DETERMINATION OF SILVER BY CHEMICAL VAPOUR GENERATION AND ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

DETERMINATION OF SILVER BY CHEMICAL VAPOUR GENERATION AND ATOMIC ABSORPTION SPECTROMETRY

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A method for determination of silver has been developed based on chemical vapour generation atomic absorption spectrometry (CVGAAS). Volatile species of silver in acidified medium were generated by the reduction of sodium tetrahydroborate; these species were sent to a flame-heated quartz tube atomizer (QTA) following isolation by using a gas-liquid separator. Flow injection (FI) was used for sample introduction. Optimization of parameters such as; concentrations of acid and $NaBH_4$ concentration, flow rates of solutions and carrier gas were made. The influences of the well-known chemical modifier, Pd, and the effect of diethyldithiocarbomate (DDTC) were also examined. Interference study has been carried out for Ni(II), Co(II), Cu(II), Fe(III), Au(III), As(III), Pb(II), Se(IV) and Sn(II) . A detection limit of 7.5 ng mL^{-1} (n=11) was obtained with a 0.2 mL sample volume. With the FI-CVGAAS system 5.6 times sensitivity enhancement was achieved over flame atomic absorption spectrometry (FAAS).

Keywords: Hydride Generation, Chemical Vapour Generation, Flow Injection, Atomic Absorption Spectrometry, Ag

ÖZ

KİMYASAL BUHAR OLUŞTURMA VE ATOMİK ABSORPSİYON SPEKTROMETRİ İLE GÜMÜŞ TAYİNİ

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Gümüş tayini için kimyasal buhar oluşturmalı atomik absorpsiyon spektrometri (KBOAAS) temelli bir yöntem geliştirildi. Gümüşün uçucu türleri, asitli ortamda sodyum tetraborat ile indirgemeyle oluşturuldu; bu türler bir gaz-sıvı ayırıcı yardımıyla alevle ısıtılmış bir kuvars tüp atomlaştırıcıya yollandı. Örnek, sisteme akışa enjeksiyon yöntemiyle verildi. Asit ve $NaBH_4$ derişimleri, çözeltiler ve taşıyıcı gaz için akış hızları gibi parametreler optimize edildi. Kimyasal değiştirici özelliği iyi bilinen Pd ve DDTC etkileri de incelendi. Ni(II), Co(II), Cu(II), Fe(III), Au(III), As(III), Pb(II), Se(IV) ve Sn(II) için girişim çalışması yapıldı. 0.2 mL örnek hacmi için gözlenebilme sınırı 7.5 ng mL^{-1} (n=11) olarak bulundu. Alevli atomik absorpsiyon spektrometri (AAAS) yöntemine göre AE-KBO-AAS sistemi 5.6 kat duyarlılık artışı sağlamıştır.

Anahtar Kelimeler: Hidrür Oluşturma, Kimyasal Buhar Oluşturma, Akışa Enjeksiyon, Atomik Absorpsiyon Spektrometri, Ag

To My Parents

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INTRODUCTION

1.1. Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is the most widely used technique to measure the concentrations of the elements. The occurrence of atomic absorption was noted by Wollaston and Fraunhofer and explained by Kirchoff and Bunsen in the nineteenth century. In the 1955, Walsh established the foundation of modern analytical atomic absorption spectroscopy by introducing a system that consists of hollow cathode light sources, flame atomizers, photomultipliers and a modulated system. When radiation of proper wavelength passes through a vapour containing ground state atoms, some of the radiation can be absorbed by excitation of the atoms and change in the intensity of the radiation at a wavelength corresponding to the energy of the photon is detected [1]. AAS is based on the measurement of the absorption of optical radiation by atoms in gas phase. The magnitude of the atomic absorption signal is directly related to the number of ground state atoms in the optical path of the spectrometer. Ground state atoms are produced from the sample material, usually by evaporation of solvent and vaporization of the solid particles followed by decomposition of the molecular species into neutral atoms. Normally these steps are carried out using an aspirator and flame [2].

1.2. Flame Atomic Absorption Spectrometry

Walsh and Milatz proposed and demonstrated analytical flame atomic absorption spectroscopy (FAAS), in which radiation from a line source, such as a hollow cathode lamp, is absorbed by atomic vapour in the flame. The technique of FAAS became accepted in the 1960s after the introduction of the first commercial FAAS in 1959. Until recently, FAAS was the most widely used of all atomic spectral methods because of its simplicity, effectiveness, and relatively low cost. This position of supremacy is now being challenged, however, by plasma spectroscopy, an emission method.

In flame atomization, a solution of the sample is aspirated into a flame by means of a nebulizer, which converts the sample solution into a mist made up of tiny liquid droplets. A complex set of interconnected processes then occurs; these processes eventually lead to a mixture of analyte atoms, analyte ions, sample molecules of the analyte, and certainly a variety of atomic and molecular species formed by reactions among the fuel, the oxidant, and the sample. With so many complex processes occurring, it is not surprising that atomization is the most critical step in flame spectroscopy and the one that limits the precision of such methods. Because of the critical nature of the atomization step, it is important to understand the characteristics of flame and the variables that affect these characteristics [3].

Generally air-acetylene flame and nitrous oxide-acetylene flame are used in AAS. The nitrous oxide-acetylene flame is the hotter flame (3150 K), in comparison to the cooler air-acetylene flame (2500 K). The sensitivity of conventional FAAS is limited by several factors. Free analyte atoms generated in the flame in which they absorb radiation from the external source pass rapidly; its residence time is around 0.1 ms. A further limitation is the poor nebulization efficiency; that is a maximum of 10% of the aspirated solution reaches the burner [4]. FAAS normally allows the qualification of the elements only at an mg L^{-1} level. Thus, a pre-concentration step, which may include solvent extraction and co-precipitation, is often required before FAAS analysis [5]. Sensitivity could be improved by forcing the atomic vapour to remain longer time in the source beam and also if the sample could be introduced with numerous trapping devices [6].

1.3. Hydride Generation

The achievement of analytical atomic spectrometry often depends on the method of sample introduction. Most generally used sample introduction is nebulization of liquid solution by pneumatic nebulizers. These devices are convenient to operate; on the other hand, efficiency of nebulization of sample solution is less than 10 %, with 90% of sample being wasted. They also present difficulties with viscous, high salt content and micro-volume solutions. The hydride generation (HG) technique is another commonly used means of introducing liquid samples [7]. HG is a special form of sample introduction which is wholly reserved for a limited number of elements that are capable of forming volatile hydrides. HG has been employed for over 100 years for the determination of arsenic in methods known as the Marsh reaction or the Gutzeit test. The introduction of atomic absorption spectrometry to laboratories throughout the world was an incentive for a massive application of hydride generation in AAS. It was introduced around 1970 to overcome problems associated with flame AAS determinations of arsenic and selenium. In the following years, the unquestionable advantages of the method led to its application to virtually all elements forming volatile hydrides, namely arsenic, antimony, bismuth, germanium, lead, selenium, tellurium, and tin. Hydride generation of indium and thallium was also described. Most hydride forming elements are of a certain biological, environmental and technological importance as well as being among the analytes which are more problematic with alternative techniques of AAS. Owing to the significant instrumental and methodological process in the last decade, this technique is widely applied to analysis of diverse sample types: environmental, biological, agricultural, geological, metallurgical, food, plastics, etc. [8].

The popularity of hydride generation arises for several reasons. One of these is its relative simplicity and low cost of the apparatus. However, the main reason lies with the principle of the method. It involves analyte pre-concentration and separation from the sample matrix. This results in a superior sensitivity, and mainly, in an outstanding suppression of interferences during atomization. A serious disadvantage of the method, interferences in hydride evolution from the sample, takes place under laboratory temperature and in aqueous solutions. In principle, they can be more easily studied than interferences in a graphite furnace or in a flame [8].

The conventional procedure for HG is to generate volatile analyte species by reducing the acidified sample solution with sodium tetrahydroborate (III) solution; afterward the gaseous hydride is liberated. These volatile hydrides are consequently swept the generated gas into the atomizer; so that quantitative measurement can be done.

The basic design of a hydride generation system with following AAS detection may be expediently well thought-out as four steps [9]:

i) generation of the hydride
ii) collection of the hydride (if necessary)
iii) transfer of the hydride
iv) atomization of the hydride

The main advantages of the hydride generation technique include that it provides chemical pre-separation of the analyte from possible matrix interferences; secondly a more efficient sample introduction system and good powers of detection. HG can afford several methods of inorganic and/or organic speciation for As, Ge, Sb, Se, Sn and Te. It can be used with emission sources which have poor vapourization characteristics. HG can further be easily automated. But on the other hand disadvantages of the hydride generation technique include being prone to interferences by concomitants which reduce the hydride generation efficiency. Another disadvantage is that HG rate can be kinetically controlled and slowed, in some cases, necessitating collection apparatus prior to introduction of the hydrides to the source or atom cell. In addition, pH and reagents concentration of generation solution can be critical for some elements. Another disadvantages is that in some cases oxidation state of interest may be critical, e.g., Se (IV) and Se (VI).

1.3.1. Hydride Generation Reactions

Several reducing agents and sources of nascent hydrogen have been investigated in order to convert the analyte element into its hydride. In the early work, most frequently a metal/acid measuring system was employed, such as $SnCl_2$-HCl, HCl-KI-Zn and $TiCl_3$-HCl-Mg [10]. Generally, Zn-HCl reaction metal-acid system, known as March reaction, is used to produce nascent hydrogen.

$$Zn + 2HCl \rightarrow ZnCl_2 + 2H\bullet \qquad (1)$$
$$H\bullet + E^{m+} \rightarrow EH_n + H_2 \text{ (excess)} \qquad (2)$$

Where E is the analyte concerned and m may not be equal to n.

Presently, more effective and newer method to produce hydride is the usage of sodiumborohydride, $NaBH_4$-acid reaction. Reduction is effected as shown in the following equation [7]:

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H\bullet \qquad (3)$$
$$H\bullet + E^{m+} \rightarrow EH_n + H_2 \text{ (excess)} \qquad (2)$$

Where E is the analyte of interest and m may not be equal to n. The $NaBH_4$-acid reduction system has some advantages over prior metal-acid reduction system regarding the reduction yield, reaction time, contamination of the blank and applicability to the elements concerned. Therefore, the $NaBH_4$-acid reaction has greater potential for use in multi-element determinations. At first, $NaBH_4$ pellets were favorites, but currently its water solution stabilized either by potassium or sodium hydroxide is the most popular and most convenient agent. A freshly prepared solution of $NaBH_4$ is more efficient and now preferred. Even alkaline $NaBH_4$ solutions slowly decompose to form hydrogen. Recommended range of $NaBH_4$ is usually 0.5 – 10 % aqueous solutions stabilized by 0.1 – 2 % KOH or NaOH [7]. In the $NaBH_4$ –acid system, hydrochloric acid is exclusively used, although H_2SO_4 and HNO_3 are suitable in some cases. Optimum acidity ranges appear to be depending on interest and the type of hydride generators [7-8]. Owing to rapid reaction between sodium tetrahydroborate and hydrochloric acid, foam may be generated, mainly when undigested biological fluids like urine or blood plasma are being analyzed. In these cases, antifoaming compounds can be used [10]. The efficiency of hydride generation is strongly depended on the use of optimized chemical and physical parameters, both the method of hydride generation and the design of the apparatus.

1.3.2. Hydride Transport

Hydride released from sample solution is transported by a flow of the purge gas to an atomizer. Separation and transport are achieved with a carrier gas such as N_2, Ar, He. So as to increase the signal, it is essential to generate and transport the hydride as rapidly as possible to the atomizer. This reduces the dilution of the hydride by the carrier gas [9]. During the transport, losses of hydride can be severe. Loss or delays of transported hydrides are probably due to their decomposition or sorption. The magnitude of hydride interaction with surfaces obviously decreases with increasing the carrier gas flow rate and with decreasing the surface area, that is, with decreasing diameter of tubing and the size of the generator vessel.

Hydride transport losses can be made negligible in an optimized experimental set-up. The tubing serving for the transport of hydrides to the atomizer should be as short as possible to avoid the transport losses. The interaction of hydride with the tubing surface is obviously reduced in narrower tubings; however, too narrow tubing increases the risk of overpressure problems. The flow of gases also transports together with generated hydride a certain amount of spray of the reaction mixture stripped out of the reaction vessel. Condensation of the reagent mist and/or water vapour in the transfer line should be avoided due to the losses or delay of hydrides [8].

1.3.3. Hydride Atomization

Hydride atomizers are expected to convert the analyte hydride to free atoms with maximum efficiency which should be independent of the sample composition, with minimum dilution and, because of achieving high sensitivity, to keep free atoms in the observation volume as long as possible [8]. The following atomizers have been used in HGAAS.

1.3.3.1. Inert Gas-Hydrogen Diffusion Flames

The first time HG was used as a sample introduction technique in atomic spectrometry was in 1969 by Holak to determine arsenic [11]. Holak used a conventional air-acetylene flame supported on a three-slot Boling burner. This type of flame will be called diffusion flame. The flow of hydride supported by the purge gas could be easily introduced into such a flame. The air-acetylene flame was used by many workers in the early stages of the development of the technique, but it was soon replaced by the argon-hydrogen-entrained air flame usually called the argon-hydrogen diffusion flame [10]. The advantage of this type of flame over the air-acetylene flame is much lower background absorption at lower wavelengths characteristic for hydride forming elements. However, the background absorption is still significant and its flicker noise increases the limit of detection [8]. Shielded flames (using solid plates) have also been employed [12, 13, 14] in order to minimize drafts from the atmosphere and thus to improve flame stability and to reduce the noise. Diffusion flames produce low temperature- in the range of 350 °C to 1000 °C. An additional disadvantage of diffusion flames is a marked dilution of the hydride with flame gasses [8]. As a result, they were used commonly in the past, and they were inferior to the other atomizer so not often been employed in recent years.

1.3.3.2. Flame-in Tube Atomizers

Flame-in-tube atomizer, in which hydrogen used as a carrier gas, is partially combusted in the inlet arm of a T-shaped furnace by introducing a limited amount of oxygen or air [15]. They are most often externally unheated quartz tubes with a flame burning inside. Flame-in-tube atomizer was first described by Siemer and Hagemann [10]. Since then, quartz tubes have become the most commonly used hydride atomizers; the externally heated quartz tube is by far more popular than flame-in-tube and all commercial quartz-tube atomizers are of this kind.

1.3.3.3. Externally Heated Quartz Tubes

The earliest reported use of an electrically heated or a flame heated quartz tube for hydride atomization was Chu et al. in 1972 [16] and Thompson and Thomerson in 1974 [17]. Since then, externally heated quartz tubes have become the most accepted used atomizers. The design is usually very similar to the flame-in tube atomizer, consisting of a T-tube with its bar-tube align in the optical path and the central arm of the T serving for delivery of hydrides carried by a flow of gas from a generator. The bar-tube is heated either by a chemical flame or, electrically, either by a resistance wire wound around it or by a tailored furnace. The two outlets of the bar-tube are either open or closed with optical windows. Oxygen or air is often introduced into the atomizer mainly because of the beneficial effect on sensitivity. Compared with flame atomizers, externally heated quartz tubes have the following advantages: the flame background is almost eliminated and better sensitivity is achieved owing to the longer residence time of the atom cloud in the optical path, the lower dilution and the much lower noise levels since the flame is not directly on the light path [10]. The temperature of quartz atomizers is limited by the thermal durability of quartz and, in case of electrically heated ones, of the heating device. Maximum sensitivity is typically reached at temperatures much lower than in a graphite furnace; below 1000°C. In contrast to flame-in-tube atomizers which typically employ a continuous supply of hydrogen to maintain the flame there is no need to use a separate supply of hydrogen to externally heated quartz tubes. For the purging of hydrides from the generator, the most popular gas is argon but nitrogen is also often utilized.

1.3.3.4. Graphite Furnace Atomizers

The first report on the use of the graphite furnace atomizer for atomization of hydrides was by Knudson and Christian in 1974 [18]. After that, atomization of hydrides in a heated graphite furnace has been carried out by other workers. There are two approaches to using graphite furnaces. First one is on-line atomization and the second one is in situ trapping of hydrides in the furnace.

The on-line atomization approach utilizes a direct transfer of the hydride from the generator to the furnace, which is preheated to a temperature usually over 2200°C [10,19,20]. The hydrides are almost exclusively introduced to the internal gas line of commercial furnaces. This method is simple but the hydride can be captured on cooler metal or graphite parts. A similar drawback, hydride capture in the connection tube, can result from introduction of hydrides to the sampling port of the graphite furnace by a sealed graphite tube [21, 22]. There is a feasible alternative for introducing hydrides to the furnace using a quartz tube interfaced to the sampling port, which does not retain hydrides and can endure temperatures above 2300°C, for a reasonable time, if cooled by a gas flow. Naturally, the sensitivity for on-line atomization is generally lower than with in situ trapping [10].

In-situ trapping approach was first described by Drasch et al. [23]. This technique uses the graphite furnace as both the hydride trapping medium and the atomization cell. The hydride purged from the generator is trapped in the preheated graphite furnace, usually in the range 300-600°C, until the evolution of hydride is completed. The trapped analyte is then atomized at temperatures generally over 2200°C. This technique has been shown to enhance the sensitivity significantly and to eliminate effectively the possible influence of the hydride generation kinetics on the signal shape.

1.3.4. Hydride Generation Methods

There are two basic modes of hydride generation. First one is the direct transfer mode and the second one is the collection mode. In the direct transfer mode, hydride released from a sample solution is directly transported to the atomizer. Three direct transfer methods are currently employed:

i) Continuous Flow (CF)
ii) Flow Injection (FI)
iii) Batch

In CF, a constant flow of sample solution is mixed with a constant flow of tetrahydroborate solution and of the purge gas. They are delivered continuously at a constant rate to the generator using a peristaltic pump. The use of the CF hydride generation system had been described as early as 1973 [24]. Presently it is the most popular mode of hydride generation. The first FI hydride generation system was described by Aström [25] in 1982. Sample is injected to a carrier stream and subsequently merged with reductant solution. A plug of hydride was transported to atomization cell and transient signal was measured. Most of the systems use a peristaltic pump to drive the reactant solutions. FI system generally employs a special valve to inject a volume of sample to the flow of carrier. In a few applications, sample is injected manually to a sampling cup from where it is sucked by the carrier flow. FI mode enhance the performance of HGAAS by providing reduction in sample and reagent consumption, two-to-three fold higher sample frequencies, better precision, enhanced sensitivity and automated operation [26].

Batch system is the earlier system used for CVAAS and HGAAS consisted of normal laboratory apparatus, such as flasks, dropping funnels, gas inlet tubes, etc., assembled to meet the requirements. The measurement solution is placed in the flask, the air is driven out by an inert gas (not necessary for CVAAS), the reductant is added, and the gaseous analyte species is transferred in the inert gas stream to the atomizer or absorption cell. A tyime dependent signal is generated in these techniques and the profile is largely determined by the kinetics of the release of the gaseous analyte from the solution [27]

In the collection mode, the hydride is trapped in a collection devise, considered as a part of the generator, until the evolution is completed and is then transported to an atomizer at all once. The collection methods are:

i) In Absorbing Media
ii) Pressure
iii) Cryotrapping

Collection methods were employed much more frequently in the early years of the application of hydride generation since the metal/acid system used then was relatively slow so that it could take several minutes for the reaction to reach the completion. Obviously, it was advantageous to collect the released hydride and then to sweep it to the atomizer in the shortest possible time. It should be stressed that when using the BH_4^-/acid system as the reducing agent the need to collect released hydride is much less pressing, so that the simpler direct transfer methods are more often make use of presently [8].

1.4. Chemical Vapour Generation

Chemical vapour generation (CVG) techniques are widely utilized for trace element detection. CVG-AAS has become popular for the determination and speciation of difficult analytes and their organoelement species, particularly in the important application field of biological and environmental monitoring [29] due to enhancement of the sample introduction efficiency for solution based measurements. The most common and well established procedure is the reduction and conversion of analyte ions into an atomic vapour or a volatile hydride species [30]. Although vapour generation methods date back to the Marsh Test, which was developed in the middle of the 19th Century, hydride generation remains an active area of research. Dedina and Tsalev surveyed the chemistry of HG in an extensive monograph published in 1995 [8]. Since a limited number of analytes are transformed into volatile species, another benefit of vapour generation is realized when spectral interferences from line-rich elements, such as iron, are eliminated from the atom source. Mercury, which readily forms a monatomic vapour, is easily determined by reduction with either tin (II) or sodium tetrahydroborate(III). Germanium, tin, selenium and tellurium were also studied. Over the last two decades, however the list of elements that can be determined by transforming into vapour phase species has grown considerably. Lead, cadmium, thallium were determined from their hydrides [8], nickel was determined by transforming it into its tetra carbonyl, and osmium was determined from its volatile oxide [31]. Within the last five years several more elements were added to the list of elements that can be determined from volatile species. These elements include Ag, Au, Co, Cr, Cu, Fe, Mn, Ni, Pd, Rh [32-34]. It is not clear at this point in what form some of these elements are delivered to the excitation source, but it is clear that mass transfer efficiencies are significantly greater than those from solution nebulization. All of these advantages aside, vapour generation is often perceived as difficult because of its poor reproducibility of results and need for separate introduction system for vapour generation and nebulization. CVG encounters complex chemistry and transfer line problems; therefore it can be applied to limited number of analytes. Besides the description of the chemistry of vapour generation and interferences can be complex, it is also needs to be understood mass transfer processes from the gas liquid separator [35].

1.5. Interference

In atomic spectrometric methods, three types of interferences are encountered: spectral interferences, chemical interferences and physical interferences.

1.5.1 Spectral Interferences

These interferences are due to radiation absorbed by species other than free atoms of the analyte on analytical wavelength. In other words, when the absorption or emission of an interfering species either overlaps or lies so close to the analyte absorption, emission, luminescence or scattering that resolution by the monochromator becomes impossible [3].

Fortunately, spectral line overlap does not very commonly occur. The risk of spectral interferences increases in the case where multielement line sources are employed in atomic absorption. Continuum source atomic absorption, like flame emission, depends highly on the spectral resolution of the wavelength selection device for selectivity. If the spectral band pass is large, the probability of absorption by other atomic species is enhanced [2].

1.5.2 Chemical Interferences

These are the dominant type of interference in flame FAAS. Chemical interferences arise when the element to be determined form thermally stable compounds with certain molecular or ionic species that are present in the solution [4]. These interferences can occur in the conversion of the solid or molten particles that remain after dissolution into free, neutral, ground-state analyte atoms [2]. Their effects can occasionally be minimized by a suitable choice of operating conditions. Since all the analytes and interferants are confined into a small volume, chemical interferences are even more severe in ETAAS.

1.5.3 Physical Interferences

Physical interferences in FAAS are related to the transport of the sample solution to the flame. This type of interference is related to the nature of the sample solution such as viscosity, surface tension, or density of the solution. They can be positive as well as negative. Interferences of this type can be controlled by careful matrix matching of sample and standard solution. If this is not possible, method of standard additions must be used. To successfully utilize the standard additions method it is essential that calibration is linear over the absorbance range to be covered. By plotting an aqueous calibration plot alongside the standard additions plot it is possible to visually observe the physical matrix effects. If the two plots are not parallel then, some physical matrix interference is occurring with either an enhanced or suppressive effect.

1.5.4 Interference in HGAAS

Due to the separation of analyte from matrix, spectral inferences in hydride generation AAS are much less serious than for liquid sampling AAS. Line interferences do not occur at all, nonselective background absorption can be observed when a significant amount of a species is transported to the atomizer from a hydride generator. This may typically happen in the presence of an excess of other hydride forming elements in the sample matrix or in the case of hydride generation from non-homogeneous media.

Liquid phase interferences are due to changes in the rate of hydride release from the liquid phase and/or due to a decreased efficiency of hydride release. Gaseous phase interferences are obviously caused by volatile species most often by hydrides but also by other compounds, or by liquid spray, produced in a hydride generator. These interferences can take place on the surface or in the dead volume of generator, the connective tubing and/or the atomizer. Gaseous phase interferences could have either a direct effect or a memory effect. Standard addition method may 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 obviously possible only for samples with higher analyte concentration or when employing pre-concentration methods of hydride generation or in-situ trapping in graphite furnaces.

1.5.5 Interference Studies of Silver

Most of the reported interferant studies of silver were done with the FAAS and ETAAS techniques [36-38]. Dadfarnia et al. [36] reported about trace enrichment and determination of silver by immobilized diethyldithiocarbomate (DDTC) micro column and flow injection FAAS. The deposition efficiency of micro column in pre-concentration of silver was tested in presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, Cr^{3+}, Cd^{2+}, Pb^{2+}, Ni^{2+}, As^{3+}, Co^{2+}, Mn^{2+}, Zn^{2+}, Sn^{2+}, Fe^{3+}, Cu^{2+}, V^{5+}, Mo^{6+}. In that study, except Cu, no significant interference was observed in the determination of silver at trace level. Mao et al. [37] also investigated interferences from the common elements potentially existing in geological samples, in the study of determination of trace amount of silver by FAAS-Coupled FI on-line co precipitation, pre-concentration, using DDTC-copper as a co-precipitation carrier. They observed, although the tolerance to iron (III) and copper (II) interference was quite good, the iron content in geological samples usually gave a final iron concentration in the test solution greater that 1000 mg L^{-1}. Thus, ascorbic acid was employed to reduce the iron interference with the addition of 0.16% ascorbic acid; at least 2000 mg L^{-1} Fe(III) can be tolerated. Rahman et al. [38] made a study about interference effects on Ag by preconcentrating the analyte by a tungsten wire by ETAAS; elements contained in river water such as Al, Ca, Cu, Fe, K, Mg, Na and Zn (0.5-5 mg metal L^{-1} for 0.5 µg $L^{-1}$of Ag) were selected. It is claimed that even if 10^3 to 10^4 fold matrix elements are presented in the water, the change in signal for Ag was of the order of 95-107% and they claimed that the atomic absorption signal for Ag absorbed on the tungsten wire appears to be unsusceptible to being affected by the matrix elements. Duan et al [34] reported over a range of concentration for interferences on silver. During its determination by CVG in the case of Ag and Au, interferences from iron were reduced by complexing with phosphoric acid (2% (v/v)) especially; Cu, Ni, and Co suppressed the signal.

1.6. Silver

Silver is known by the mankind since Pre-history, it was discovered after gold and copper about 4000 BC, when it was used in jewelry and as a medium of exchange. The earliest known workings of significant size were those of the Pre-Hittites of Cappadocia in eastern Anatolia.

The Egyptians considered gold to be a perfect metal, and gave it the symbol of a circle. Since silver was the closest to gold in perfection, it was given the symbol of a semi-circle. Later this semi-circle led to a growing moon symbol, probably due to the likeness between the shining metal and the moon glow. The Romans called silver, argentum, keeping this as the international name of the element, from where its chemical symbol derives.

The main silver mineral is the argentite (Ag_2S), which usually occurs associated to other sulfides as copper or lead sulfide. Other silver minerals are cerargirite ($AgCl$), proustite ($3Ag_2S.Ag_2S_3$), pirargirite ($3Ag_2S.Sb_2S_3$), stefanite ($5Ag_2S.Sb_2S_3$) and native silver. Silver occurs in most of the lead and copper ores, and associated to cobalt and gold arsenide. Most of the produced silver is a by-product of the extraction process of these metals. However, there are some mines especially devoted to the extraction of this element.

Silver is one of the most useful metals and has uses in decorative arts, industry and photography. It is the world's best conductor of electricity and heat and is used to make coins and bullion, jewelry silverware, photographic film. The typical concentration of silver used in coins is 90% with the other 10% being copper for added strength. Dentistry mixtures and electrical contacts use Silver alloys and photographic emulsions contain silver halides that are sensitive to light. Medical uses for silver include dentistry and surgical implants. Its malleability and conductive characteristics make it ideal for these purposes.

Silver is a non-toxic element, most forms of silver, such as those found in nature or used commercially, do not possess such irritant properties. However, most of its salts are poisonous due to the presence of its anions. These compounds are absorbed by the body and remain in the blood stream until they are deposited in the mucous membranes, forming a grayish film. However, there are some silver compounds, like the nitrate, with an antiseptic effect. Solutions of silver nitrate are used in treating irritations of mucous membranes in the mouth and throat. Generations ago, pioneers trekking across the Wild West in the US faced many hardships. Keeping safe drinking water was one of them. Bacteria, algae, etc., found a fertile breeding ground in wooden casks, which were carried by the wagons. They placed silver coins in the casks to retard the growth of the spoilage organisms. They also placed silver coins in their milk to keep it fresh. While silver has been used for centuries to purify water, modern ionization technology was developed by the National Aeronautic and Space Administration (NASA) in the early days of the space program as a lightweight method of purifying recycled water on spacecrafts [39, 40].

1.6.1. Determination of Silver

Direct determination of trace amount of silver samples can be determined by expensive analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and electro thermal atomic absorption spectrometry (ETAAS). Although FAAS is often accepted because of its speed and ease of operation, its sensitivity is not enough to meet the need in some cases. A method has been developed by Sun et al.[41] for the direct determination of trace silver in water samples using derivative atom trapping FAAS with modified water cooled stainless steel trapping equipment. For one min. collection, c_0 is 0.18 ng mL^{-1} and 3σ is 0.29 ng mL^{-1} [41]. In another pre-concentration study for silver, carried by Mao et al. [37], FAAS coupled FI on-line co precipitation pre-concentration using DDTC-copper as co precipitate carrier was studied [37]. The 3σ value is 0.6 ng mL^{-1} for 30s loading period. For the determination of silver in environmental samples, pre-concentration method involving adsorption on tungsten wire, followed by electro thermal AAS with tungsten tubing described by Rahman et al. [38] with the detection limit 5.0 ng L^{-1}. Recently, chemical vapour techniques are widely utilized for the trace element detection. Several attempts have been made to determine silver by vapour generation technique. First report on the generation and characterization of volatile species of Ag was studied Luna et al. [28]. In this study volatile species of Ag was generated at room temperature by the addition of sodium tetrahydroborate (III) to an acidified solution of the analyte and sent to electrically heated QTA. They have found the LOD is 33 ng and m_0 is 3.7 μ 0.2 ng with 8% RSD using peak height. Matousek and Sturgeon developed CVG procedure for the production of volatile species of Ag and studied using AAS and ICP-OES detection [42]. A characteristic mass of 0.12 ng was achieved by means of ICP-OES. Luna et al. [43] generate volatile species by the addition of sodium tetrahydroborate (III) to an acidified solution and rapidly send these species to the graphite tube; the detection limit was found 10 ng with the 10% RSD. In addition to these studies, Duan et al. [34] also investigate the CVG of silver and determined by ICP-AES together with ICP-MS. Detection limit was superior to nebulization for Ag that was 0.6 ng mL^{-1} for CVG and for nebulization it was 1.6 ng mL^{-1}.

1.6.2. Mechanistic Studies of Silver

Despite the published studies, very little is known about the nature and mechanism of production of volatile species except that in most cases they are relatively unstable and appear to be molecular in nature [44]. At present, there is no published proof of identity of the volatile metal species formed during CVG process. Sturgeon and Matousek worked on the mechanism in order to obtain a deeper insight into the process [42, 45]. According to the suggested mechanism for the production of volatile Ag species, most probably proceeds in two steps. The first step; formation of the volatile species or, more likely, their precursor, may correspond to the reduction of Ag^+ to Ag^0. This is a rather fast process. The second step, formation of the actual volatile species and / or its release from liquid phase, is much slower. According to Sturgeon and Matousek the volatilization of Ag from the liquid pool requires the presence of decomposing $NaBH_4$, either as the agent for further reduction, as a source of atomic (nascent) hydrogen, or simply as a source of very fine gas bubbles assisting release of the volatile compound. Panichev and Sturgeon [45] investigated the optical changes in the UV-visible region in solution during such reduction reactions has led to the observation of transient absorption spectra attributed to short-lived precursors of the metallic colloids. The temporal characteristics of these absorption transients appear consistent with the growth of larger clusters at the expense of smaller ones and may be generically described by sequences such as

$$Ag^+ + e_{aq}^- \rightarrow Ag^0 \qquad (4)$$

$$nAg + Ag^+ \rightarrow Ag_{n+1}^+ \qquad (5)$$

$$mAg \rightarrow Ag_m \qquad (6)$$

Finally, larger particles of metallic silver are formed:

$$nAg + mAg \rightarrow Ag_{n+m} \quad (n+m >> 10) \qquad (7)$$

1.7. Purpose of This Study

The main purpose of this work is chemical vapour generation of silver with AAS. To determine silver, hydride generation system with quartz tube atomizer will be employed. Optimizations for vapour generation system parameters such as the concentration of the acid, reducing agent flow rate that affect the sensitivity of silver determination will be carried out. Different types of gas-liquid separators will be studied.

The interference effects due to Ni, Co, Cu, Fe, Au, Se, Pb, As and Sn will be examined in CVG system.

Lastly, in order to check the accuracy of the system analyses of standard reference materials will be performed.

CHAPTER II

EXPERIMENTAL

2.1 Reagents and Chemicals

All reagents used were of analytical grade. Ag standard solutions were prepared by dilution of 1000 μg mL^{-1} stock solution (Spectrosol) with 3 M HNO_3 (Merck). The reductant, 0.5% (w/v) $NaBH_4$ (Merck) in 0.1% (w/v) NaOH (Carlo Erba Reagents), was prepared fresh daily or more frequently if required. For the interference studies, nine standard solutions were used. Among these, Ni, Co and Se were Plasma-Pure Leeman Abs, Inc. stock solutions (100 mg L^{-1}); Cu was Aldrich; Fe was Ultra Scientific; Au, As, and Sn were Spectrosol and Pb was Aldrich stock standard solutions (1000 mg L^{-1}). The solutions were diluted to a final volume using de-ionized water from a Milli-Q water system and solutions were stored in Dupont polyethylene containers. Glassware and plasticware were cleaned by soaking them in dilute nitric acid (1+9) for 24 hours and rinsing with distilled water before use.

2.2 Apparatus and Materials

25, 50, 100, 250, 500 mL DuPont polyethylene containers were used for the storage and preparation of the solutions. 5-50 µL, 25-250 µL and 100-1000 µL adjustable micropipettes (Transferpette, Treff Lab) with disposable polyethylene tips were used to dispense the reagents.

Quartz tubes were supplied form Quartz Scientific Inc., Fairport Harbour, Ohio. The quartz T-tube (QTA) used for hydride generation had an optical arm length of 145 mm and inlet arm length of 80 mm. The outer and inner diameters of the optical arm were 15 mm and 8 mm respectively and the outer and inner diameters of the inlet arm were 6 mm and 4 mm respectively. The quartz T-tubes used, were prepared in the glass shop of our chemistry department. The QTA was routinely cleaned using 1:5 diluted solution of HF. Transfer lines and connectors were made of polytetrafluoroethlene (PTFE) (Cole Parmer). A Milestone, model Ethos Plus oven was employed for microwave oven dissolutions.

2.3 Atomic Absorption Spectrophotometer

A Perkin Elmer Atomic Absorption Spectrophotometer, model 305B, equipped with a 10 cm air-acetylene burner was used with the hydride generation system. A Perkin Elmer Ag hollow cathode lamp was employed. Operating conditions were listed in Table 2.1

Table 2.1 Operating Conditions for Ag Hollow Cathode Lamp and Atomic Absorption Spectrophotometer

Wavelength	328.1 nm
Lamp Current	12 mA
Spectral Band pass	0.7 nm

The output was monitored using a Kipp&Zonen 7943 recorder; model TBAG-1230, operated at 10 mV range with a chart speed of 0.2 mm/sec. A Gilson Minipuls 3 peristaltic pump was employed for FI analysis. Rheodyne 6 way injection valve and Ismatec peristaltic pump tubings were used. Air was supplied by a Pye-Unicam 9003 air compressor. Air and acetylene flow rates were controlled by Perkin Elmer air and fuel regulator. Argon was used as a carrier gas and Cole Parmer gas flowmeter was used to adjust the flow of argon.

2.4 Gas-liquid Separator (GLS)

At the very beginning of this study; the U-shaped GLS as shown in Figure 2.1, was used. But then it was replaced by the cylindrical GLS shown in Figure 2.2, due to the problems that will be discussed in the result and discussion part of this study. U-shaped GLS and cylindrical GLS have approximately 6 mL and 2 mL solution volume capacities, respectively. Consequently U-shaped GLS has larger surface area than the cylindrical GLS. Larger volume GLS was discharged by the gravitational force; on the contrary, in order to discharge the smaller volume GLS a pump is needed. These GLS's were made of glass and fabricated by the Chemistry Glass Shop.

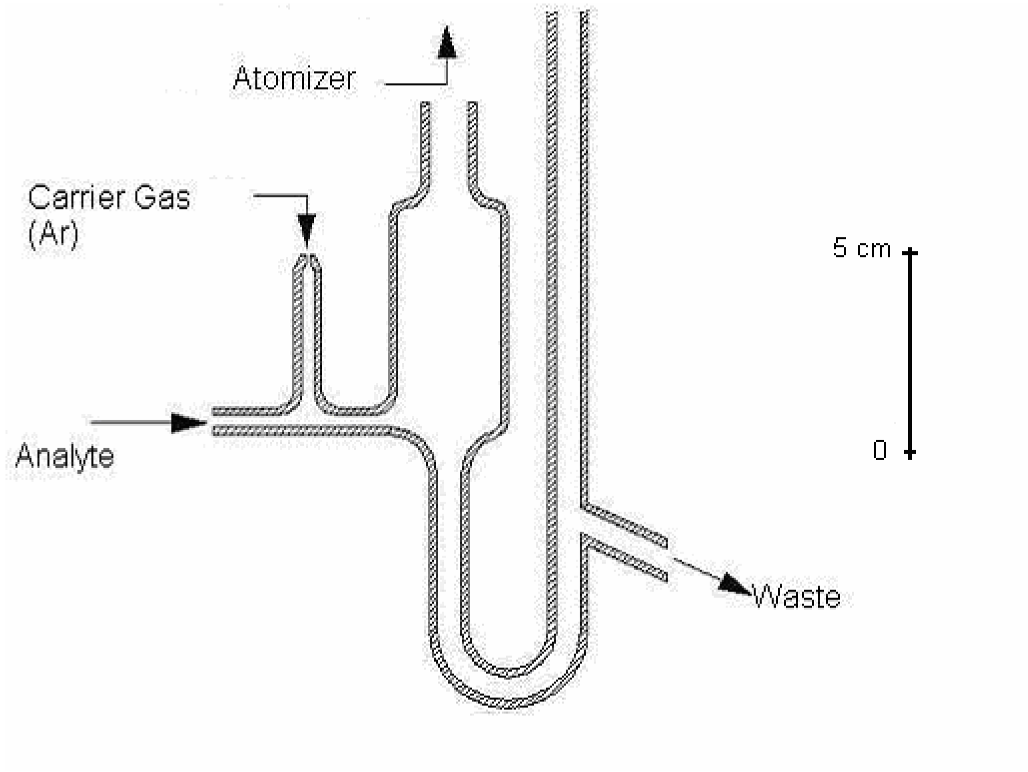

Figure 2.1 U-shaped Gas-Liquid Separator Design

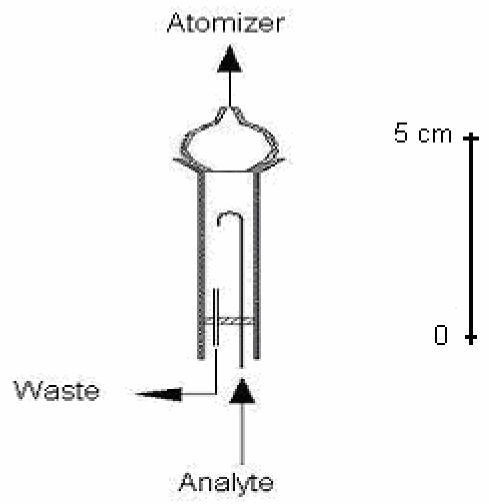

Figure 2.2 Cylindrical Gas- Liquid Separator Design

The generation of silver vapour was accomplished by pumping sodium tetrahydroborate solution and carrier acid, HNO_3 , solution into the reaction coil with Gilson Minipuls 3 pump (figure 2.3). Blue-yellow Tygon pump tubings with the outer diameter (o.d.) of 2.38 mm and inner diameter (i.d.) of 1.52 mm were used. The flow rates of both the reductant and carrier acid were 2.57 mL min^{-1}. For waste, purple-orange Tygon tubing having 2.54 mm i.d. was used. A six port valve used for the injection of fixed volume of sample solution that was introduced into the carrier stream. Argon was used as carrier gas at a flow rate of 85 mL min^{-1} through the system. The transfer lines were made of PTFE tubing having 0.8 mm i.d. Two tubings were inserted into the rubber septum which was placed 30 mm above the cylindrical GLS. One of the tubing was for the silver vapour and the other one was for the waste. The outlet of the GLS was connected to the QTA via 150 mm PTFE tubing 40 mm of which was placed into the inlet arm of the QTA. The flow injection vapour generation atomic absorption spectrometry (FI-VGAAS) is shown schematically in Figure 2.3.

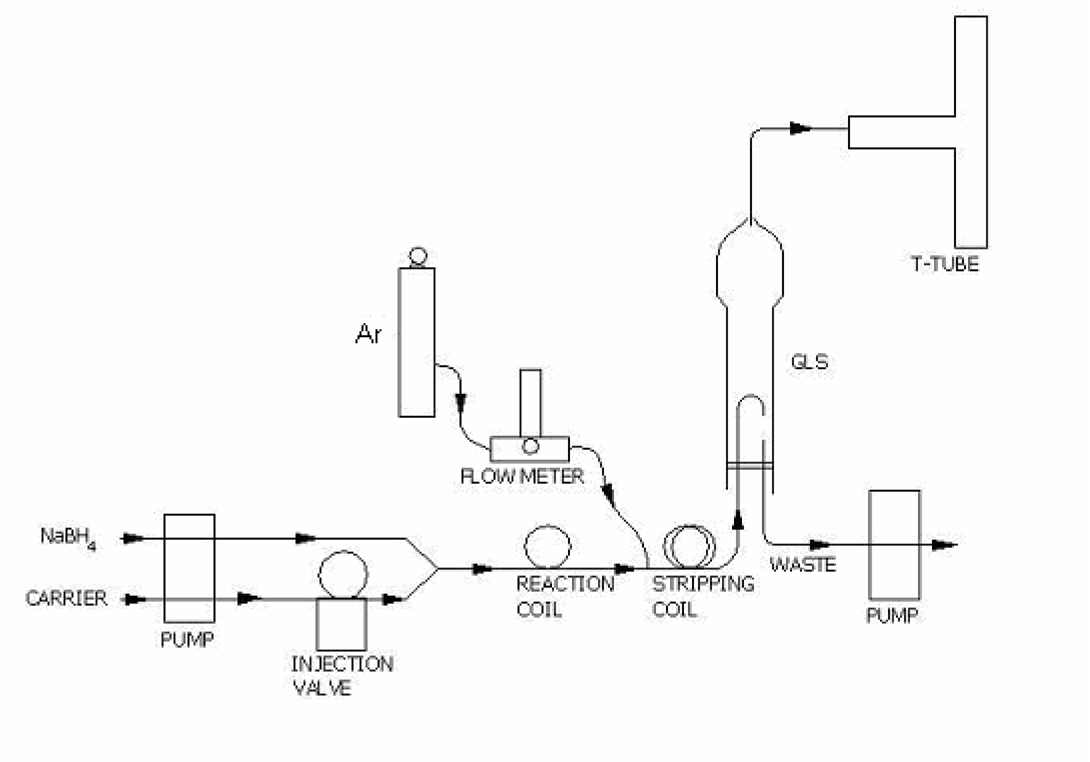

Figure 2.3 Schematic Diagram of the FI-VGAAS System.

2.5 Procedure

2.5.1 Pd Coating Procedure

First of all CVG system; reaction coil, stripping coil, GLS, T-tube; needs cleaning before coating with Pd. The CVG system was cleaned with 20% aqua regia passed through the system for 5 minutes and then the whole tubings and the GLS fulled with aqua regia and were left for another 5 minutes. Then, the system was rinsed with deionized water. Afterwards, 6 mL volume of a 20 mg L^{-1} solution of Pd was injected to the system using 1 mL injection loop six times.

2.5.2 Procedure for FI-CVGAAS

Under the optimized conditions, in order to generate chemical vapour of silver, 0.5% (w/v) $NaBH_4$ in 0.1% (w/v) NaOH was used as reductant and 3M HNO_3 was used as a carrier acid. Both reductant and carrier the acid solutions were pumped into the system at a flow rate of 2.57 mL min^{-1}. In case of FI experiments, 100 µL sample loop was used in order to merge the sample to the carrier acid stream. Then, the two streams were mixed along the 40 mm reaction coil; then argon flow of 85 mL min^{-1} was introduced to the system and the liquid-gas phase transport to the GLS was realized through the 250 mm stripping coil. The gas phase was sent to inlet arm of the QTA by 150 mm PTFE tubing.

2.6 Interferences

To investigate the interference effects of transition metal and hydride forming elements on CVG of silver; nickel, copper, cobalt, iron, gold, arsenic, tin, lead and selenium were studied. The effect of every interfering ion was observed by preparing standards with Ag/interferant mass ratios of 1:1, 1:10 and 1:100. The experiments are performed so that the signal for 1 mg L^{-1} Ag in 3 M HNO_3 was normalized to 100%.

2.7 Accuracy Check

To validate the accuracy of the proposed method, two standard reference materials from National Institute of Standard and Technology (NIST SRM 2710 and 2711, Montana Soil) were analyzed for their Ag contents.

For digestion; about 0.5 g of three replicates SRM's were weighed into PTFE vessels of microwave oven, 5.0 mL of concentrated HNO_3 and 2.0 mL of concentrated HF were added and program given in Table 2.2 was applied. The clear solution obtained after microwave treatment was placed on medium hot plate in PTFE vessels and the contents were vaporized for 3 hours until complete dryness. Then, the contents were diluted to 10 mL using 3M HNO_3.

Blank solutions were prepared by the same procedure. Standard addition method was employed for the analysis.

Table 2.2 Microwave Oven Program

Step	Time, min	Temperature, C^0	Power, W
1	10	150	500
2	5	200	500
3	35	200	500

CHAPTER III

RESULTS AND DISCUSSION

3.1 Optimization of Parameters for the Determination of Ag by CVG

To achieve the best detection limit, the conditions were optimized before determination. Sensitivity of CVG is influenced by parameters such as; flow rate of the carrier gas, reductant concentration, concentration of carrier acid, sample acidity, reaction coil length, stripping coil length and tubing between GLS and QTA. These parameters were optimized.

3.1.1. Carrier Gas Effects

Argon was chosen as the carrier gas used for the transportation of volatile silver species to the optical path. Besides transportation of species to the atomizer, argon enhances the separation of the resultant volatile species from the liquid phase. In addition, carrier gas makes sure that analyte and the reductant solutions are well mixed. The influence of carrier gas flow rate on the absorbance of the silver is shown in Figure 3.1. A maximum response was found at 85 mL min^{-1}.
With further increasing flow rate of the carrier gas signal was decreased, due to the dilution of the species in the observation volume.

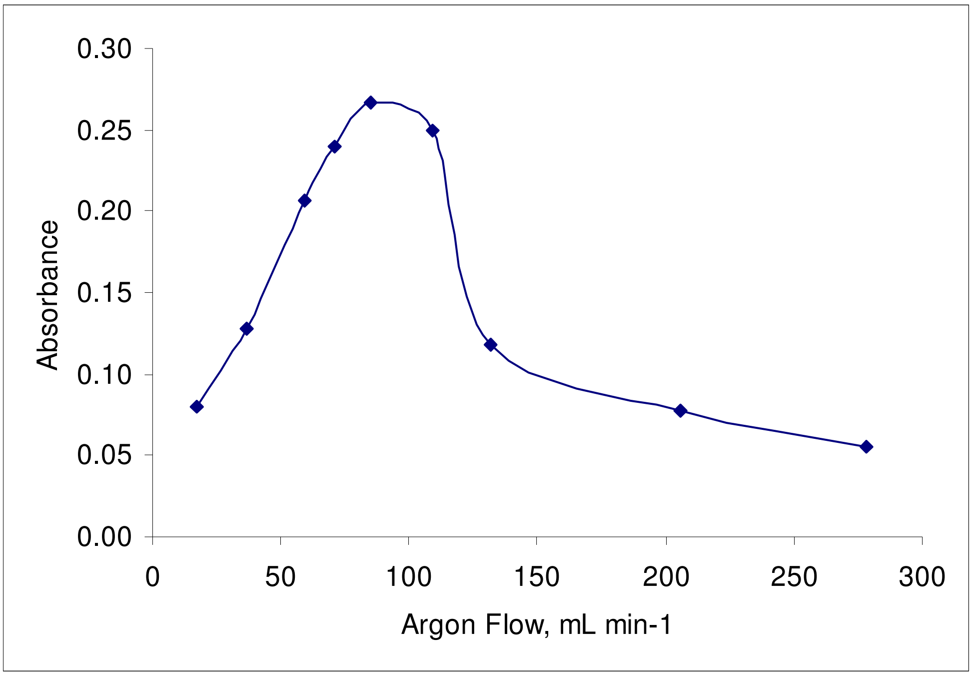

Figure 3.1 Effect of the Argon Flow Rate, using 0.2 mL of 1.0 mg L^{-1} Ag in 3.0 M HNO_3, 0.5% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, carrier acid 1.5 M HNO_3, reaction coil 4.0 cm, stripping coil 25.0 cm.

3.1.2 Reductant Effects

In the determination of Ag with CVG, the concentration of the employed $NaBH_4$ was a very important factor. In order to find the optimum value $NaBH_4$ concentration was varied between 0.25 to 2% (w/v) [8]. As it is shown in Figure 3.2, the optimum concentration of $NaBH_4$ was found to be 0.5% (w/v). According to the observed data, less than 0.25% (w/v) $NaBH_4$ consumption was not enough to generate volatile silver species. The decrease in the absorbance values may be due to the inadequate hydrogen. On the contrary, increasing the concentration of tetrahydroborate (III) resulted in broadened and noisy peaks. Bubble generation was also increased so droplets entered into atomization transfer line. Similar problems were reported elsewhere [28, 30 and 42]. The range of 0.05-2.0% (m/v) of NaOH or KOH is sufficient for stabilization [8]. Therefore, in this study NaOH concentration was chosen as 0.1% (w/v).

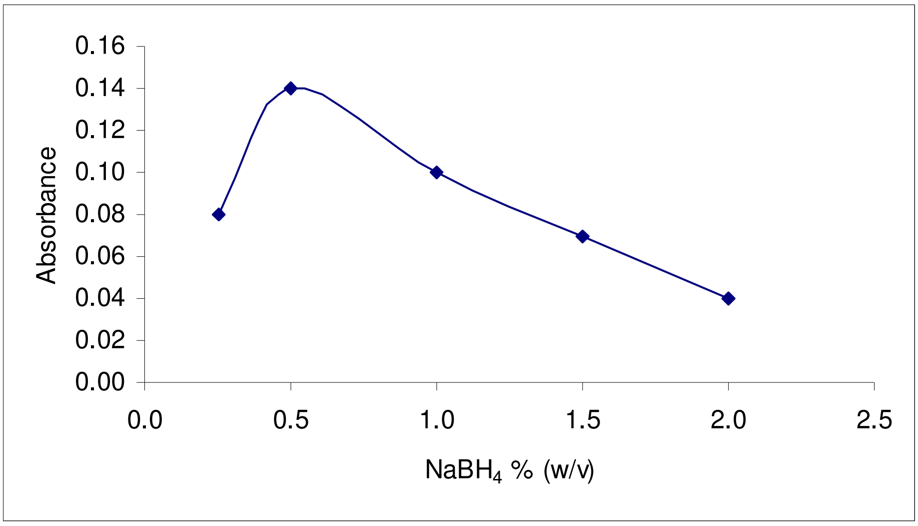

Figure 3.2 Effect of $NaBH_4$ Concentration, using 0.1 mL of 1.0 mg L^{-1} Ag in 3.0 M HNO_3, argon flow 85 mL min^{-1}, carrier acid 1.5 M HNO_3, reaction coil 4.0 cm, stripping coil 25.0 cm.

3.1.3 Effect of Nature of Acid and Its Concentration

The efficiency of the generation of the chemical vapour is dependent on the nature of the acid and acidity. Firstly, hydrochloric acid was used in this study; but later on, nitric acid was employed. In literature, both HCl and HNO_3 were used for the determination of silver. Luna et al. [28] studied both types of acid and figured out that there is no sensitivity difference for the silver signal but chose HNO_3 for his study as the many other researchers also did [38, 42 and 46].

In this study HCl and HNO_3 were examined. Some troubles were encountered due to the HCl usage. While studying with HCl, signal increased gradually, the peaks were getting broader and did not turn to the baseline. The peak shapes for HCl and HNO_3 are shown in Figure 3.3 and Figure 3.4, respectively. These problems may be due to the precipitation of Ag^+ and Cl^- as AgCl. At high concentration of HCl a white cloud could be seen. Because of these problems, the studies were continued with HNO_3. Besides, the cylindrical-GLS was chosen rather than the U-shaped GLS, so the surface area and the transfer time were minimized. With these choices the problems mentioned were eliminated.

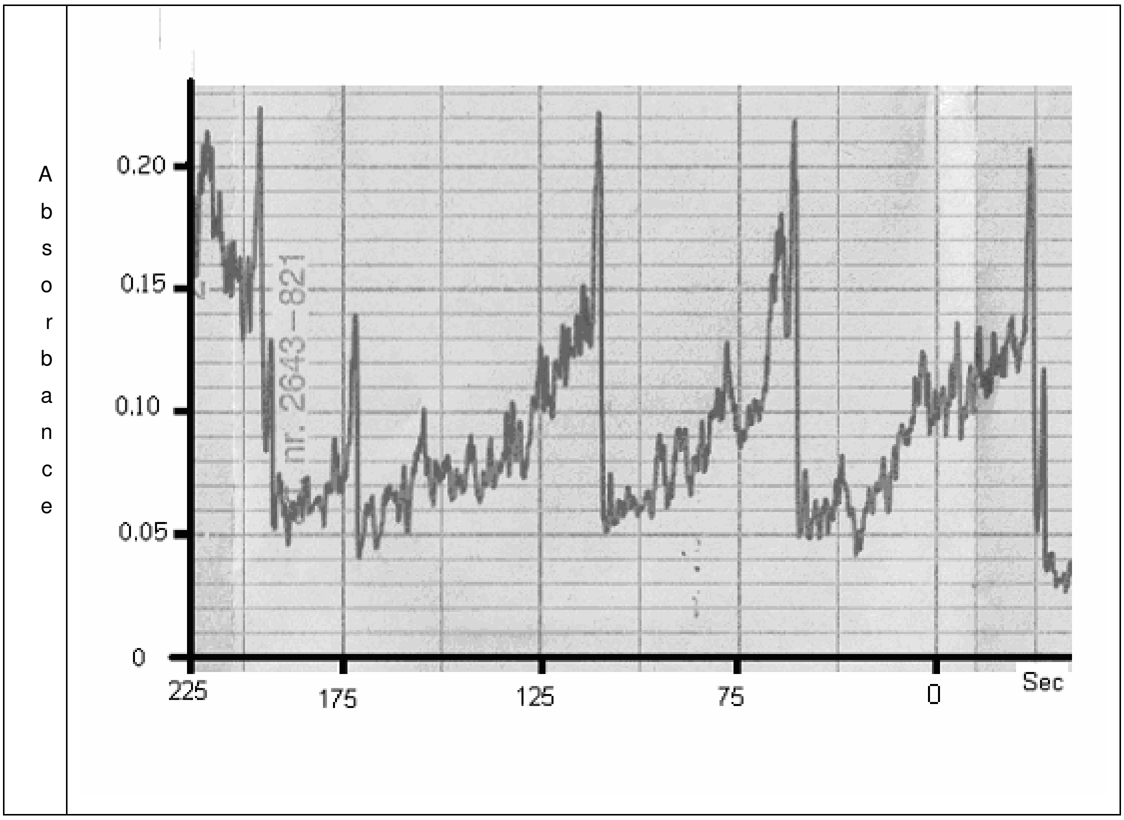

Figure 3.3 Transient Signal of Ag using 1.0 M HCl as a carrier acid with U-shaped GLS, for 0.1 mL of 1.0 mg L^{-1} Ag in 0.6 M HCl, 0.8% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 357 mL min^{-1}.

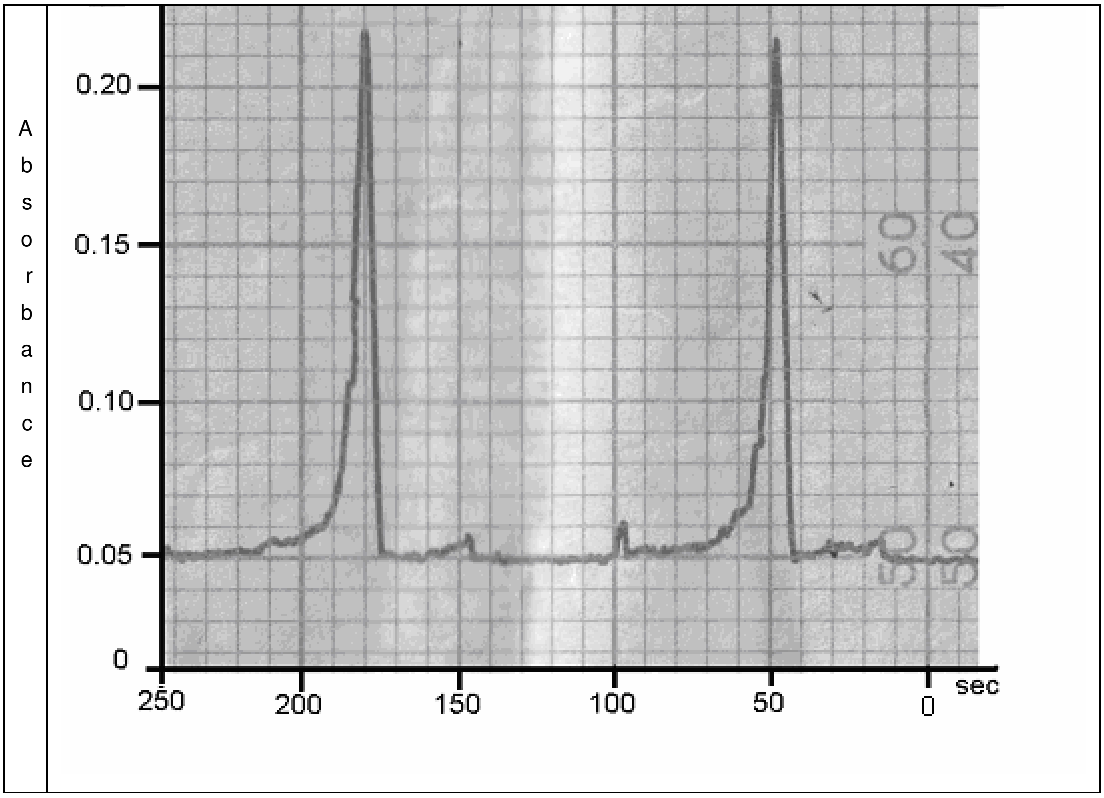

Figure 3.4 Transient Signal of Ag using 1.0 M HNO_3 as a carrier acid with U-shaped GLS, for 0.1 mL of 1.0 mg L^{-1} Ag in 0.6 M HNO_3, 0.8% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 357 mL min^{-1}.

In order to select the optimum acid concentration, in a range of 0.5 to 8.0 M HNO_3, signals were measured. It can be seen from the Figure 3.5 that the best concentration for carrier acid was around 3.0 M HNO_3 which was chosen as the best value. In Figure 3.6 effect of sample acidity concentration is shown. Although when the sample acidity was around 5.0 M HNO_3, measurements were more sensitive. However due to the degraded reproducibility and economical reasons, 3.0 M HNO_3 was chosen for the sample acidity. Besides, the double peaks occurred if the HNO_3 concentrations were not same for carrier and sample solutions. Acid concentrations below the optimum value leads to lower sensitivity.

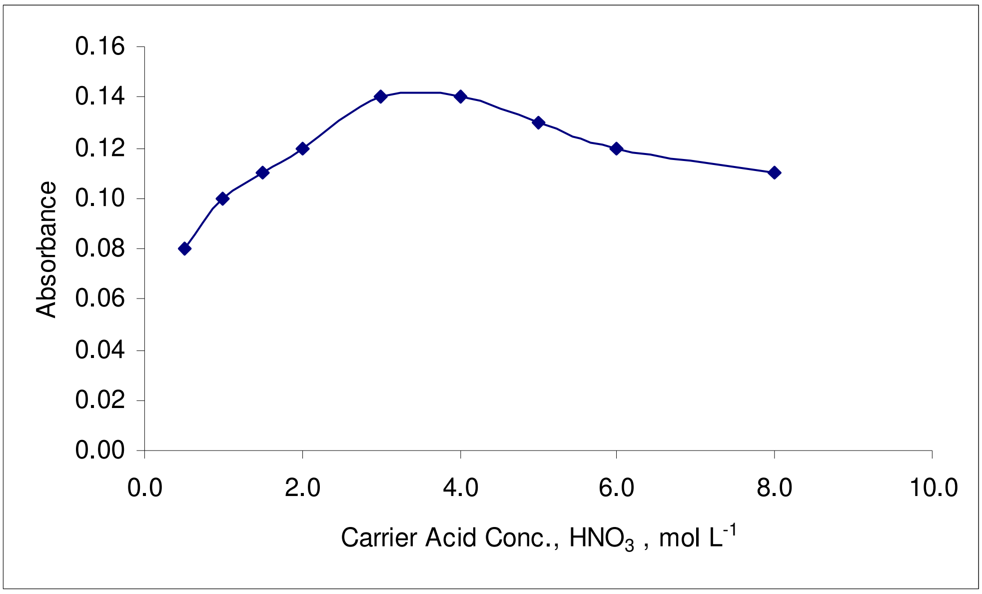

Figure 3.5 Effect of Carrier Acid, HNO_3, using 0.1 mL of 1.0 mg L^{-1} Ag in 3.0 M HNO_3, 0.5% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 85 mL min^{-1}, reaction coil 4.0 cm, stripping coil 25.0 cm.

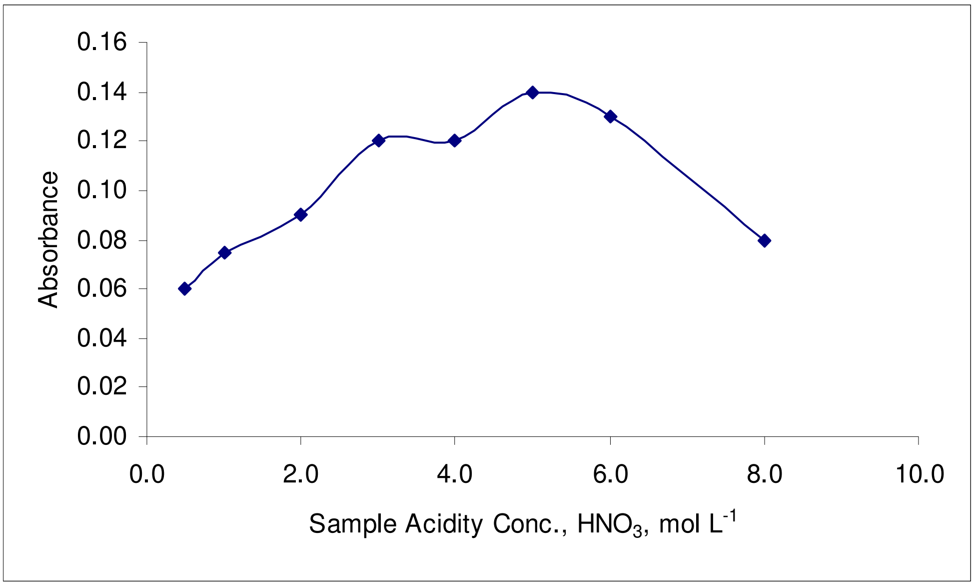

Figure 3.6 Effect of Sample Solution Acidity, HNO_3, using carrier acid 3.0 M HNO_3, 0.5% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 85 mL min^{-1}, reaction coil 4.0 cm, stripping coil 25.0 cm.

3.1.4 Effect of Transfer Tubing

The generated volatile silver species transported to the T-tube with PTFE tubings. Obviously the transfer tube diameter and the surface quality play an important role in the sensitivity. At the beginning of the experiments, low sensitivity was observed while the sensitivity increased with time. Inner wall of the reaction coil and the stripping coil were getting blacker while the signal was getting bigger. This may be due to the loss of analyte to walls of the transfer lines by adsorption. After the system was coated with the analyte by itself, the signal sensitivity and reproducibility increased. When the system was cleaned, the signal was dropped and showed the same behavior as above as the time passes. It is better to use the tubings as short as possible to keep the volume minimum and to minimize the transportation loss. In the same manner small volume GLS was chosen. The analyte species should be transferred in a short time and through a minimum length.

Length of reaction and stripping coil were investigated. The results are shown in Figure 3.7 and Figure 3.8, respectively.

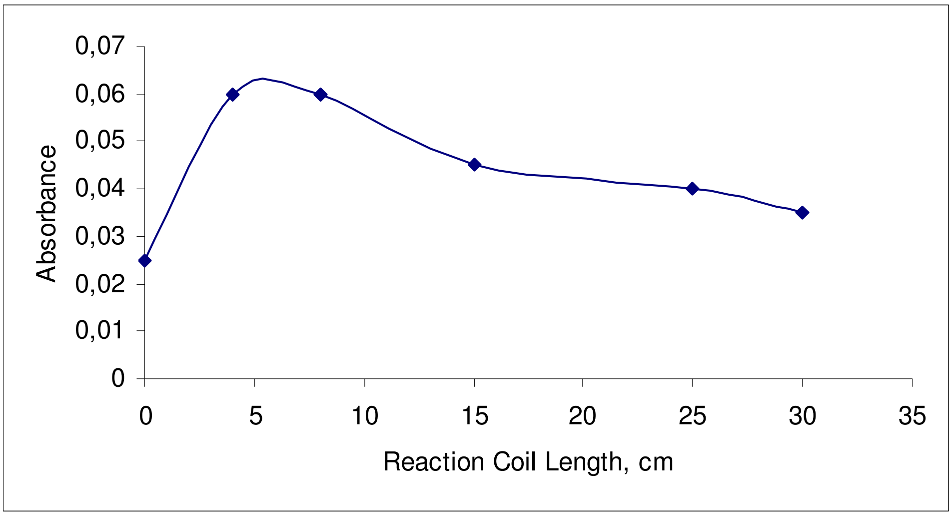

Figure 3.7 Effect of Reaction Coil Length, using 0.1 mL of 1.0 mg L^{-1} Ag in 1.5 M HNO_3, carrier acid 1.5M HNO_3, 1.0% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 76 ml min^{-1}, stripping coil 35.0 cm.

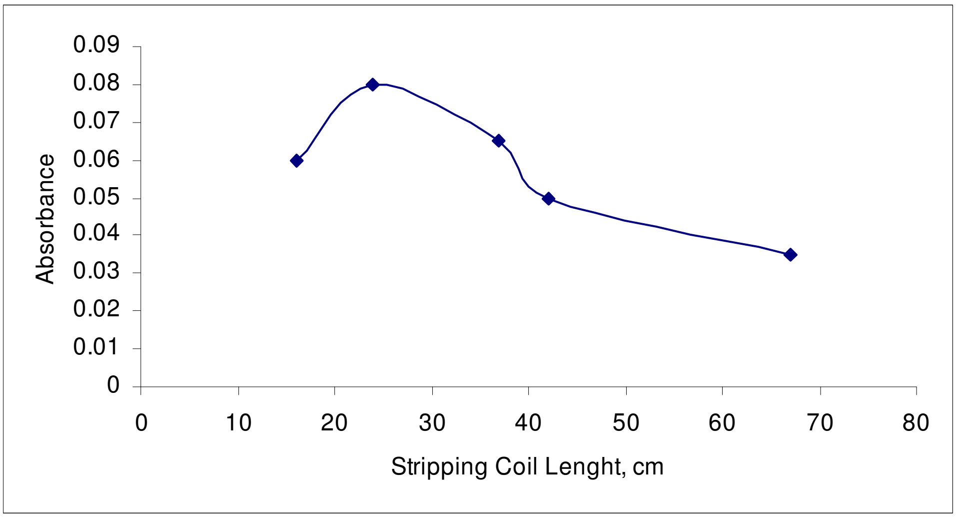

Figure 3.8 Effect of Stripping Coil Length, using 0.1 mL of 1.0 mg L^{-1} Ag in 1.5 M HNO_3, carrier acid 1.5 M HNO_3, 1.0% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 76 mL min^{-1}, reaction coil 4.0 cm.

Decreasing the reaction coil length below the optimum value may lead to incomplete reaction between the pumped solutions but on the other hand the longer transfer line may allow decomposition.

3.1.5 Effect of Type and Length of Tubing between GLS and QTA

Both Tygon and PTFE tubing of the same length were examined. No significant changes on Ag signal were observed. Because the minimum volume is better from transportation loss point of view, PTFE tubing was chosen, and the optimum length was chosen to be 15 cm.

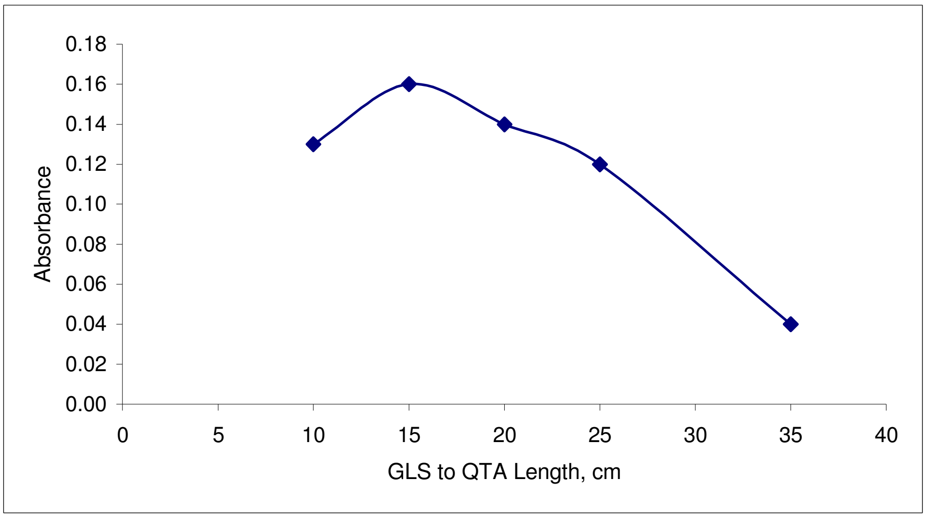

Figure 3.9 Effect of Tubing Length between GLS and QTA on Ag Signal; using 0.1 mL of 1.0 mg L^{-1} Ag in 3.0 M HNO_3, carrier acid 3.0 M HNO_3, 0.5% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 85 mL min^{-1}, reaction coil 4.0 cm, stripping coil 25.0 cm.

3.2 Sample Volume

Sample size for optimum signal was investigated and as it is expected; first the signal increased up to a certain volume than it behave as a continuous signal. For the best line equation 0.2 mL was chosen. In the optimization studies generally 0.1 mL sample volume was chosen in order not to contaminate the system quickly and also to reduce the analyte consumptions.

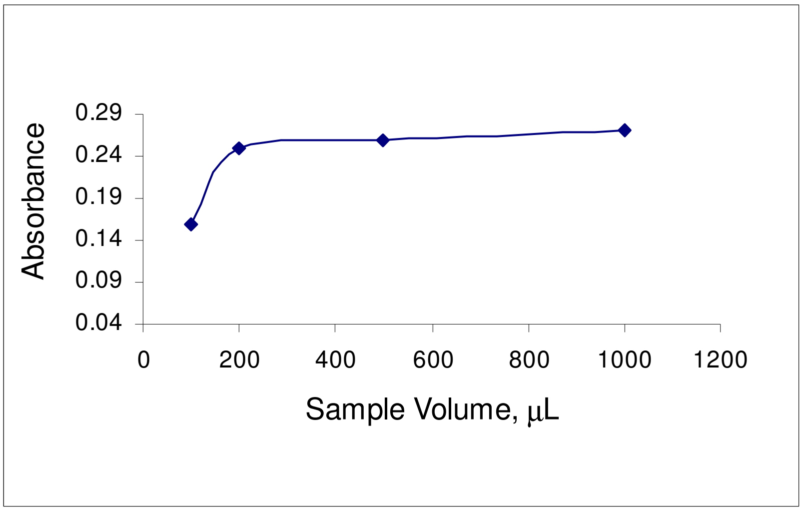

Figure 3.10 Variation of Ag Signal, with sample volumes for 1.0 mg L^{-1} Ag in 3.0 M HNO_3; using carrier acid 3.0 M HNO_3, 0.5% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 85 mL min^{-1}, reaction coil 4.0 cm, stripping coil 25.0 cm.

As a brief summary, the optimum parameters for CVG-AAS are shown in Table 3.1.

Table 3.1 The optimum parameters for CVG-AAS, 0.200 mL sample volume and 1.0 mg L^{-1} Ag

Parameter	**Optimum Value**
Argon Flow Rate	85 mL min^{-1}
$NaBH_4$ Concentration	0.5% (w/v)
Carrier HNO_3 Concentration	3.0 M
Sample HNO_3 Concentration	3.0 M
Reaction Coil Length	4.0 cm
Stripping Coil Length	25.0 cm
Length of tubing, GLS-QTA	15.0 cm

3.3 Diethyldithiocarbomate (DDTC)

Ertaş G. [47] searched the effect of DDTC to enhance the sensitivity in her study during Au determination by CVG; higher sensitivity was obtained with 1.0M HNO_3 solution containing $6x10^{-4}$ % (m/v) DDTC for in situ trapping of gold in graphite tube. Since the Au and Ag are in the same group, we thought that DDTC may increase the signal of Ag but this was not the case. $6x10^{-4}$, $6x10^{-3}$, $6x10^{-2}$ % DDTC were tested but no sensitivity increase was obtained.

3.4 Pd as Permanent Modifier

Permanent modification of the surface of a continuous flow Fsystem by reduced metals was studied for CVG of silver by Matousek and Sturgeon [48]. They have found both nickel and palladium were effective, but only palladium had sufficient stability and chemical resistance for routine use. A significant drift in sensitivity problem was noted in CVG of silver and accumulation of Ag deposited on the surface was noted.

In this study it was observed that when the CVG system was freshly cleaned the sensitivity was low and the peaks were broad as it is shown in Figure 3.11. Then the Ag signal slowly increased about 2 times after coating with Pd, with 6.0 mL 20.0 mg L^{-1} Pd solution; the signals are shown in Figure 3.12. After coating with Pd, 7.0 mL of 1.0 mg L^{-1} Ag in 3.0M HNO_3 was passed through the coated system; as a result of this treatment, 3.5 times sensitivity enhancement was observed, the signals are shown in Figure 3.13. If none of these treatment were applied, however, within time, the system accumulated a coating itself and reached the same absorbance signal with the coated one. But it takes longer time and the reproducibility was not as good as the Pd coated system. After coating with Pd, for 200 injections there was no shift in the signal; percent relative standard deviation was 1.5%.

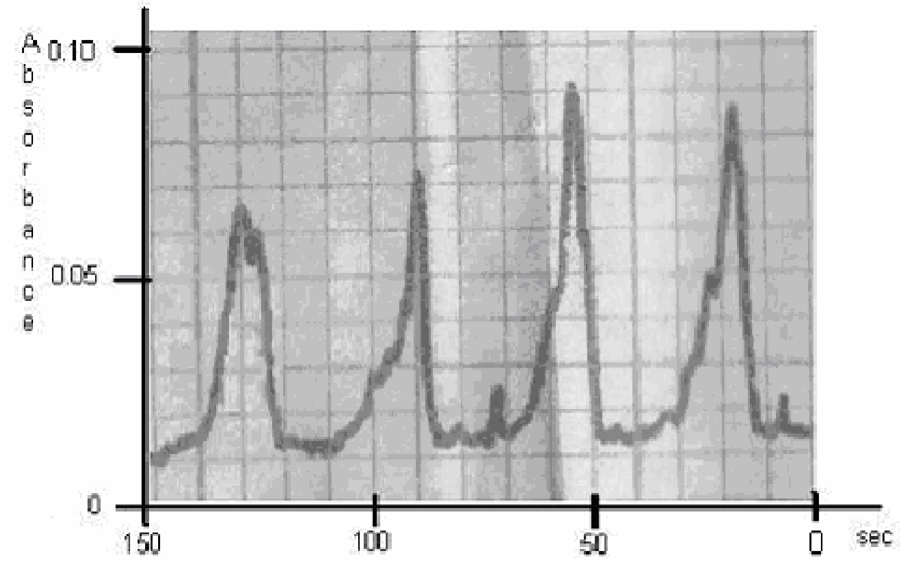

Figure 3.11 Transient Signals of Freshly Cleaned CVG –AAS System; using 0,1 mL of 1.0 mg L^{-1} Ag in 3.0 M HNO_3, carrier acid 3.0 M HNO_3, 0.5% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 85 mL min^{-1}, reaction coil 4.0 cm, stripping coil 25.0 cm.

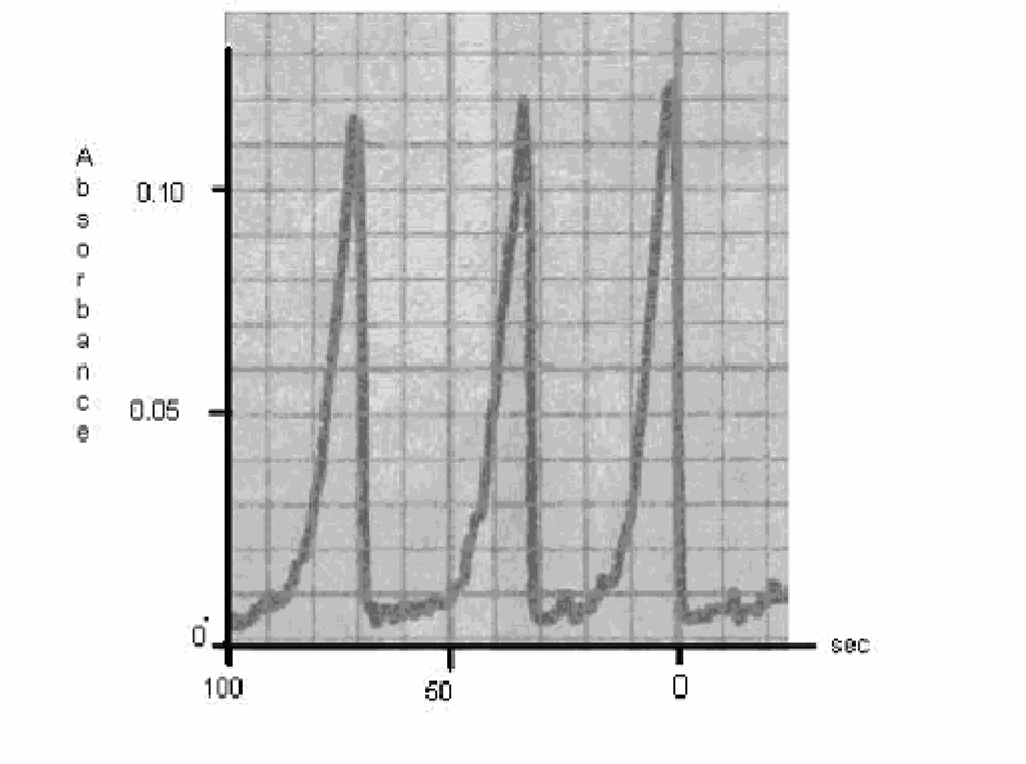

Figure 3.12 Transient Signal of CVG –AAS System Coated with 6.0 mL of 20.0 mg L^{-1} Pd; using 0.1 mL of 1.0 mg L^{-1} Ag in 3.0 M HNO_3, carrier acid 3.0 M HNO_3, 0.5% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 85 mL min^{-1}, reaction coil 4.0 cm, stripping coil 25.0 cm.

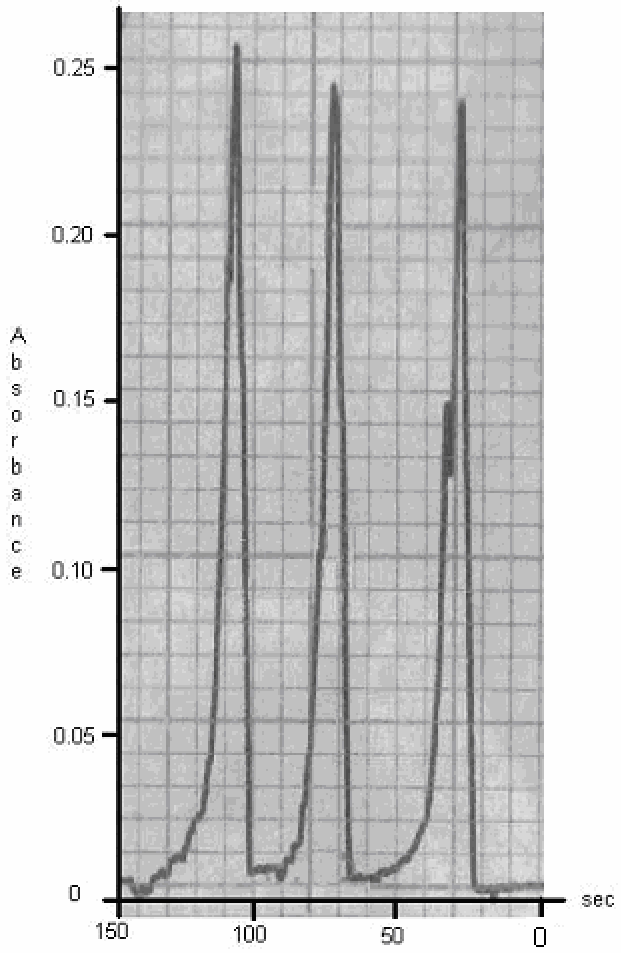

Figure 3.13 Transient Signal of CVG –AAS System Coated with 6.0 mL of 20.0 mg L^{-1} Pd and then 7.0 mL of 1.0 mg L^{-1} Ag were passed through the system; using 0.1 mL of 1 mg L^{-1} Ag in 3.0 M HNO_3, carrier acid 3.0 M HNO_3, 0.5% (w/v) $NaBH_4$ in 0,1% (w/v) NaOH, argon flow 85 mL min^{-1}, volume 0.1 mL, reaction coil 4.0 cm, stripping coil 25.0 cm.

3.5 Interference Studies

Interference studies for Ni(II) (2% nitric acid), Co(II) (2% nitric acid), Cu(II) (1% nitric acid), Fe(III) (2% nitric acid), Au(III) (gold chloride), As(III) (arsenic trichloride), Pb(II) (2% nitric acid), Se(IV) (selenous acid) and Sn(II) (8% hydrochloric acid) were carried out using chemical vapour generation atomic absorption spectrometry. The absorbance signal of pure analyte was normalized to 100 and the absorbance signal for the analyte and the interferent solutions were calculated relatively.

Standard concentrations of 1 mg L^{-1} Ag in 3.0 M HNO_3 were used for the experiments the interferent concentrations were 1, 10 and 100 folds of the Ag concentration using a weight ratio. The graphical representation of interference of Ni(II), Co(II), Cu(II), Fe(III), Au(III), As(III), Pb(II), Se(IV) and Sn(II) on the absorbance signal was shown. It can be seen from the Figure 3.14 that the presence of 1 fold of nickel decrease the signal by 3.5%, in the case of 10 and 100 folds of nickel, the signal was decreased by 18%. In the presence of copper the decrease of the signal was more than nickel as interferant. The signals decreased by 16, 47 and 87% for the 1, 10 and 100 folds of silver, respectively; as shown in Figure 3.15. In the case of cobalt, there were no changes in the absorbance signal for the ratio of 1. As shown in Figure 3.16, the absorbance signal was depressed by 22 and 11% for 10 and 100 folds of cobalt, respectively. Iron has positive effect on the signal. While 10 folds of iron did not change the signal, 1 and 100 folds of iron increased the signal by 8 and 31 %, respectively as shown in Figure 3.17. Gold had a more drastic effect; it suppressed the signal to 15, 7, and 17% of the pure analyte signal as shown in Figure 3.18. As had also an abrupt decreasing effect. For 1, 10 and 100 folds of arsenic, the signal decreased to 12, 8 and 54% respectively as shown in Figure 3.19. Lead first increased than suppressed the signal. 1 and 10 folds of Lead increased the signal by 20, 3%; while signal was decreased by 21% for the concentration of 100 folds; this is shown in Figure 3.20. In the case of selenium, the signal gradually decreased by 12, 42, and 89% as shown in Figure 3.21. Regarding increasing Sn concentrations, it first suppressed analyte signal, and then it gave an increasing rise to the signal. The percentages of decrease in the signal were 89 and 74% for 1 and 10 folds and it gave rise 19% for 100 folds of tin these are shown in Figure 3.22. In order to lessen the interferences method of standard additions may be used in case the signal of analyte was not reduced much due to the interference. The other generally applicable method is to dilute the sample if it is applicable. The effects of interferences are summarized in Table 3.2

Table 3.2 Effect of Interferences of Various Elements on the CVGAAS of Ag.

Interferant /Ag (w/w) Elements	1	10	100
Ni(II)	96	82	82
Cu(II)	87	53	13
Co(II)	100	78	89
Fe(III)	108	100	130
Au(III)	15	7	17
As(III)	12	8	54
Pb(II)	119	103	89
Se(IV)	88	57	11
Sn(II)	11	26	118

Numbers represent percent values of the Ag signal, without interferant.

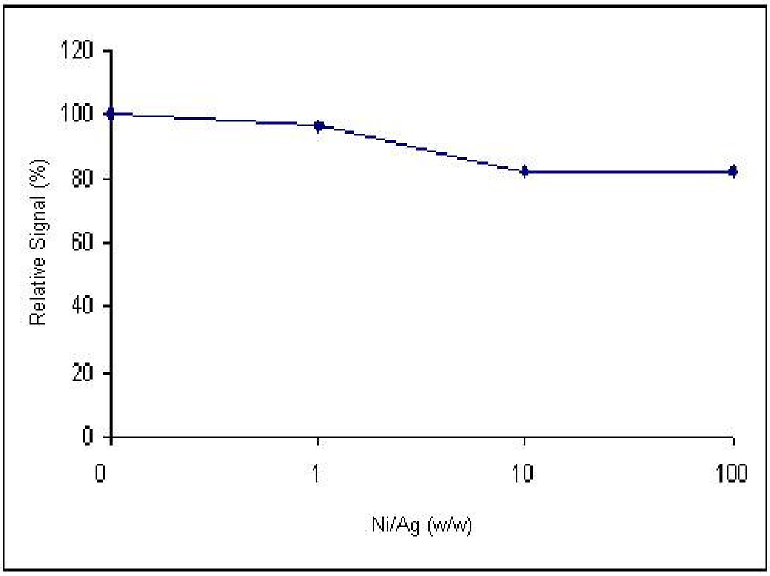

Figure 3.14 Interference of Nickel on Ag CVG Signal

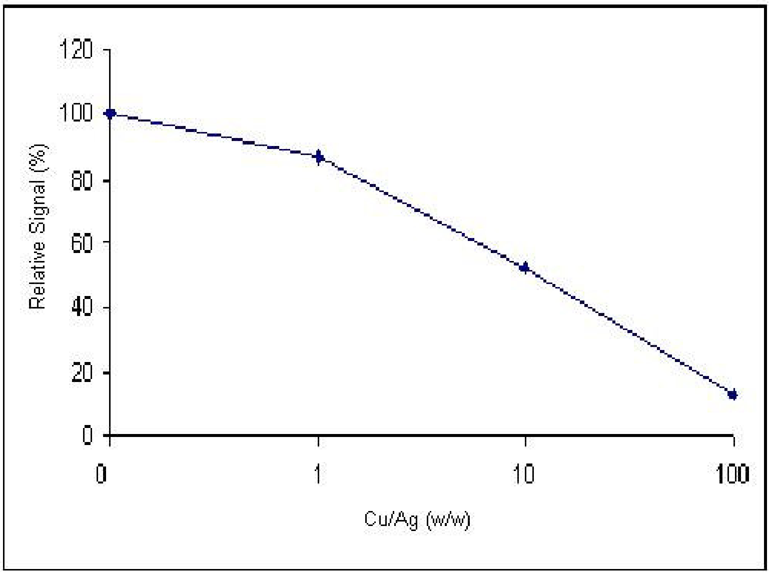

Figure 3.15 Interference of Copper on Ag CVG Signal

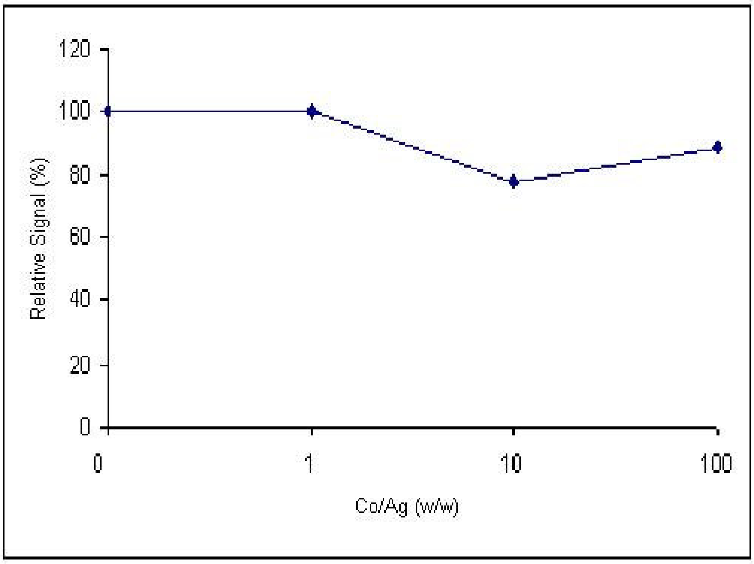

Figure 3.16 Interference of Cobalt on Ag CVG Signal

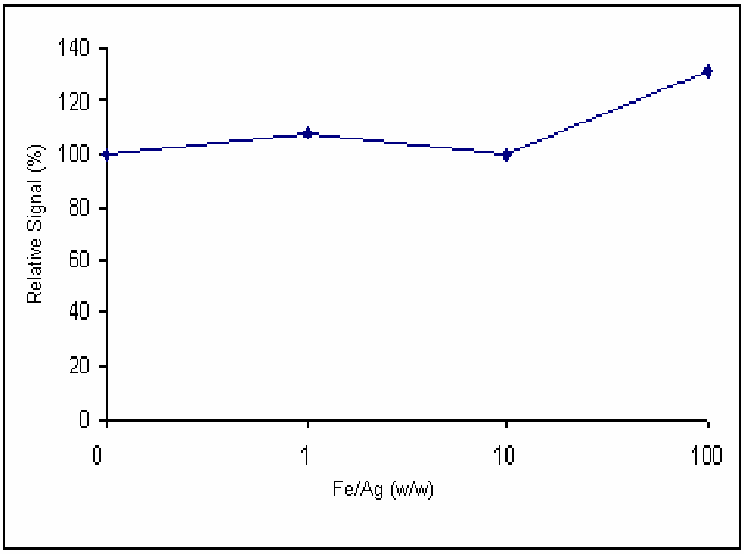

Figure 3.17 Interference of Iron on Ag CVG Signal

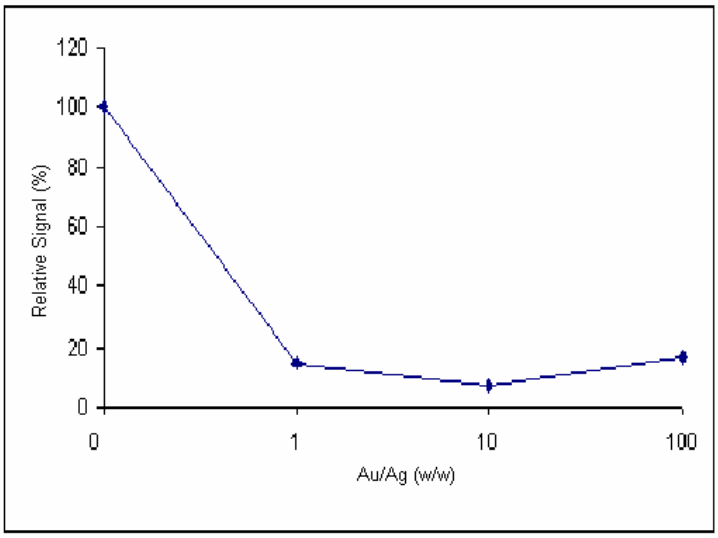

Figure 3.18 Interference of Gold on Ag CVG Signal

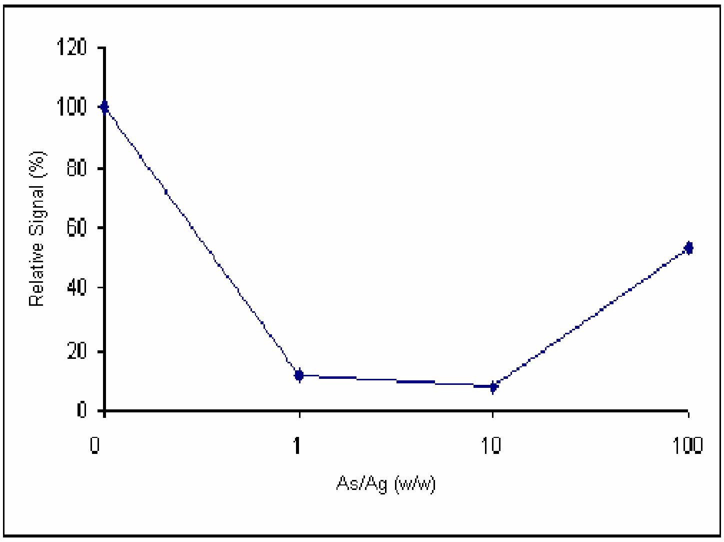

Figure 3.19 Interference of Arsenic on Ag CVG Signal

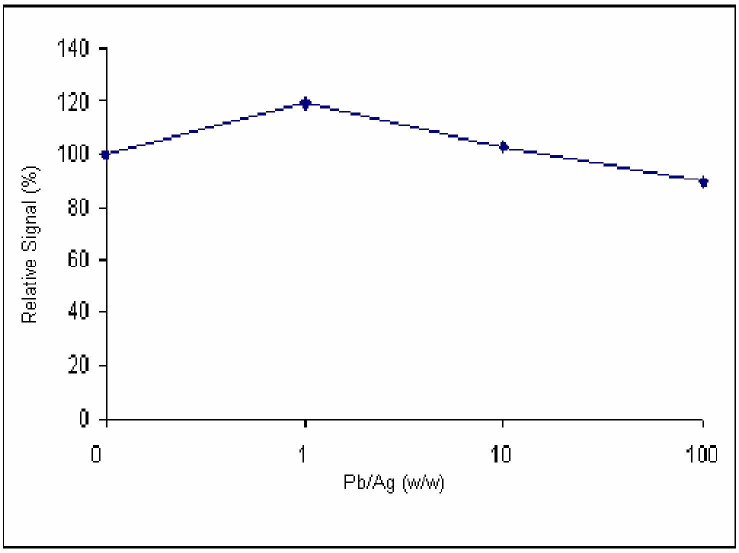

Figure 3.20 Interference of Lead on Ag CVG Signal

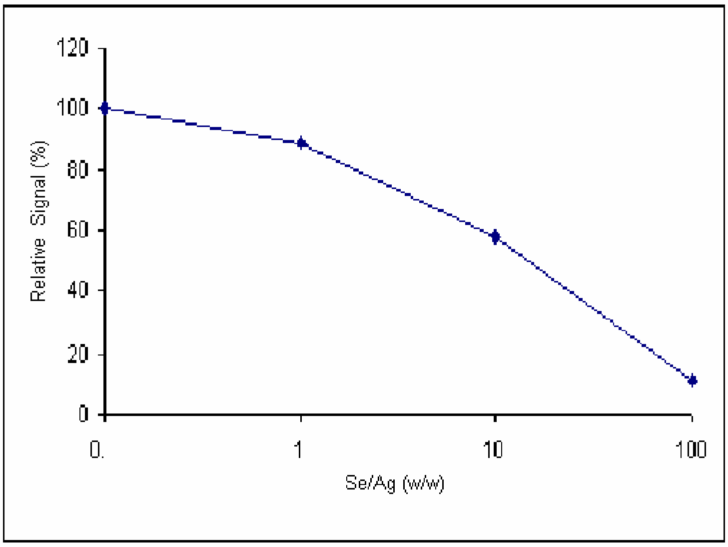

Figure 3.21 Interference of Selenium on Ag CVG Signal

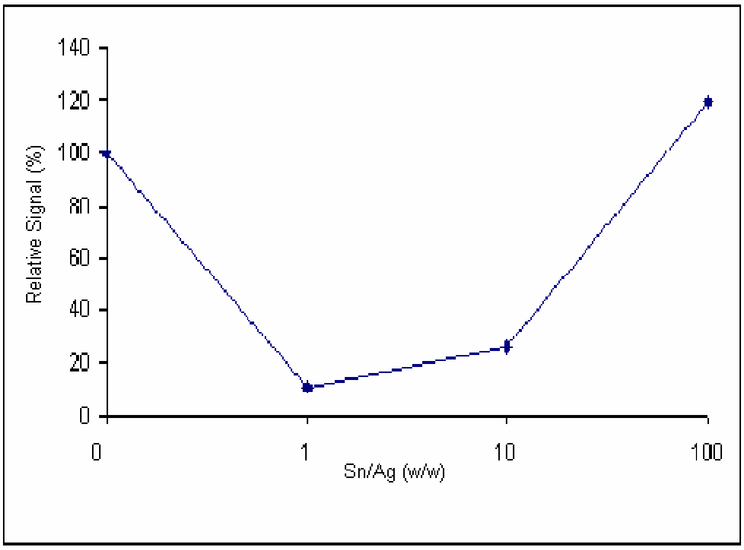

Figure 3.22 Interference of Tin on Ag CVG Signal

3.6 Analytical Figures of Merit

Under the optimum conditions the calibration plot was drawn for Ag. The calibration plot for chemical vapour generation with QTA-AAS, as shown in Figure 3.23 was linear up to 1.3 mg L^{-1} with the best line equation and coefficient of multiple correlation of $y=0.3368x+0.004$ and 0.9960 respectively. The relative standard deviation was 3.5 %. The detection limit was 7.5 ng mL^{-1} (n=11) using 0.2 mL sample volume. The characteristic concentration (C_o) for 1 mg mL^{-1} Ag was found to be 12.9 ng mL^{-1}.

The calibration plot for FAAS was shown in Figure 3.24. Relative standard deviation was 0.4 % and the C_o was 72.3 ng mL^{-1}. With the CVG 5.6 fold higher sensitivity was achieved compared with FAAS.

A comparison between this study and the others from the literature were shown in Table 3.3. Regarding LOD values in terms of mass, the result obtained in this study is competitive as compared to others using AAS even when a furnace atomizer was used. W-wire ETAAS results are comparable to the one obtained in this study. On the other hand, as compared to systems using ICP-OES, the system used in this study provided less sensitive results. The advantage of preconcentration methods, expectedly make these systems more sensitive than the one used in this study. It should not be forgotten, however, that the system used here has the advantages of lower cost and simplicity as compared to ICP-OES and preconcentration systems.

Table 3.3 Comparison of Results for Ag with Different Systems

Atomization Mode	**LOD, conc.**	**LOD, mass**	**C_o**	**m_o**	**Reference**
FAAS (discrete)	22 ng mL^{-1}	4.4 ng	72.3 ng mL^{-1}	15 ng	This Study
On-line coprecipitation with DDTC-Cu(II) by FAAS	0.6 ng L^{-1}				37
Preconcetration using DDTC by FAAS	0.29 ng mL^{-1}		0.18 ng mL^{-1}		41
CVG with QTA-AAS		33 ng		3.7 ng	27
CVG with QTA-AAS	7.5 ng mL^{-1}	1.5 ng	12.9 ng mL^{-1}	2.5 ng	This Study
W wire ETAAS	5.0 ng L^{-1}				38
CVG-ETAAS	1 mg L^{-1}	10 ng			43
Nebulization by ICP-OES	1.6 ng mL^{-1}				34
CVG with ICP-OES	0.6 ng mL^{-1}				34
CVG with ICPOES		0.12 ng			42

3.7 Comparison between CVGAAS and FAAS

Evaluation of CVGAAS and FAAS in terms of their linear range, limit of detection (LOD) and reciprocal sensitivity was explored.

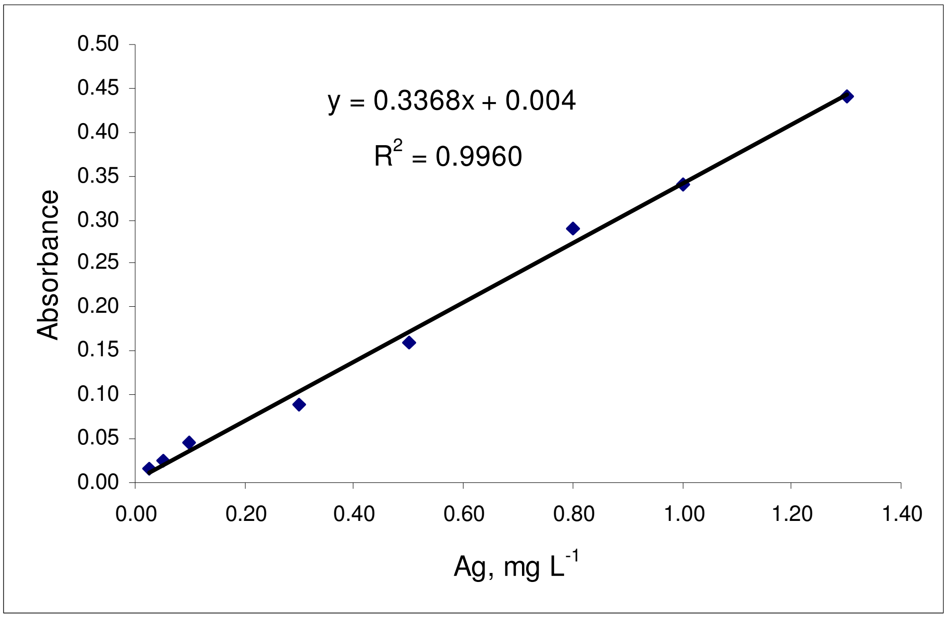

Figure 3.23 Calibration Graph for Ag Determination by CVG-FIAAS.

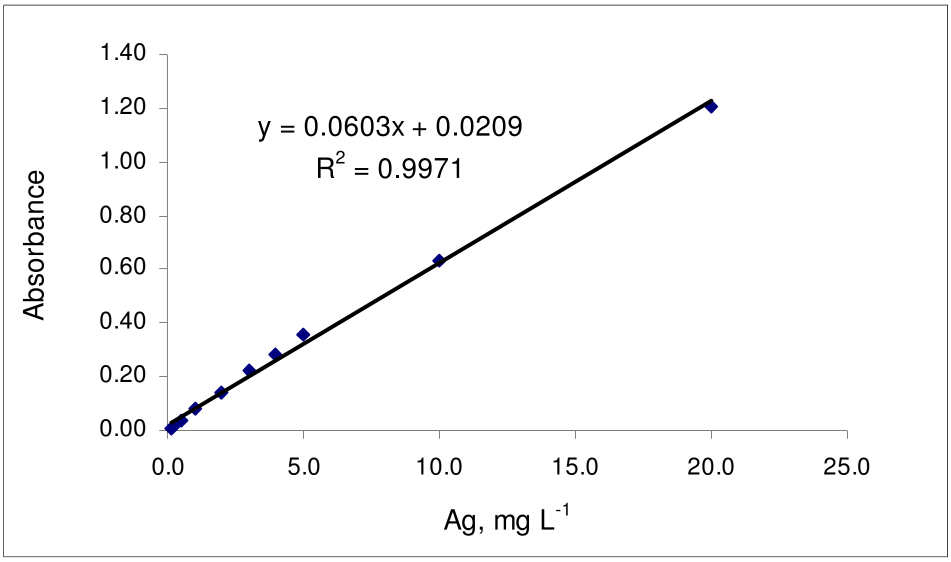

Figure 3.24 Calibration Graph for Ag Determination by FAAS.

In both techniques, sample volumes were 0.200 mL.

Table 3.4 Comparison of CVG and FAAS

	CVGAAS	FAAS
Linear Range	0.025-1.3 mg mL^{-1}	0.125-20 mg mL^{-1}
Best Line Equation	y=0.3368x+0.004	y=0.0603x+0.0209
LOD (ng mL^{-1})	7.5	22
LOD (ng)	1.5	4.4
C_o (ng mL^{-1})	12.9	72.3

Application of CVG results in 5.6 fold enhancement in the sensitivity over FAAS. In terms of LODs compared 2.93 fold lower LOD was achieved with CVG as compared to FAAS. Duan et al. [34] had 2.66 fold lower LOD with vapour as compared to nebulizer.

3.8 Analysis of Standard Reference Materials

In Table 3.5 the certified and found values for the standard reference materials (SRM) used in this study are given. The Ag concentrations in SRMs were found to be in good agreement with the certified values.

Table 3.5 Results of the Analysis of Standard Reference Materials

Standard Reference Material	Certified Ag, mg/kg	Found Ag, mg/kg
NIST SRM 2710 Montana Soil (Highly Elevated Trace Element Concentrations)	35.3 ± 1.5	33.56 ± 1.40
NIST SRM 2711 Montana Soil (Moderately Elevated Trace Element Concentrations)	4.63 ± 0.39	5.93 ± 0.38

Certified Values for SRM 2710 and SRM 2711 shown in Table 3.6 and Table 3.7, respectively. The Student's t test was employed for the results . At 95 % confidence level, the result found for SRM 2710 was found to have no significant difference as compared to the certified value. For SRM 2711, the result was rather high, significant difference was indicated at 95% confidence level, while the difference was not significant at 98 % confidence level.

The results found by direct calibration for SRM 2710 and 2711 were found to be 21.88 ± 2.34 and 7.02 ± 1.13, respectively. These results reflect the dominant interference effects.

Comparing the slopes of direct calibrations (aqueous standards) with the standard addition methods, for the SRM 2710 the slope of standard addition is lower than the direct calibration, indicating a suppressive effect. As a result of interference study, 100 fold Cu concentration yielded 85%

decrease in the sensitivity. And in SRM 2710 contains approximately 80 fold higher concentration of Cu than Ag. In addition, SRM 2710 contains 17 times higher concentration of As than Ag. According to the interference study, even 1 fold of As decrease the sensitivity by 88%. Presence of 100 fold Fe increased the sensitivity by 30% and the concentration in reference material is nearly 900 times higher than Ag concentration. For the SRM 2711 the slope of standard addition is higher than the direct calibration, indicating an enhancing effect. Looking at the interference studies, this increase may be owing to 78 fold higher concentration of Fe. When the Fe concentration was 100 fold of than Ag concentration 30% increase in sensitivity was observed. On the other hand 1 fold of the Cu decreased the signal 15% and in this SRM has nearly 3 times more Cu concentration than Ag concentration. 1 fold of As decreased 90% of the signal and the SRM 2711 has 3 times more As concentration than Ag concentration.

The interferences can be of widely varying nature and often depend on the apparatus used. Interferences can take place during vapour generation, during transport, and in the atomizer. Interferences can be either caused by concomitants in the actual sample, or they can be caused by residues from a previous determination (memory).Interferences due to the amalgamation with heavy metals may also occur [27].

Table 3.6 Certified Values for SRM 2710

Element	wt. (%)		Element	mg/kg	
Aluminum	6.44	± 0.08	Antimony	38.4	± 3
Calcium	1.25	± 0.03	Arsenic	626	±38
Iron	3.38	± 0.10	Barium	707	± 51
Magnesium	0.853	± 0.042	Cadmium	21.8	± 0.2
Manganese	1.01	± 0.04	Copper	29580	± 130
Phosphorus	0.106	± 0.015	Lead	5532	± 80
Potassium	2.11	± 0.11	Mercury	32.6	± 1.8
Silicon	28.97	± 0.18	Nickel	14.3	± 1.0
Sodium	1.14	± 0.06	Silver	35.3	± 1.5
Sulfur	0.24	± 0.006	Vanadium	76.6	± 2.3
Titanium	0.283	± 0.010	Zinc	6952	± 91

Table 3.7 Certified Values for SRM 2711

Element	wt. %	Element	µg/g
Aluminum	6.53 ± 0.09	Antimony	19.4 ± 1.8
Calcium	2.88 ± 0.08	Arsenic	105 ± 8
Iron	2.89 ± 0.06	Barium	726 ± 38
Magnesium	1.05 ± 0.03	Cadmium	41.70 ± 0.25
Phosphorus	0.086 ± 0.007	Copper	114 ± 2
Potassium	2.45 ± 0.08	Lead	1162 ± 31
Silicon	30.44 ± 0.19	Manganese	638 ± 28
Sodium	1.14 ± 0.03	Mercury	6.25 ± 0.19
Sulfur	0.042 ± 0.001	Nickel	20.6 ± 1.1
Titanium	0.306 ± 0.023	Selenium	1.52 ± 0.14
		Silver	4.63 ± 0.39
		Strontium	245.3 ± 0.7
		Thallium	2.47 ± 0.15
		Vanadium	81.6 ± 2.9
		Zinc	350.4 ± 4.8

CHAPTER IV

CONCLUSIONS

Chemically generated vapour species of silver were sent to a flame-heated quartz tube atomizer (QTA) by using a gas-liquid separator. Flow injection (FI) was used for sample introduction. The experimental parameters in chemical vapour generation were optimized. Both HCl and HNO_3 were employed in the system and it was found that HNO_3 was more convenient for the determination of silver.

Application of the CVGAAS system yields 5.6 times sensitivity enhancement was achieved employing chemical vapour generation technique, 3σ limit of detection was 7.5 ng ml^{-1}. The system needs conditioning, absorbance signals gradually increased and reached a plateau after several injections. Using Pd as a permanent modifier increases the sensitivity and decrease the time of conditioning. Silver species were coated on the inner surface of the tubings and GLS. When the systems were compared due to their time needed to reach the conditioning, modifier used system reached the conditioning in shorter time than not used one. The sensitivity increases as silver coating gets blacker. Since the species could not stand for a long time the transfer tubing and the GLS surface length should be as short as possible.

The interferences of some hydride forming elements and some transition metals on chemical vapour generation were investigated. Both positive and negative interferences were occurred. If needed these interferences can be eliminated using standard addition method. Evaluating this study is competitive with the others in the literature studied by the method of CVG, with AAS and ETAAS. But this study has lower sensitivity than the ICP methods. On the other hand this method is easy to apply and has lower cost.

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