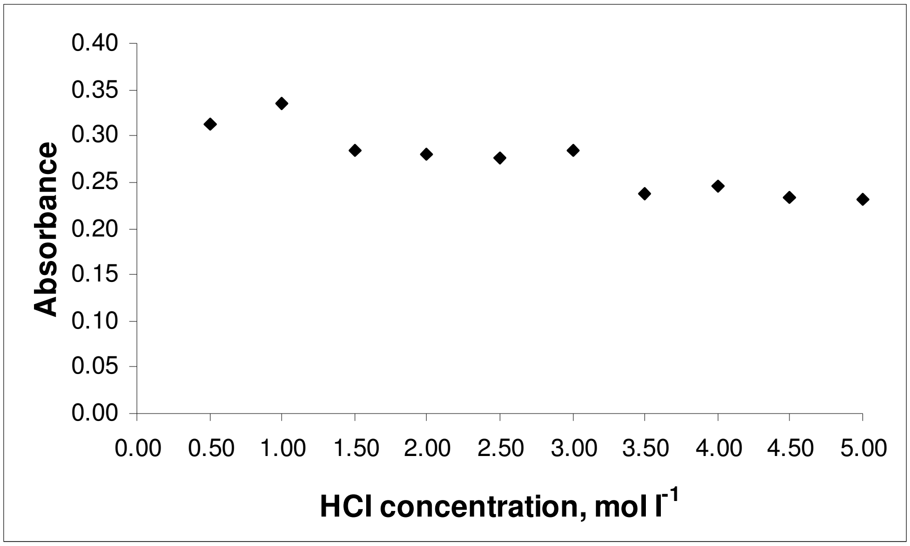

Figure 3.2 Optimization of catholyte acidity

Anolyte: 2 mol l^{-1} H_2SO_4, Ar flow: 45 ml min^{-1}, Current: 1200mA, Catholyte and Anolyte Flow: 4ml min^{-1}

3.1.3 Optimization of Anolyte Flow Rate

The effect of the flow rate of the anolyte solution was investigated in the interval of 1 – 9 ml min^{-1}. It was observed that there was no significant difference in the absorbance values obtained with the change in the anolyte flow rate (Figure 3.3). The reproducibility of the signals was influenced from the change of the anolyte flow rate by 9-11 %, so as the optimum flow rate value; 4 ml min^{-1} was selected where the relative standard deviation of the signals were lower than those of the other flow rate values.

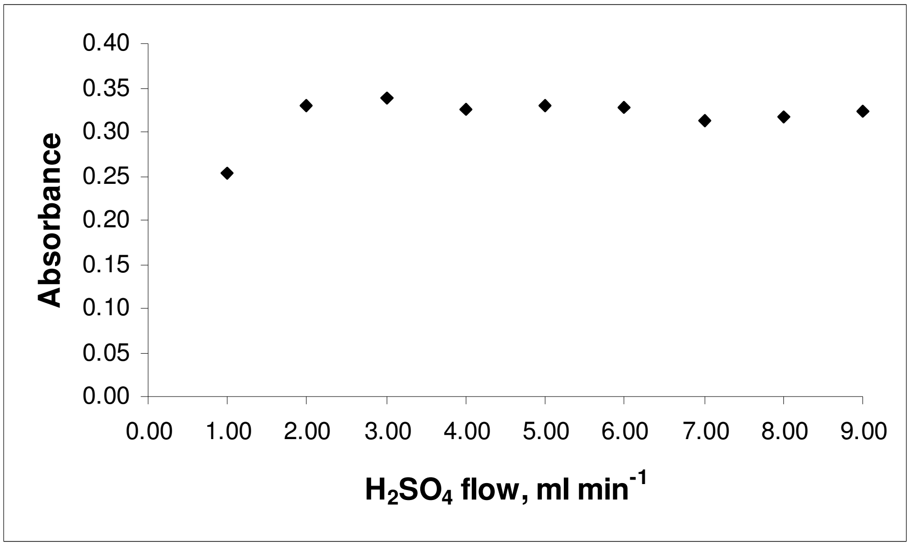

Figure 3.3 Optimization of anolyte flow rate

Anolyte: 2 mol l^{-1} H_2SO_4, Catholyte: 50 ng ml^{-1} Sb in 1 mol l^{-1} HCl, Ar flow: 45 ml min^{-1}, Current: 1200mA, Catholyte Flow: 4ml min^{-1}

3.1.4 Optimization of Catholyte Flow Rate

The flow rate of catholyte is an important parameter for electrochemical hydride generation as the hydrides are produced on the cathode surface. Figure 3.4 shows that the absorbance signals increase with increasing catholyte flow rate. This observation can be explained by the fact that, at higher flow rates, the amount of antimony that reaches the electrode surface is increased and more antimony hydride is produced. Although the absorbance values increase with the flow rate, the reproducibility of the signals decreases; so catholyte flow at 3 ml min^{-1} was chosen as the optimum flow rate.

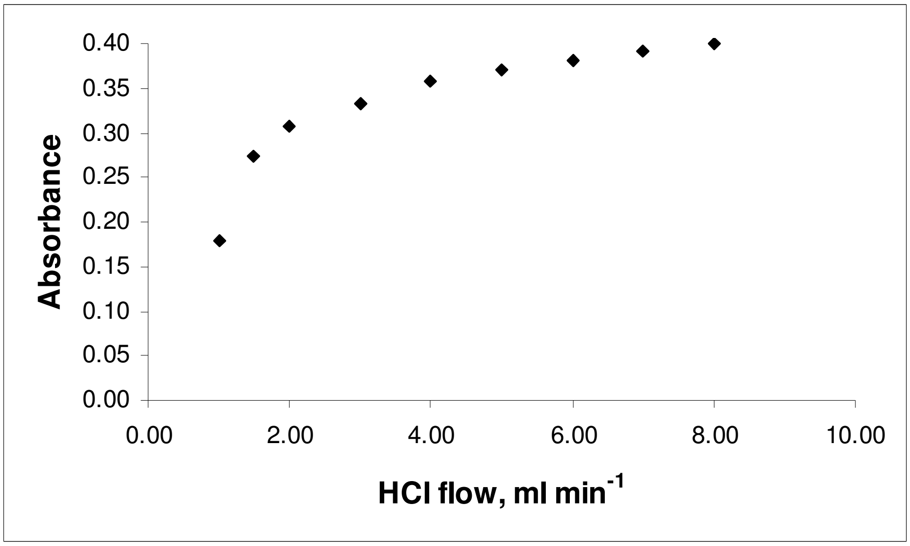

Figure 3.4 Optimization of catholyte flow rate

Anolyte: 2 mol l^{-1} H_2SO_4, Catholyte: 50 ng ml^{-1} Sb in 1 mol l^{-1} HCl, Ar flow: 45ml min^{-1}, Current: 1200mA, Anolyte Flow: 4ml min^{-1}

3.1.5 Optimization of Carrier Gas Flow Rate

The carrier gas flow through the system is one of the basic parameters influencing the sensitivity of antimony determination. Argon is used as the carrier gas. Argon, introduced into the catholyte stream, carries the cathode products into the gas-liquid separator. Argon, together with the excess of hydrogen produced during the electrochemical reduction aids in separation of the volatile compounds from the liquid phase and transports the generated antimony hydrides into the quartz tube atomizer. The influence of argon flow rate on the absorbance signal is shown in Figure 3.5.

The argon flow rate was chosen as 45 ml min^{-1} during the studies as the relative standard deviations of the signals were lower at this flow rate.

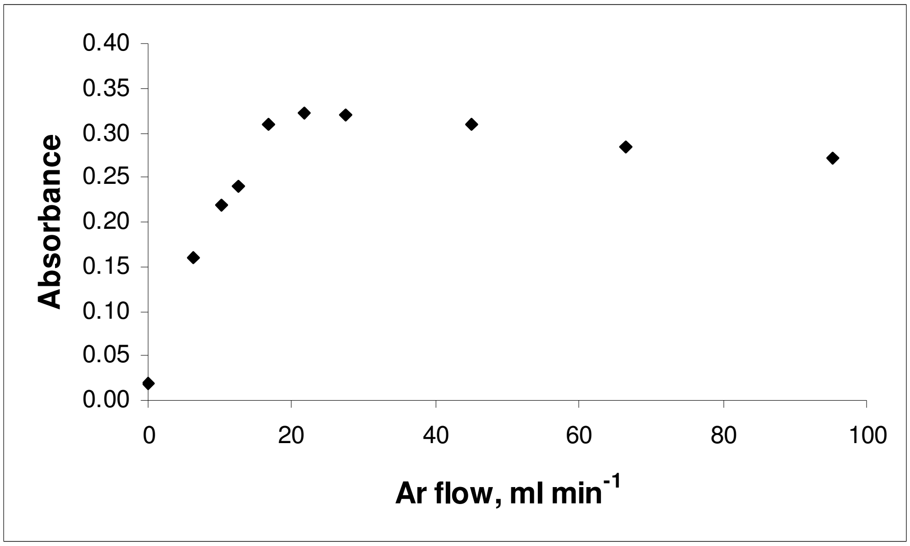

Figure 3.5 Optimization of carrier gas flow rate

Anolyte: 2 mol l^{-1} H_2SO_4, Catholyte: 50 ng ml^{-1} Sb in 1 mol l^{-1} HCl, Current: 1200mA, Anolyte Flow: 4 ml min^{-1}, Catholyte flow: 3 ml min^{-1}

3.1.6 Influence of Applied Electric Current

The generation of stibine is highly dependent on the magnitude of the electric current applied to the electrochemical cell. Figure 3.6 shows the influence of the generation current applied on the analytical signal. It is evident from the graph that the analytical signal rapidly increases with increasing generation current; however currents higher than 1.4 A were not applied as the electrolyte solutions heat up excessively. In addition to the heating of the electrolytes, the reproducibility of the signals decreases at currents higher than 1.2 A, therefore 1.2 A was selected as the operating current throughout the experiments.

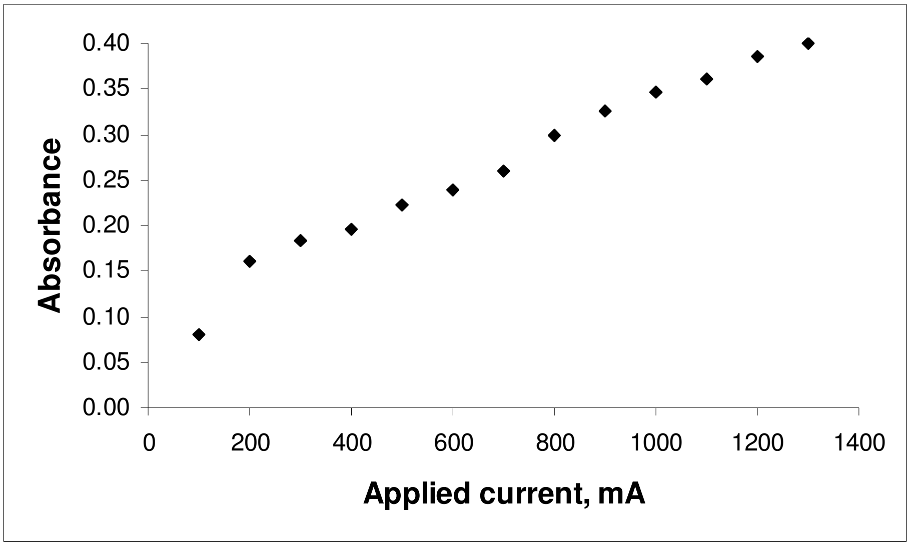

Figure 3.6 Influence of the applied electric current on the absorbance signal

Anolyte: 2 mol l^{-1} M H_2SO_4, Catholyte: 1 mol l^{-1} M HCl, Ar flow: 45 ml min^{-1}, Anolyte Flow: 4 ml min^{-1}, Catholyte flow: 3 ml min^{-1}

3.2 Determination of Sb (V) by ECHG

The absorbance signals of Sb (V) solution were taken by generating the hydrides of 50 ng ml^{-1} Sb (V) in 1 mol l^{-1} HCl electrochemically. 100 ml of 500 mg l^{-1} Sb (V) stock solution was prepared by dissolving 0.116 g of potassium antimonate ($KSb(OH)_6.1/2\ H_2O$) with deionized water and the standard solutions were prepared from this stock solution.

The mixtures of the two forms of the element were prepared with 0, 20, 40, 60, 80 and 100% of the solution being Sb (III) and the rest Sb (V) in 1 mol l^{-1} HCl. The total concentration of each solution was 50 ng ml^{-1}. It was observed that the signals were identical for all of the six solutions. This observation indicates that, using lead cathode, direct determination of total antimony with electrochemical hydride generation can be performed without the need of a pre-reduction step to reduce Sb (V) to Sb (III).

Table 3.1 Absorbance Signals for Sb (III) and Sb (V) mixtures

Sb (III) percentage (%)	Sb (V) percentage (%)	Absorbance Signal
100	0	0.277
80	20	0.275
60	40	0.278
40	60	0.276
20	80	0.274
0	100	0.276

3.3 Analytical Figures of Merit

Under the obtained optimum conditions, Sb (III) standards in 1 mol l^{-1} HCl at a concentration interval of 5 – 200 ng ml^{-1} were used as the catholyte solutions. The calibration plot for this interval was taken. The calibration plot (Figure 3.7) was linear between 5 – 120 ng ml^{-1} with a best line equation and correlation coefficient of $y = 0.0055x - 0.0063$ and 0.9953, respectively.

The relative standard deviation was better than 5% for electrochemical hydride generation. The 3σ limit of detection was calculated as 1.03 ng ml^{-1}. The characteristic concentration (C_0) for 50 ng ml^{-1} Sb was found to be 0.81 ng ml^{-1}.

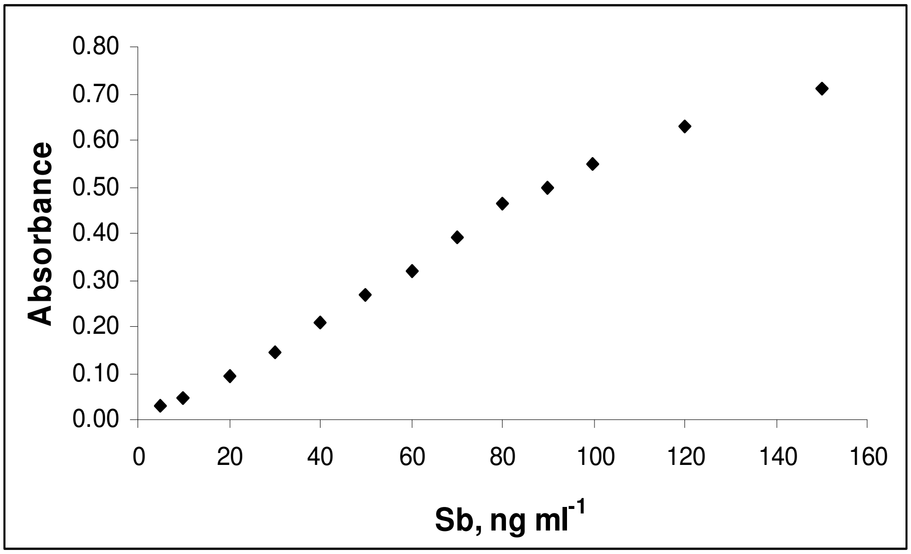

Figure 3.7 Calibration plot for electrochemical hydride generation of Sb

3.4 Comparison of Electrochemical Hydride Generation and Chemical Hydride Generation

The differences between electrochemical hydride generation and chemical hydride generation techniques in terms of their linear range, 3σ limit of detection and reciprocal sensitivity were investigated. SbH_3 was generated with 0.5% $NaBH_4$ in 0.4% (m/v) NaOH as described in reference [8]. The concentration range of Sb (III) was 5 – 200 ng ml^{-1} as it was in electrochemical hydride generation. Figure 3.8 is the calibration plot for chemical hydride generation of Sb in the continuous flow mode.

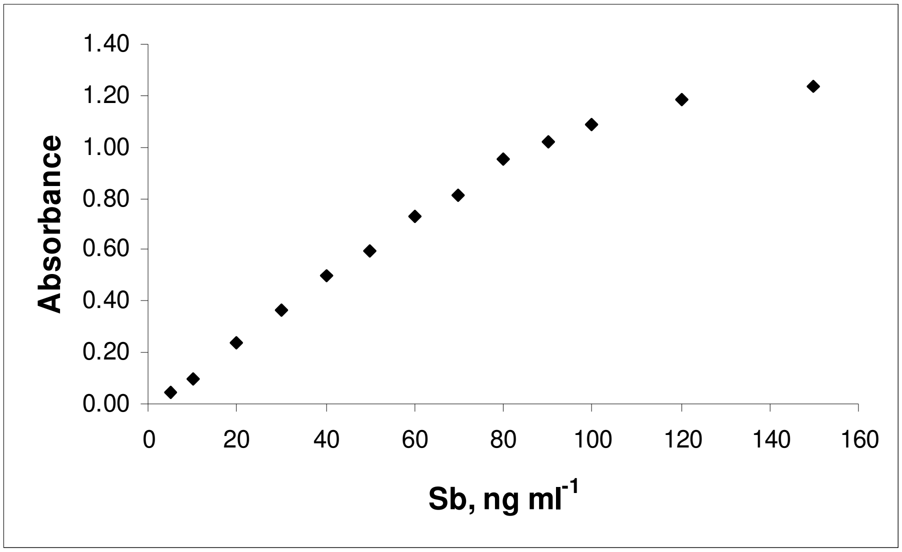

Figure 3.8 Calibration plot for chemical hydride generation of Sb

As it is can be seen from figure 3.8, the absorbance signals obtained with chemical hydride generation are slightly higher than those obtained with electrochemical hydride generation. The linear range of the calibration plot is in between 5 – 100 ng ml^{-1} with a best line equation and correlation coefficient of $y = 0.0113x + 0.0139$ and 0.9935, respectively. The 3σ limit of detection was calculated as 0.69 ng ml^{-1}. The characteristic concentration (C_0) of 50 ng ml^{-1} Sb was found as 0.36 ng ml^{-1}.

Table 3.2 Comparison of Chemical and Electrochemical Hydride Generation techniques

	Chemical Hydride Generation (HG)	Electrochemical Hydride Generation (ECHG)
Best line equation	$y = 0.0113x + 0.0139$	$y = 0.0055x – 0.0063$
LOD (ng ml^{-1})	0.69	1.03
C_0 (ng ml^{-1})	0.36	0.81

3.5 Efficiency of Electrochemical Hydride Generation

A relative efficiency of the electrochemical hydride generation can be estimated in relation to the chemical hydride generation. In order to calculate the efficiency, SbH_3 was generated both electrochemically and chemically from 50 ng ml^{-1} Sb (III) in 1 mol l^{-1} HCl solution. Chemical hydride generation was performed under the experimental conditions given in section 3.4. While generating the hydrides electrochemically, the waste pumped away from the gas-liquid separator was collected. After obtaining the absorbance values of the electrochemical generation, the amount of antimony in the waste solution was determined by chemical hydride generation. Assuming that the efficiency of chemical hydride generation is 100%, the signal obtained from the waste solution and the total signal were compared. It was seen that 40% of antimony remained in the waste solution. By comparing the signal of chemical hydride generation with the signal of electrochemical hydride generation, it was observed that 47% of total signal was obtained with the electrochemical hydride generation technique. The rest of the total, which was 13%, could be lost in various parts of the generation system which could be the transport tubing upstream, the electrochemical cell, the cathode surface, the tubing transferring the waste solution and the tubing transporting the cell to the atomizer.

3.6 Optimization of Trap Conditions

Throughout the trap experiments, 1 ng ml^{-1} Sb (III) in 1 mol l^{-1} HCl was used and the trap was placed three centimeters away from the junction point of the inlet and optical arms of the quartz tube atomizer. The distance of the trap from the junction point was chosen as 3 centimeters as at that distance the temperature of the trap was not affected from the flame of the atomic absorption spectrometer. Before starting the optimization of the trap conditions, the relation between the voltage applied to the trap and the trap temperature (Table 2.1) was investigated. Also, whether the introduction of hydrogen gas to the system during the revolatilization step had an effect on the temperature of the trap was investigated and it was observed that introducing hydrogen gas had no effect on the temperature of the trap. Introduction of hydrogen into the system was necessary because merely heating the trap was not sufficient to revolatilize the trapped species and sent them into the atomizer.

The optimizations of collection and revolatilization temperatures and H_2 flow rate were performed with 30 seconds of collection time. The absorbance signals are given as peak height.

3.6.1 Optimization of Collection and Revolatilization Temperatures

Figure 3.9 shows the peak height values during the optimization of collection and revolatilization temperatures.

During the optimization of collection temperature, the revolatilization temperature was 1030 ^{0}C and during the optimization of revolatilization temperature the collection temperature was 400 ^{0}C.

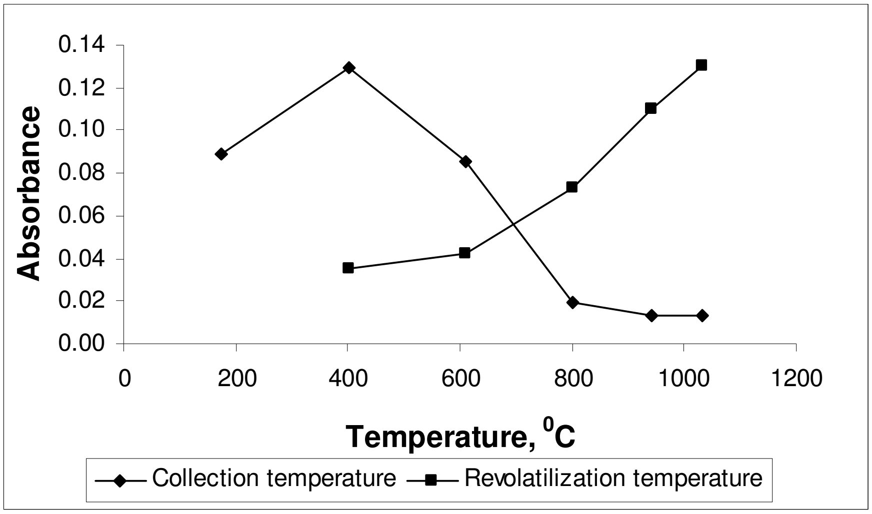

Figure 3.9 Influence of collection and revolatilization temperatures

Catholyte: 50 ng ml^{-1} Sb in 1 mol l^{-1} HCl, H_2 Flow: 100 ml min^{-1}, collection time: 30 s

Using the inlet arm of the quartz tube atomizer as the trapping medium, the maximum temperature used as the revolatilization temperature was 1030 ^{0}C. It was not necessary to heat the trap further as the collected species could be volatilized at once at this temperature.

3.6.2 Influence of the Time Period between Turning the Heat on and Introducing H_2 flow at Revolatilization Step

The change in temperature of the trap with time after increasing the voltage applied to it is given in Figure 2.4. The time passed before the introduction of H_2 flow into the trap and after increasing the temperature to volatilization temperature is an important parameter that influences the absorbance signal. Figure 3.10 illustrates this influence.

It is obvious from Figure 3.10 that the absorbance values are the highest at the tenth second, so H_2 flow was introduced into the system at the end of this time interval and the absorbance signals were obtained. Although a plateau was reached after 30 seconds, 10 seconds was used at further experiments as the percent relative standard deviations of the obtained results did not change. The % RSD of the measurements were 4-6 % for all the data obtained at different time periods between turning the heat on and introducing H_2 flow at revolatilization step.

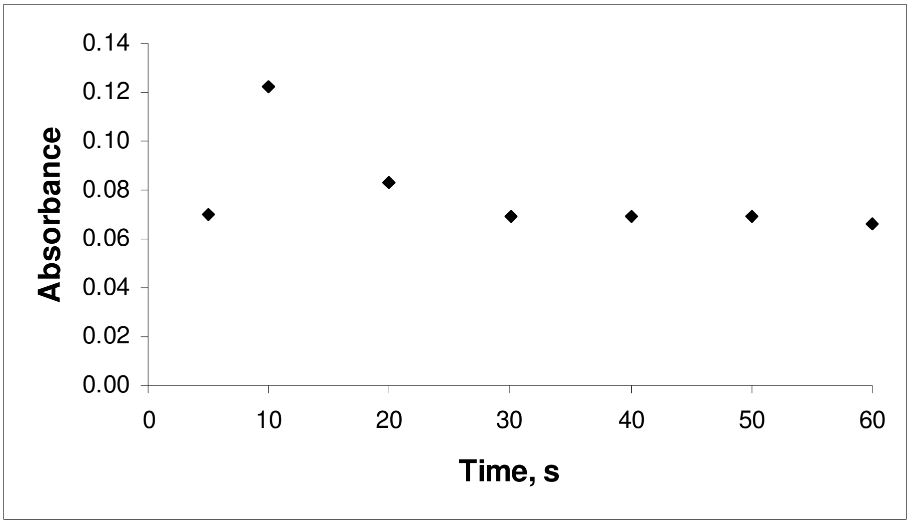

Figure 3.10 Influence of time period between turning the heat on and introducing H_2 flow at revolatilization step

Collection T: 403 ^{0}C, Revolatilization T: 1030 ^{0}C, H_2 flow: 100 ml min^{-1}, collection time: 30 s

3.6.3 Optimization of Hydrogen Flow Rate

For the revolatilization of the collected analyte species, introduction of hydrogen flow into the trap is necessary. Figure 3.11 represents the effect of hydrogen flow rate on the signal. The optimum hydrogen flow rate was found to be 100 ml min^{-1} and the total gas flow into the quartz tube has become 145 ml min^{-1} after the introduction of hydrogen.

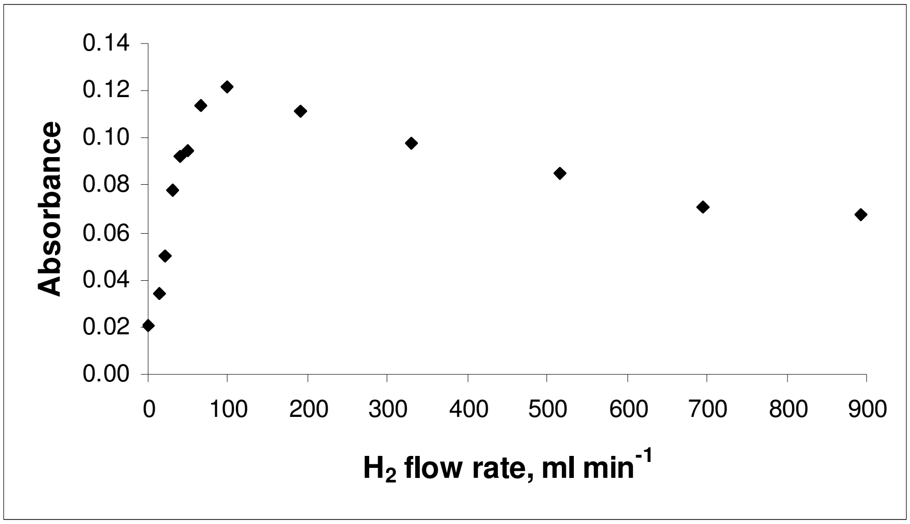

Figure 3.11 Optimization of H_2 flow rate

Collection T: 403 ^{0}C, Revolatilization T: 1030 ^{0}C, collection time: 30 s

In order to investigate whether hydrogen flow is necessary to revolatilize / reatomize the collected antimony species or to transport the species into the atomizer, some experiments were performed. The hydrogen flow rate was decreased but at the same time the total gas flow into the system was held constant by increasing the argon flow rate. The same trend that is seen in Figure 3.11 was observed; the absorbance values were lower at hydrogen flow rates that were both lower and higher than 100 ml min^{-1}. As a result of this observation it can be stated that the necessity of hydrogen flow into the system is not for the transportation of collected analyte species, but to revolatilize the analyte species from the surface of the inlet arm of the quartz tube atomizer.

Figure 3.12 is the typical signal shape observed for 1 ng ml^{-1} Sb in 1 mol l^{-1} HCl solution after 30 seconds collection.

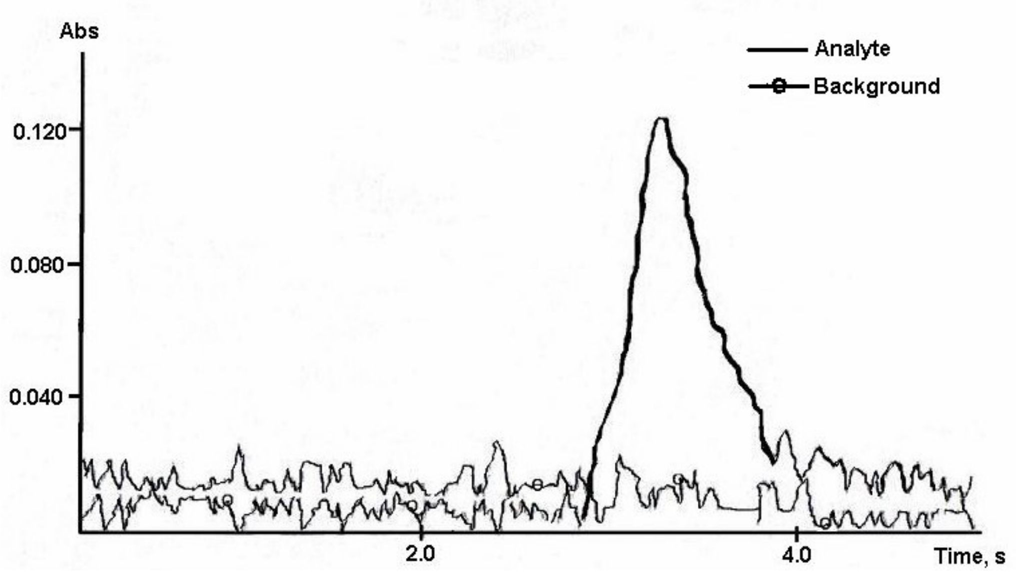

Figure 3.12 The typical signal shape observed for 1.5 ng Sb.
Collection T: 403 ^{0}C, Revolatilization T: 1030 ^{0}C, H_2 flow: 100 ml min^{-1}

In figure 3.12 the background signal is also seen. As it is obvious from the figure background signal is not important, so background correction was not employed for further studies.

3.7 Effect of Collection Time on the Absorbance Signal

The increase in the peak height signals with increasing collection time can be seen in Figure 3.13. The collection volume ranges from 0.5 ml to 12 ml which corresponds to 0.5 – 12 ng Sb. For collection times longer that 120 seconds, the blank signals also start to increase, so employing collection times longer than 120 seconds is not feasible.

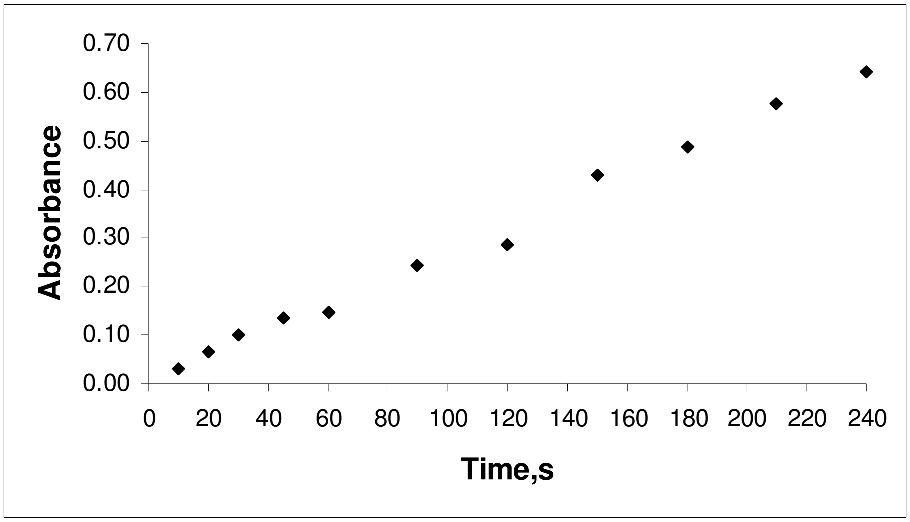

Figure 3.13 Peak height absorbance values for different collection times

Collection T: 403 ^{0}C, Revolatilization T: 1030 ^{0}C, H_2 flow: 100 ml min^{-1}

3.8 Determination of Sb (V) with the Quartz Trap

The signals for the two oxidation states of Sb were taken by electrochemical hydride generation as it was explained in Section 3.2 and it was found that the results were identical. The hydrides generated from Sb (V) solution were collected in the trap and it was investigated whether the efficiency of the trap was the same for this oxidation state of the analyte. The signals identical to the ones obtained with collection of Sb (III) were obtained. This indicates that the efficiency of the trap is same for both of the oxidation states.

3.9 Quartz Trap Leached in HF

The inlet arm of the quartz tube atomizer that is used as the trapping medium was leached in HF for 20 minutes, rinsed with distilled water and then left to dry. Employing this quartz tube atomizer, the generated hydrides were trapped as explained in Section 2.6. It was observed that the trapping was the same as the trap not leached in HF (Figure 2.5), but revolatilization signals were 8-10% lower under the same hydrogen gas flow rate introduced into the system. The results indicate that a smooth surface should be used for better trapping.

3.10 Analytical Figures of Merit

The calibration plot, for collection of hydrides with standard solution introduction time of 120 seconds is shown in Figure 3.14. The results given in this graph are not blank-corrected. The linear portion of the calibration plot extended up to 1 ng ml^{-1} Sb, corresponding 6 ng of sample. The best line equation and the correlation coefficient for the calibration plot are $y = 0.09x + 0.0047$ and 0.9949 respectively.

The relative standard deviation was better than 6% for peak height measurements. The 3σ limit of detection was calculated as 0.053 ng ml^{-1}. The characteristic concentration (C_0) found using 0.5 ng ml^{-1} Sb was calculated as 0.044 ng ml^{-1}.

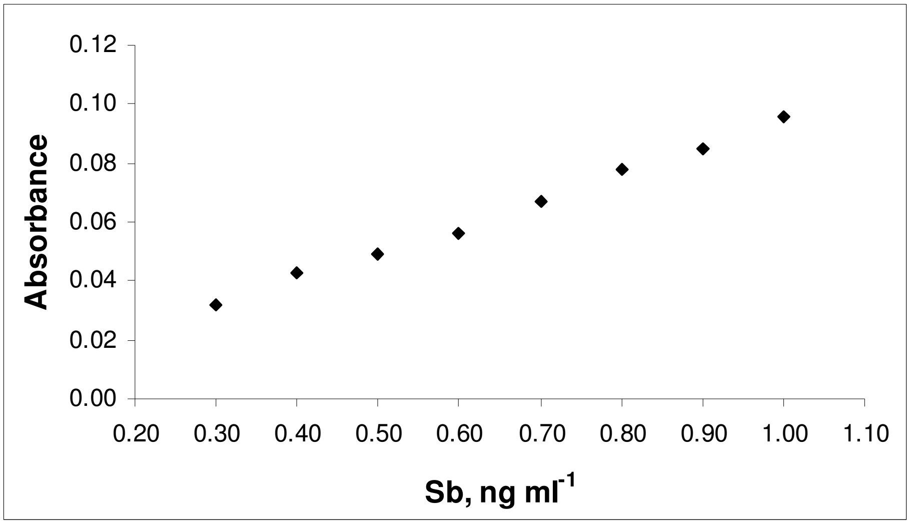

Figure 3.14 Calibration plot for collection of hydrides

Collection T: 403 ^{0}C, Revolatilization T: 1030 ^{0}C, H_2 flow: 100 ml min^{-1}, Collection time: 120 seconds

Table 3.3 gives the results obtained for Sb (III) with different electrochemical hydride generation systems employing different cathode materials and also different techniques. As it can be seen from this table, the results obtained in this study without employing the trap is better than those obtained in reference [51] and also the results obtained by employing the trap are comparable with the results of reference [50] which were obtained by electrothermal atomic absorption spectrometry with in-situ concentration in Pd-coated graphite furnace.

Table 3.3 Comparison of Results for Sb with Different ECHG Systems

Cathode Material	Technique	LOD (3σ)	Ref.
lead	ETAAS	0.02 ng ml^{-1} (a)	50
fibrous carbon	ICP-TOFMS	0.2 ng ml^{-1}	52
lead	AAS	1.03 ng ml^{-1} 0.053 ng ml^{-1}(b)	This study
vitreous carbon	AAS	1.4 ng ml^{-1}	51

(a) in-situ trapping in Pd-coated graphite furnace
(b) trapping on quartz surface

3.11 Interference Studies

During the interference studies, standards at concentrations of 50 and 1 ng ml^{-1} Sb in 1 mol l^{-1} HCl were used for without trap and with trap experiments respectively. The interferent concentrations were 10, 100 and 1000 folds of these concentrations.

Figures 3.15 and 3.16 are the graphical representations of the interference effects of arsenic, selenium, tin and lead on the absorbance signals without trap and with trap respectively. As it can be seen from Figure 3.15, the presence of ten fold arsenic, resulted in 40% increase in the signal, when the arsenic amount was increased to 100 fold of the antimony amount, no change in the signal was observed and when the interferent amount was 1000 fold of analyte, the signal decreased by 23%. In the presence of selenium, the signals decreased by 28, 46 and 50% at selenium concentrations that are 10, 100 and 1000 folds of antimony, respectively. The signals increased by 11, 37 and 40% in the presence of tin at 10, 100 and 1000 folds of antimony concentration, respectively. The same increase trend was observed in the presence of lead. The percentages of the increase in the signals were 10, 17 and 24 for lead concentrations that were 10, 100 and 1000 folds of antimony.

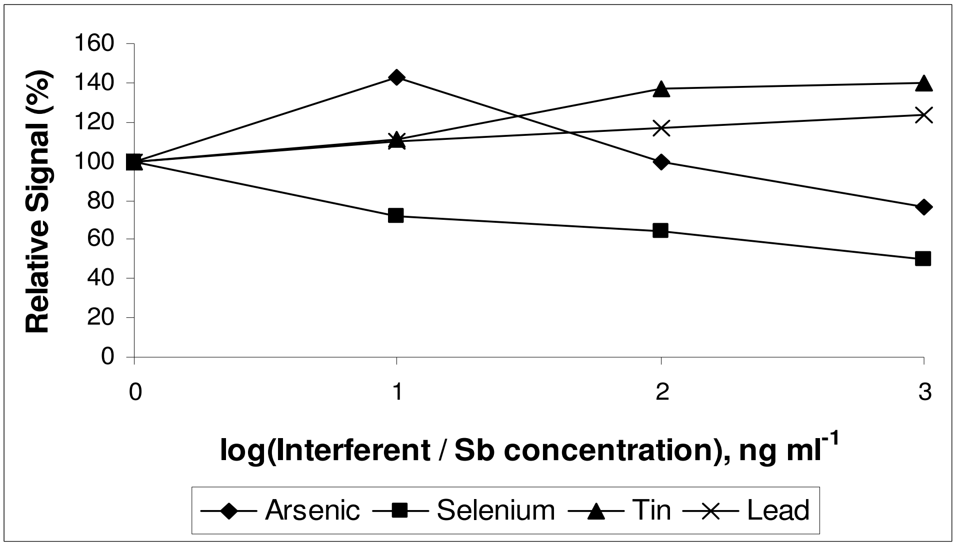

Figure 3.15 Interference of arsenic, selenium, tin and lead on electrochemical hydride generation without trap

With the trap, the same trend for each individual element was observed but the effects were 5 – 10% lower compared to the case without trap. At arsenic concentrations that were 10, 100 and 1000 folds of antimony concentration the signals were 35% higher, same and 15% lower than those obtained from the solutions containing no arsenic respectively. For the same interferent and antimony concentrations, the results were 23, 40 and 42% lower for selenium respectively. For tin, the absorbance signals were 10, 30 and 35% higher and finally for lead the increases in the signals were 7, 15 and 20% respectively for 10, 100 and 1000 folds of interferent concentrations.

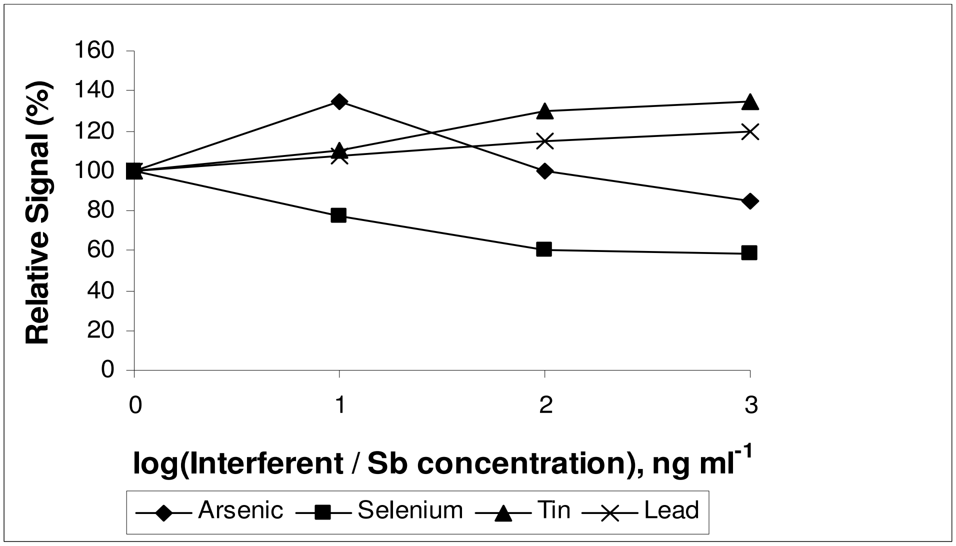

Figure 3.16 Interference of arsenic, selenium, tin and lead on electrochemical hydride generation with trap

Figures 3.17 and 3.18 are the graphical representations of the interference effects of nickel, copper, cobalt and iron without and with trapping respectively. The presences of all of the four interferents individually cause a signal depression. By employing the trap, the effects of these metals on the electrochemical hydride generation were reduced. As it can be seen from figure 3.17, the presence of nickel at 10, 100 and 1000 folds of antimony concentration, decreased the absorbance signals by 20, 73 and 77% respectively. The presence of copper at the same concentrations caused 65, 80 and 85 % decreases in the signals. In the presence of cobalt at 10, 100 and 1000 folds of the analyte, the signals were decreased by 42, 60 and 70 %, respectively. The presence of iron at 10, 100 and 1000 folds of the antimony concentration decreased the signals by 65, 75 and 80 %, respectively.

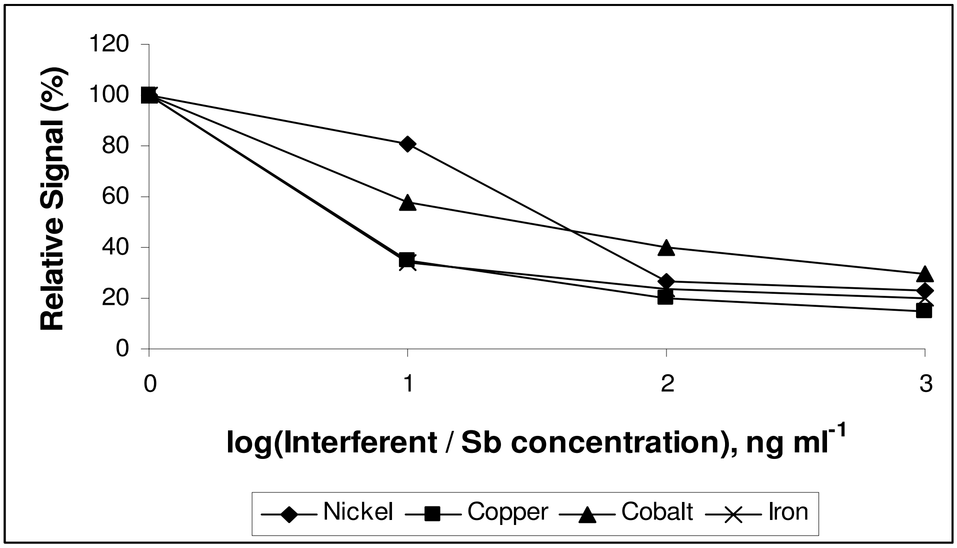

Figure 3.17 Interference of nickel, copper, cobalt and iron on electrochemical hydride generation without trap

Employing the trap, the interferences of nickel, copper, cobalt and iron were reduced. As it can be seen from figure 3.18, the presence of 10 fold nickel, did not cause any interference; nickel concentrations that are 100 and 1000 folds of antimony decreased the absorbance signals by 5 and 20 % respectively. The presence of copper at 10, 100 and 1000 folds of antimony decreased the signals by 15, 22 and 30 % respectively. The presence of cobalt resulted in 10, 12 and 24% signal depressions at the same interferent/antimony ratios. In the presence of iron, the decreases in the signals were 20, 32 and 40 % at the same interferent concentrations.

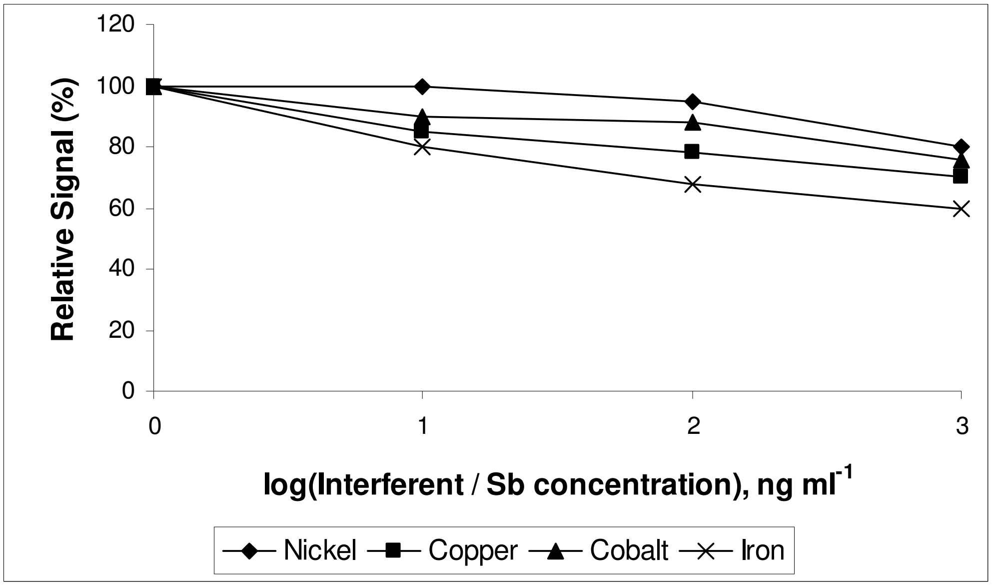

Figure 3.18 Interference of nickel, copper, cobalt and iron on electrochemical hydride generation with trap

Comparing the results obtained without and with trap, it was observed that employing the trap decreased the interference effects of nickel, copper, cobalt and iron significantly. Presence of transition metals cause nonspectral interferences and these metals are present in great excess relative to the analyte. The extent of the interference does not depend on the analyte concentration but on the interferent concentration. A consequence of the independence of interference magnitude on analyte concentration is that the method of standard additions may, in principle, be employed to alleviate the interferences. However, it is usable only when the interference does not reduce the observed signal too much. The other generally applicable method is to dilute the sample. This approach is possible only for samples with higher analyte content or when employing collection methods of hydride generation or in-situ trapping [20]. It is thought that this decrease was observed as a result of dilution of the interferent ions as well as the analyte.

3.12 Analysis of Standard Reference Materials

Table 3.4 gives the certified and found values for the standard reference materials (SRM). The amount of Sb in SRMs was found to be in good agreement with the certified values.

Table 3.4 Results of the analysis of standard reference materials

SRM	Certified Value	Found
Soil/Sediment #4, mg kg^{-1}	2.55	2.51 ± 0.3
CRM-TMDW, µg l^{-1}	10 ± 0.5	9.8 ± 0.5

CHAPTER IV

CONCLUSIONS

Electrochemical hydride generation of antimony and trapping the generated hydrides in the inlet arm of the conventional quartz tube atomizer was studied. The experimental operation parameters in electrochemical hydride generation were optimized. Employing electrochemical hydride generation technique, 3σ limit of detection was calculated as 1.03 ng ml^{-1}. Determination of the two oxidation states of Sb was performed and it was concluded that employing lead as cathode material, hydrides of both of the oxidation states were generated with the same efficiency, which is an advantage for total antimony determination in real samples. Speciation can be performed with the electrochemical hydride generation technique by selecting the cathode material according to its influence on the efficiency of hydride generation depending on the analyte oxidation state.

The inlet arm of the conventional quartz tube atomizer was used as atom trap by external heating. The trap parameters were optimized and 3σ limit of detection was calculated as 0.053 ng ml^{-1}. These results represent that trapping the generated hydrides on the quartz surface causes a 20 fold improvement in limit of detection.

The interferences of some hydride forming elements and some transition metals on electrochemical hydride generation with and without employing the trap were investigated. It was observed that, hydride forming elements Sn and Pb have caused an increase in the absorbance signals with and without trap. On the other hand, the presence of As, have caused an increase in the signal when its concentration is 10 fold of the analyte concentration and no difference was observed when the arsenic concentration was 100 fold of the analyte concentration and a signal suppression was seen at 1000 fold arsenic concentration. The presence of Se resulted in signal suppression at all the three interferent concentrations. With the hydride forming elements, employing the trap did not have any significant effect.

The presence of Ni, Cu, Co and Fe had the same effect on the absorbance signals; signal suppressions of 20 – 85% were observed without employing the trap. The levels of signal suppressions were decreased by using the trap; that is, the suppressions were in the range of 10 – 40%. These observations indicate that, by diluting the sample, the effects of interferences can be reduced. This is a common characteristic and advantage of sensitive techniques.

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