DETERMINATION OF SILVER BY SLOTTED QUARTZ TUBE ATOM TRAP FLAME ATOMIC ABSORPTION SPECTROMETRY USING METAL COATINGS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

GAMZE KARAMAN

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMISTRY

SEPTEMBER 2011

Approval of the Thesis;

DETERMINATION OF SILVER BY SLOTTED QUARTZ TUBE ATOM TRAP FLAME ATOMIC ABSORPTION SPECTROMETRY USING METAL COATINGS

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ABSTRACT

DETERMINATION OF SILVER BY SLOTTED QUARTZ TUBE ATOM TRAP FLAME ATOMIC ABSORPTION SPECTROMETRY USING METAL COATINGS

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September 2011, 76 pages

Silver is a precious metal having antibacterial property and widely used in industry mostly for water purification and medicinal products. Therefore, the determination of trace levels of silver is important for industrial applications. Flame atomic absorption spectrometry (FAAS) is a popular technique for the determination of relatively low concentration levels. This mature technique owes its widespread application to its simplicity and low cost. However, for some occasions, FAAS technique suffers from its low sensitivity because of low nebulization efficiency and relatively short residence time of analyte atoms in the measurement zone. In order to overcome this sensitivity problem, atom traps have been developed in recent years. Slotted quartz tube (SQT) is an accessory designed to use as an atom trap in conventional flame atomic absorption burner head. This thesis study involves the development of a sensitive, simple and economical technique with the help of the SQT for the determination silver. Firstly, the technique known as SQT-FAAS was used to increase the residence time of analyte atoms in the measurement zone. In this case, limit of detection (LOD) and characteristic concentration (C_0) values were found to be 19 ng/mL and 35 ng/mL, respectively. Enhancement in sensitivity with respect to

FAAS was found to be 2.31 fold using SQT-FAAS. Regarding the angle between the two slots of the SQT, 180° configuration was used. Secondly, in order to improve sensitivity further, the SQT was used as an atom trap (AT) where the analyte is accumulated in its inner wall prior to re-atomization. The signal is formed after re-atomization of analyte atoms on the trap surface by introduction of organic solvent. For this purpose, uncoated SQT was used as a trap medium. However, there was a memory effect. Therefore, the SQT inner surface was coated with different coating elements and theoptimum conditions were found by using W-coated SQT-AT-FAAS technique. In the presence of a lean air-acetylene flame, analyte atoms were trapped in the inner surface of the SQT for 5.0 min and then revolatilized with the introduction of 25 μL isobutyl methyl ketone (IBMK); afterwards, a transient signal was obtained. These optimized parameters were used for uncoated SQT, W-coated SQT and Zr-coated SQT atom trap techniques. Sample suction rate was 6.25 mL/min in all techniques. Sensitivity was increased 54 fold using uncoated SQT-AT-FAAS technique with respect to simple FAAS technique. When W-coated SQT-AT-FAAS technique was applied, 135 fold sensitivity enhancement was obtained with respect to FAAS technique. The best sensitivity enhancement, 270 fold, was obtained using Zr-coated SQT-AT-FAAS technique. In addition, the Ag signals were more reproducible (%RSD, 1.21) when Zr was used as a coating element. After the sensitive technique was developed, interference effects of some transition and noble metals and hydride forming elements on Ag signals were investigated. Finally, surface studies were done to determine the chemical state of Ag during trapping period by using X-ray Photoelectron Spectroscopy (XPS). It was observed that the Ag analyte is retained on the SQT surface in its oxide form.

Keywords: Silver, flame atomic absorption spectrometry, slotted quartz tube, tungsten, zirconium, sensitivity enhancement.

ÖZ

YARIKLI KUVARS TÜP ATOM TUZAĞI VE METAL KAPLAMALAR KULLANARAK ALEVLİ ATOMİK ABSORPSİYON SPEKTROMETRİYLE GÜMÜŞ TAYİNİ

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Eylül 2011, 76 sayfa

Gümüş, antibakteriyel özelliğe sahip değerli bir metaldir. Endüstride yaygın bir kullanıma sahiptir; daha çok su saflaştırmada ve tıbbi ürünlerde kullanılır. Bu nedenle eser miktarda gümüş tayini endüstriyel uygulamalar için önemlidir. Alevli Atomik Absorpsiyon Spektrometri (FAAS), göreceli düşük derişimlerin tayini için popüler bir tekniktir. Bu olgunlaşmış teknik, yaygın kullanımını kolaylığına ve ekonomik oluşuna borçludur. Ancak FAAS yönteminin duyarlılığı bazı durumlar için yetersiz kalmaktadır. Bu durumun nedeni; sisleştirmenin düşük verimi ve analit atomlarının ölçüm bölgesindeki kalma süresinin oldukça kısa olmasıdır. Bu duyarlılık problemini aşmak için, son yıllarda atom tuzakları geliştirilmiştir. Yarıklı kuvars tüp (YKT), ticari alevli atomik absorpsiyon başlığında atom tuzağı olarak kullanılmak üzere tasarlanmış bir aksesuardır. Bu tez çalışması; gümüş tayini için YKT yardımıyla duyarlı, kolay ve ekonomik bir teknik geliştirmeyi amaçlamaktadır. İlk olarak analit atomlarının ölçüm bölgesindeki kalma süresini artırma amacıyla YKT-FAAS tekniği kullanılmıştır. Bu durumda gözlenebilme sınırı (LOD) ve karakteristik derişim (C_0) değerleri sırasıyla 19 ng/mL ve 35 ng/mL olarak bulunmuştur. YKT-FAAS kullanıldığında bulunan C_0 değeri, FAAS yönteminden elde edilen değer ile karşılaştırıldığında 2.31 kat duyarlılık artışı gözlemlenmiştir. YKT'nin yarıkları arasındaki açının 180° olduğu durum kullanılmıştır. Bir sonraki aşamada, duyarlılığı daha da artırmak amacıyla YKT atom tuzağı (AT) olarak kullanılmıştır. Bu yaklaşımda, analit tekrar atomlaşmadan önce YKT iç yüzeyinde toplanır. Sinyal, tuzak yüzeyinde toplanan analit türlerinin organik çözücü varlığında atomlaşmasından sonra elde edilmektedir. Bu amaçla boş YKTtuzak alanı olarak kullanılmıştır. Ancak hafıza etkisi gözlemlenmiştir. Bu nedenle, YKT iç yüzeyi farklı kaplama elementleri ile kaplanmış ve optimum şartlar W kaplı YKT-AT-FAAS tekniği kullanılarak bulunmuştur. Düşük asetilen akış hızında; analit atomları, 5.0 dakika boyunca YKT iç yüzeyinde toplanır ve sonra 25 µL izobutil metil keton (IBMK) gönderilmesiyle toplanan analit türleri buharlaşır ve hızla atomlaşır. Bu hızlı atomlaşmanın ardından pik şeklinde bir sinyal elde edilir. Optimize edilen bu parametreler sırasıyla kaplamasız YKT, W kaplı YKT ve Zr kaplı YKT atom tuzağı teknikleri için kullanıldı. Örnek akış hızı tüm tekniklerde 6.25 mL/min idi. Kaplamasız YKT-AT-FAAS tekniği kullanıldığında, duyarlılık FAAS tekniğine göre 54 kat artmıştır. W-kaplı YKT-AT-FAAS tekniği uygulandığında, FAAS tekniğine göre duyarlılıkta 135 kat artış elde edilmiştir. En iyi duyarlılık artışı Zr kaplı YKT-AT-FAAS tekniği kullanılarak 270 kat olarak elde edilmiştir. Ayrıca kaplama elementi olarak Zr kullanıldığında daha tekrarlanabilir (%RSD, 1.21) Ag sinyalleri elde edilmiştir. Duyarlı bir teknik geliştirdikten sonra, bazı geçiş ve soy metaller ile hidrür oluşturan elementlerin Ag sinyali üzerindeki girişim etkileri incelenmiştir. Son olarak; Ag elementinin YKT yüzeyinde hangi formda toplandığını belirlemek için, X ışınları fotoelektron spektroskopisi (XPS) kullanılarak yüzey çalışmaları yapılmıştır. Gümüş analitinin YKT yüzeyinde oksit formda tutunduğu gözlenmiştir.

Anahtar Kelimeler: Alevli Atomik Absorpsiyon Spektrometri, gümüş, yarıklı kuvars tüp, tungsten, zirkonyum, duyarlılık artışı.

To My Family

ACKNOWLEDGEMENTS

I would like to record my gratitude to my supervisor Prof. Dr. O. Yavuz Ataman for his guidance, advice, support and encouragement throughout this research.

I gratefully acknowledge Dr. Yasin Arslan for his endless patience, guidance and contribution in each part of this study.

I would like to thank Dr. Sezgin Bakırdere for his encouragement and guidance.

I am deeply grateful to Selin Bora, Pınar Akay, Emrah Yıldırım, Feriye Şenol and Engin Şimşek for their help, support and friendship.

I want to thank Necati Koç for his help, all AtaMAn Research and C-50 group members for their understanding and friendship.

I would like to show my gratitude to Gönül Hızalan, Merve Kolay, Nalan Korkmaz and Sevgi İpekçioğlu for their support, love and friendship.

I owe my deepest gratitude to Buğrahan Dikici for his love, trust, patience and support.

Finally, my special thanks to my mother, father, sisters and brother for their trust, patience, support and love.

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LIST OF ABBREVIATIONS

ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
CVG-AAS	Chemical Vapor GenerationAtomic Absorption Spectrometry
ETAAS	Electrothermal Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
IBMK	Isobutyl Methyl Ketone
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
SQT	Slotted Quartz Tube
SQT-AT	Slotted Quartz Tube Atom Trap
SQT-AT-FAAS	Slotted Quartz Tube Atom Trap Flame Atomic Absorption Spectrometry
SQT-FAAS	Slotted Quartz Tube Flame Atomic Absorption Spectrometry
W Coated SQT-AT-FAAS	Tungsten Coated Slotted Quartz Tube Atom Trap Flame Atomic Absorption Spectrometry
XPS	X-Ray Photoelectron Spectroscopy
Zr Coated SQT-AT-FAAS	Zirconium Coated Slotted Quartz Tube Atom Trap Flame Atomic Absorption Spectrometry

CHAPTER 1

INTRODUCTION

1.1 Silver and its Properties

Silver is a soft and lustrous white transition metal which is the sixty-fourth most abundant element in the Earth's crust. Its atomic number is 47 and atomic mass is 107.9 amu. The word *Silver* derives from the Anglo-Saxon *seolfor* or *siolfur* and its symbol comes from Latin *argentum* [1].

It is not known when silver is discovered, however there are some evidences related with historical background of silver. Some objects that are made up of silver have been recovered from sites of ancient civilizations of China, Egypt, South America and Middle East dating from 2000BC. The largest producers of silver in the world include Mexico, Peru, the United States, Canada, Poland, Chile and Australia [2].

Silver occurs in association with other metal ores; gold, copper, lead, zinc, mercury, arsenic, antimony, molybdenum and tellurium [1, 3]. It is also found in some 60 minerals including: argentite (silver sulfide), proustite (complexed with arsenic and sulfur), cerargyrite (silver chloride) and hessite (complexed with tellurium) [1, 4].

Silver is a metallic element having the lowest contact resistance and therefore it has the highest thermal and electrical conductivity of all metals in the Periodic Table [1].

Silver extracted commercially is 99.9% pure. Pure silver is stable in air but it tarnishes when exposed to air containing sulfur or hydrogen sulfide, ozone [1].

Silver is rarely found in the Earth's crust and its abundance is thought to be 0.1 mg/L. It is also found in sea water and its abundance there is estimated to be 0.01 mg/L. It occurs as cubic crystals and there are two naturally occurring isotopes of silver exist: ^{107}Ag and ^{109}Ag. These occur in similar proportions. Totally thirty five isotopes of silver are known and about sixteen of them are radioactive [1].

1.2 Silver and its Uses

Silver is unique metal with its antibacterial property [5-7]. Through this property, silver has widespread usage in industry. This element with its compounds and alloys are used in medicinal science and surgery [8-10] for processing drugs [11-13], production of dental fillings [6]. In addition to these, implants and many medical devices are treated with silver to prevent infection risk [5, 14].

Silver is probably the first metal known to have antimicrobial activity, so for many years it was also used for water purification. Moreover its compounds are added to different products such as foods, beverages and clothing for disinfection [15]. The production of clothing for hospitals and some domestic products is a new science for silver uses [1].

On the other hand, silver has an important role in industrial applications for use in preparation of high-strength and corrosion-resistance alloys and jewellery. It is also used in the production of electronic devices, photographic films and mirrors [6, 12, 13].

1.3 Silver in Health

Silver is ubiquitous in the human environment. It is found everywhere; in the soil, in drinking water, in the air we breathe and in foods. It is absorbed into the human body through drinking water, diet and by inhalation. The greatest majority of people exhibit low levels of silver in their blood plasma or body tissues without any metabolic disturbances or clinical signs. The amount of silver in the human body is very low (<2.3 μg/L), however for the people who are working in silver industries higher amounts can be observed [1].

Metallic silver is inert in the presence of human tissues but in the presence of body fluids and secretions it readily forms silver ion (probably Ag^+) which is biologically active and is metabolized to most part of the body [16, 17].

Silver has a worldwide acceptance as a broad spectrum antibiotic. Laboratory studies have shown that it can be used to control most pathogenic bacteria and parasitic infections including the methicillin-resistant strains of Staphylococcus aureus (MRSA) which is a bacterium responsible for several infections and have proved fatal in many aged and immunocompromised people [1].

As mentioned in section 1.2, silver is frequently used for industrial applications. In addition, silver impregnated filters are used in the preparation of drinking water [15]. Therefore, its concentration increases in aquatic ecosystems. World Health Organization (WHO) permits 0.1 mg/L of silver ions as a maximum concentration in drinking water disinfection, on the other hand United States Environmental Protection Agency (USEPA) recommends 0.05 mg/L silver ions as a maximum [18, 19].

Silver deposition by chronic ingestion or inhalation of colloidal silver leads to argyria which is characterized by gray to gray-black staining of the skin and mucous membranes. Silver may be deposited in the skin either from industrial exposure or a result of medications containing silver salts. Deposition of silver particles can be observed in the skin (argyria), eye (argyrosis) and other organs. These are not malignant diseases but cosmetically undesirable [1, 20].

1.4 Determination of Silver

The widespread use of silver in industry especially in water purification is an important requirement for the determination of trace amounts of silver for many areas of chemical analysis [21]. This is why several studies focus on the development of highly sensitive and precise methods of silver determination.

The widespread methods for the determination of silver are flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), chemical vapor generation atomic absorption spectrometry (CVG-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The sensitivities of the techniques were compared in section 3.7.

1.4.1 Atomic Absorption Spectrometry

Atomic absorption is based on the absorption of light by atoms. Atomic absorption takes place only if the light of the characteristic wavelength of the element of interest is absorbed by ground-state atoms, promoting them to an excited state [22]. The intensity of light is decreased after the absorption process and the absorbance is proportional to the number of atoms in ground state and so to the concentration of analyte.

The basic components of an atomic absorption spectrometer are; a radiation source, an atomizer, a monochromator, a detector and a readout device. Hollow cathode lamps (HCL) are the most widely used radiation sources in Atomic Absorption Spectroscopy (AAS). Electrodeless discharge lamps and lasers are other sources that are also popular in this technique. Atomizer is used to produce the ground state atoms from the analyte molecules or ions. Most commonly used atomizer is flame atomizer which is employed with air/acetylene and nitrous oxide/acetylene flames. Graphite furnace is also used as an atomizer in AAS systems [23].

Flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS) and chemical vapour generation atomic absorption spectrometry (CVG-AAS) are the techniques used for the determination of silver. Among all, FAAS is still the most preferred technique in the determination of trace metals because of its high specificity and low cost [24].

1.4.1.1 Flame Atomic Absorption Spectrometry

Flame AAS can be used for the determination of trace levels of analyte in a wide range of sample types [22]. Typically, in FAAS the sample solution is aspirated into the flame in the form of an aerosol generated through a nebulizer which forms fine droplets. This step is known as nebulisation. Then, the aerosol reaches the flame (atomizer) where desolvation, volatilization and dissociation steps take place to produce ground state atoms of the analyte [25]. Most common flames are air-acetylene and nitrous oxide-acetylene flames. An air-acetylene flame at 2100-2400 °C has been mostly used for the determination of majority of elements. A nitrous oxide-acetylene flame at 2600-2900 °C has been preferred for refractory elements due to its high temperature [26]. In case of silver determination, air-acetylene flame is used.

FAAS is quite popular; however the sensitivity of the technique is limited by two factors. The first one is poor nebulization efficiency of the system, only 1-10% of the sample solution reaches the flame. A further limitation is the relatively short residence time of analyte atoms in the measurement zone during sample aspiration; this is estimated to be in the order of few milliseconds when flame atmosphere is considered [27].

Despite its low sensitivity, FAAS is still an important technique for analysis of trace elements owing to its simplicity, low cost and its convenience to sensitivity improvements.

1.4.1.2 Electrothermal Atomic Absorption Spectrometry

Electrothermal atomization is performed by graphite furnace, open filament, or vertical crucible furnace devices [23]. Among them graphite furnace atomizer which was first introduced by L'vov in 1959 is the most widely used ETAAS technique [28]. This is the reason why ETAAS is also known and often named as graphite furnace atomic absorption spectrometry (GFAAS).

In ETAAS or GFAAS technique, a small amount of sample (5-100 µL) is placed in an electrically heated graphite tube which is shaped like a cylinder having a hole in the center of the tube wall for sample introduction. The tube ends are open for the passage of light from source and removal of the sample constituents [25]. The ETAAS determination consists of three stages. The drying stage is applied to remove the solvent from sample at temperatures near the boiling point of the solvent (around 100°C). The aim of second stage known as ashing is to remove the sample matrix as much as possible; this involves heating the tube between 350 and 1200°C. In atomization stage, free atoms of the element are produced in the presence of high temperatures (2000-3000°C) and then the absorption by atomic vapor is measured [29]. In drying and ashing stages, an inert gas (Ar or N_2) is passed through the system in order to remove any extraneous material. However, the flow must be stopped during atomization in order to prevent dilution and analyte loss [22].

In atomization stage, the residence time of analyte atoms in the measurement zone is relatively longerwith respect to FAAS. Hence the sensitivity also increases and µg/L working ranges may be possible. Also, the transport efficiency of the system reaches 100% which is considerably higher than FAAS technique. Even though ETAAS seems better when compared with FAAS, it has important deficiencies. One of them is the presence of interferences especially in case of heavy matrices. Another disadvantage is the cooler ends of the tube which hold the analyte atoms that are volatilized. Since the atomization is not homogeneous, multiple peaks and peak broadening may be observed [30]. This disadvantage has been largely eliminated by the recently developed transversely heating techniques.

1.4.1.3 Chemical Vapor Generation

Chemical vapor generation is a sample introduction technique based on separation of analyte element from the matrix by the generation of gaseous species. In acidic environment analyte is reduced by sodium tetrahydroborate (III) and is liberated in the form of volatile species. This volatilized analyte can be detected by different methods of atomic spectroscopy [31].

The technique has significant advantages. One of them is reduction or elimination of interferences after efficient separation of matrix. Another advantage is the high efficiency of transport of analyte to the detector. Moreover this vapor generation system enables to use of gas phase separation methods for speciation analysis [32].

There are several studies in literature where this technique was used for the determination of silver [33-38].

1.4.2 Plasma Techniques

ICP-OES is a type of plasma technique that can be used for the determination of trace elements. The technique enables to measure different elements at the same time [39]. In ICP-OES, generally liquid samples are analyzed. Sample is nebulized into the plasma and evaporation is followed by conversion of sample into excited free atoms and ions. These excited free atoms and ions emit electromagnetic radiation at wavelengths that is characteristic for a particular element. This radiation at particular wavelengths is used for qualitative analysis and the measured intensities at these wavelengths are used for quantitative analysis of the elements [23]. The technique has several advantages such as there is no need to use a hollow cathode lamp, simultaneous multi-element detection is possible and since the sample flow rate (~ 1 mL/min) is lower than the sample flow rate of AAS techniques (~ 6 mL/min), volume of sample in the analysis is smallerthan AAS techniques. In addition to these it has high sensitivity and large dynamic range [30].

ICP-OES is applied with different sample introduction techniques for the determination of silver; chemical vapour generation-ICP-OES (CVG-ICP-OES) has been frequently used in literature [37, 40].

ICP-MS which is commercialized in 1983 has unique features with its extremely low detection limits at sub-ppt levels [25]. This plasma technique is the marriage of inductively coupled plasma (ICP) which is operating at atmospheric pressure and mass spectrometry (MS) which is operating under high vacuum. An ion source (ICP) converts sample (usually in liquid form) into positively charged ions. The mass analyzer sorts ions according to their mass-to-charge ratio (m/z). Differently from other techniques like ETAAS, FAAS, ICP-OES; the technique has the ability to measure isotope ratios [29]. ICP-MS has further advantages; high-speed analysis is one of them. Another advantage is due to high sensitivity of the system further dilution can be done and then matrix interferences are reduced. In addition to these, the technique has wide linear dynamic range. Similar with ICP-OES, multiple element determination is possible simultaneously [30].

ICP-MS has been used for the determination of silver in literature [41-43].

1.5 Atom Trapping Techniques in Atomic Absorption Spectrometry

Atom traps are developed in order to improve the sensitivity of the techniques. This is done by collection of analyte atoms within the body of the atomizer. There is no need to use additional chemicals that result contamination problem when atom traps are used. In addition these traps have low cost and simple instrumentation [44].

In CVG; quartz trap, graphite furnace trap and metal trap are used for preconcentration. For FAAS, long-path absorption tube, Delves' microsampling cup and slotted quartz tube are used in order to increase residence time of analyte atoms; integrated atom trap and slotted quartz tube atom trap are used for preconcentration.

1.5.1 Atom Traps for Vapor Generation

As mentioned in section 1.4.1.3, vapor generation is popular due to matrix elimination and high transport efficiency of analyte. In addition to these its popularity based on another property; sensitivity improvement is possible by simple preconcentration techniques such as atom traps.

Atom trapping is based on collection of analyte species on the surface of an atom trap and sending the atoms to the detector as rapidly as possible. Finally a transient signal is obtained and either the area or height can be used as the analyte signal [30].

1.5.1.1 Quartz Trap

The quartz atom traps are obtained by heating the quartz pieces externally. The inlet arm of the quartz T-tube is used directly or some quartz pieces are placed for this purpose. The generated volatile analyte species are collected on the quartz surface and then the temperature is further increased for the revolatilization of the analyte atoms. At this stage, hydrogen gas is sent to the system to create a reducing environment for revolatilizaiton [45]. External heating is the critical point of the system since it takes long time [30]. Dedina [46] used microflame in addition to the external heating to overcome time problem. Oxygen gas is sent to the system and the reaction between oxygen and hydrogen forms microflame.

1.5.1.2 Graphite Furnace Trap

The volatile analyte species are trapped on the surface of the graphite tube and these collected species are revolatilized and atomized with the increasing temperature. Then a transient signal is obtained [30].

Graphite furnace trap has lower sensitivity than quartz trap because of limited surface area. Also it has higher cost than quartz trap. However it is easy to operate and provides better tolerance to atomization interferences [47].

1.5.1.3 Metal Trap

Another approach is using metal surfaces as a trapping medium. In this case no external heating is applied; metal itself is resistively heated by the passage of electricity. Since the metal has higher thermal conductivity than quartz, it is easy to reach high temperatures in a short time. Typically tungsten is used as a metal trap due to its high melting point and low cost [27].

In literature, W-coil was used as an atom trap in combination with a T-tube atomizer for the determination of Bi [48]. Also, it is used both for trapping medium and atomizer for the determination of Se [49].

Unfortunately, in metal trap systems oxidation of W-coil is inevitable and this affects the system performance. To overcome this problem hydrogen gas is sent to the system and a reducing medium is created [30].

1.5.2 Atom Traps for Flame Atomic Absorption Spectrometry

As mentioned previously in section 1.4.1.1, there are some problems in FAAS technique. Atom traps in FAAS mainly aim to overcome these sensitivity problems with in-situ preconcentration of the analyte atoms [50].

1.5.2.1 Long-Path Absorption Tube Technique

These prolonged absorption tubes are arranged on the basis of Beer's law which states that absorbance is directly proportional to the path length of the sample cell. As shown in Figure 1.1, these tubes can be T-shaped or open-ended. In the technique, since the absorption medium is confined by the tube, probable contamination from outside atmosphere is prevented and the concentration of free atoms increases. Here the critical point is the mean lifetime of free atoms which varies with the element, the temperature and also the composition of flame gases [51].

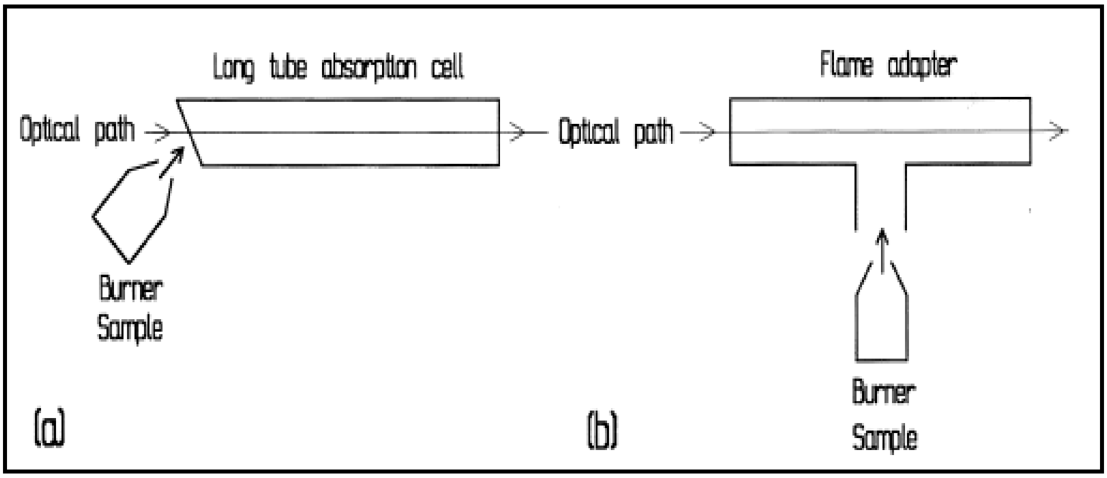

Figure 1.1 Schematic representation of a long tube absorption cell. (a) Open ended, (b) T-shaped [51].

The absorption tube technique was used for the determination of silver, copper, gold and cadmium in propane-butane-air flame and sensitivity improvement was 5-13 fold [52]. In another study, 45 cm long silica tube was used to investigate the fuel flow rate effect on several elements (copper, silver, gold, cadmium, tin, lead, antimony, bismuth, manganese and rhodium) [53].

Even though the studies with using long-path absorption tube are favorable, the tube has not been utilized commercially since it is too long to place into the burner head of standard atomic absorption spectrometer [51].

1.5.2.2 Delves' Microsampling Cup Technique

Delves' microsampling cup technique is the best method reported for microsample analysis with a flame atomizer [54]. As can be seen in Figure 1.2, sample is placed in a sampling boat and the absorption tube is above the long path flame. By this way the vaporized species from crucible are collected in absorption tube which is placed above the source [51].

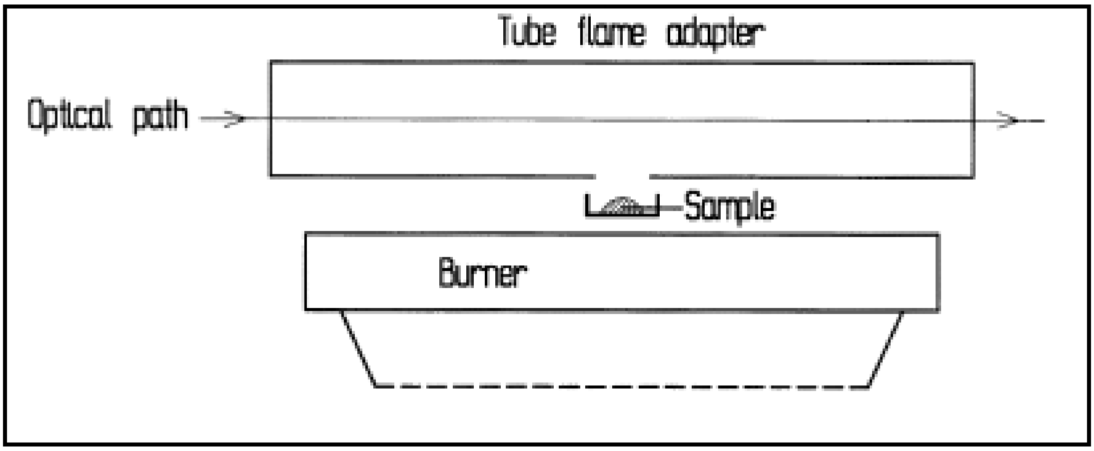

Figure 1.2 Schematic representation of Delves' microsampling cup system [51].

In 1970, the technique was used for the detection of lead in blood. In this case, 10 µL of sample is placed in micro crucible which is made up of nickel foil. The nickel absorption tube was above the air-acetylene flame which was 20 mm height from the burner head. The atomization is occurred inside the tube and the source radiation was passing along the axis of tube [54]. The sensitivity is increased when this technique is applied because the transport efficiency is high and also residence time of analyte atoms in the measurement zone is long due to prolonged absorption tube. Here, the most important point is all these are possible with small volume of samples.

The technique was proposed for the analysis of clinical, environmental and industrial samples [51]. It was particularly used for the determination of lead and cadmium at sub-ppm levels in biological samples. This trap system was manufactured in the 1970s; however, it has not been commercially available for a long time [51].

1.5.2.3 Slotted Quartz Tube FAAS

Slotted quartz tube, illustrated in Figure 1.3, was an accessory firstly designed and also used by Watling in 1977 [55]. The tube was designed to use in the conventional flame atomic absorption burner head and aimed to increase the sensitivity and precision for trace metals. This quartz tube which is aligned with the optical path of the spectrometer has two parallel slots; the entrance slot (lower), aligned directly above the flame, allows the passage of flame to the inside of the tube and the exit slot (upper) eliminates the possible damages to lens of the spectrometer [55]. The entrance and exit slots may be positioned at 120° or 180° to each other [23]. The tube is typically made up of quartz which has high melting point and low thermal expansion coefficient. However stainless steel, graphite and silicon nitride are also used while making slotted tubes [51].

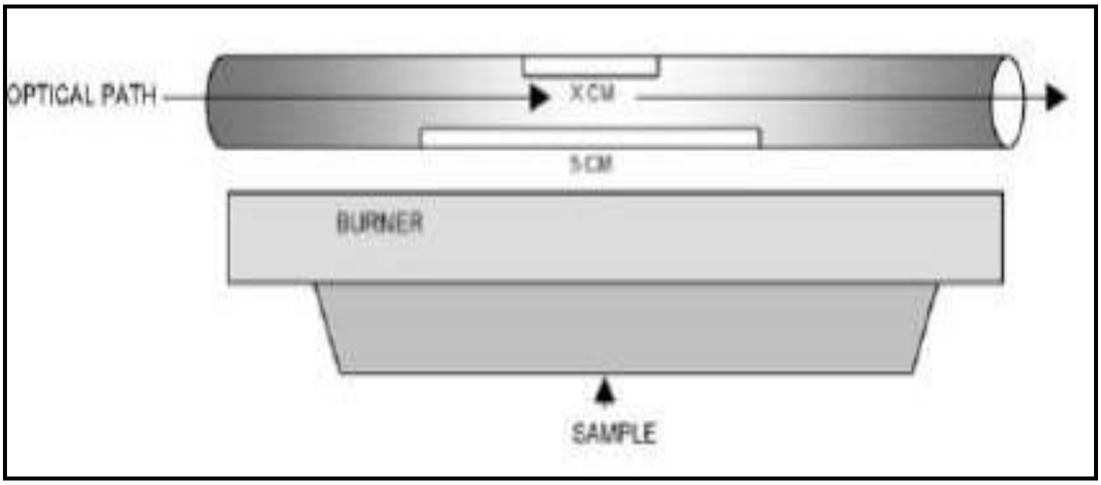

Figure 1.3 Schematic representation of slotted quartz tube [56].

This double-slotted tube, placed into air-acetylene flame with the help of asbestos blocks, was used for the analysis of trace metals in fresh water. The height of the SQT above the burner head was 5.0 mm and it was fixed. A significant increase (9 fold) in analytical sensitivity was obtained for Ag and 2-5 fold increase in sensitivity was obtained for Zn, Cd, Bi, Pb, As, Sb, Se and Hg in comparison with conventional FAAS. On the other hand for elements such as Co, Ni, Cu, Mn and Fe; a little enhancement (1-2 fold) was observed in absorbance signal. However, precision at low concentrations was improved for majority of elements since the tube walls controlled the flame dimensions through the absorption path and reduce the instrumental noise formed by flame flicker [55, 57]. In another study, the SQT was used in conjunction with different types of flames (air-acetylene, air-hydrogen, argon-hydrogen) for the determination of As, Sb, Se and Hg. When the SQT was used in conjunction with air-acetylene flame, up to 10 fold increase in sensitivity was observed [58]. These studies have shown the achievement of the SQT regarding sensitivity and precision improvement as compared to conventional FAAS. There are several reasons contribute to these results. One of the reasons is that in the presence of the SQT, flame speed through the absorption path is slower than original flame and also the optical path is longer; therefore residence time of analyte atoms in the measurement is increased. Another reason is the stability of chemical environment inside the tube because of the elimination of oxidizing species present in conventional flame. In this way, the amount of neutral atoms inside the tube is also stable [55].

Slotted quartz tubes can be used with hydride generation technique, flow injection systems and used in conjunction with discrete nebulization instead of pneumatic nebulization. On the other hand various modifications can be done such as changing dimension and length of the tube. In all cases, the aim of the SQT is sensitivity improvement [51].

To sum up, slotted quartz tube is suitable for simple and rapid analysis of samples. Quartz has low cost and is easily manufactured [55]. As mentioned at the beginning sensitivity increased with this system, however it should be underlined that slotted quartz tube provided only momentary sensitivity improvement with conventional use of flame [27].

1.5.2.4 Water Cooled U-tube Atom Trap

Water cooled U-tube atom trap, illustrated in Figure 1.4, was first proposed by Lau et al. [59]. This silica U-tube, positioned just below the optical path, was placed into air-acetylene flame. The tube was designed in U-shape for the entrance and exit of water or air into the system. In this system, the sample solution aspirated by conventional nebulizer is collected on the outer surface of the U-tube while the tube is cooled by the passage of the cold water. The analyte species are condensed on the cool surface of the tube. After collection stage, the cold water flow is replaced by pressurized air and the U-tube surface undergoes rapid heating. By this heating, analyte species are released into the flame and a transient signal is obtained [27].

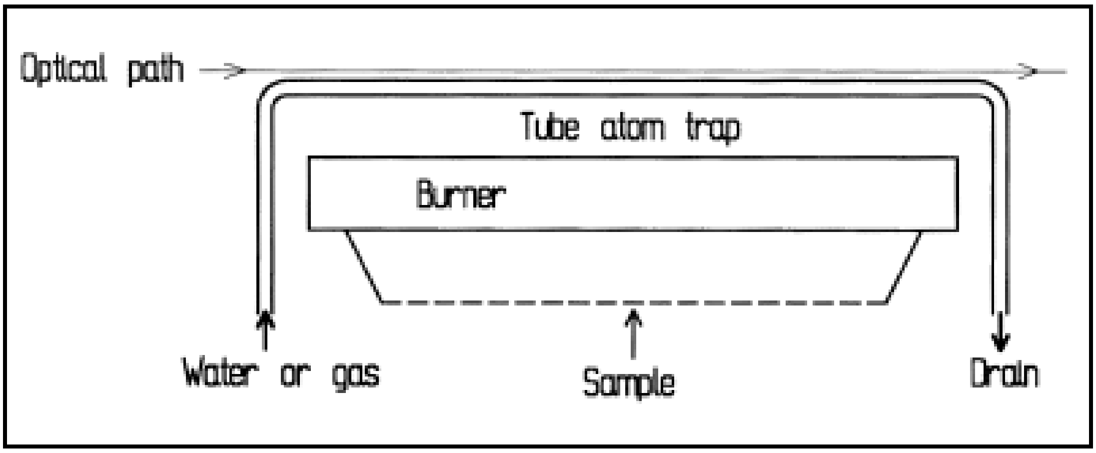

Figure 1.4 Schematic representation of water cooled U-tube atom trap [51].

The water cooled U-tube is probably the first application of quartz as an atom trap [60]. There are several studies concerning this system. In one study, the mechanism of the atomization in water cooled U-tube atom trap was investigated and found that elements such as Ag, Au, Cd, Co, Cu, Fe, Ni, Pb, Se and Zn were trapped on the cooled surface as metals while other elements such as K, Li, Na, Cr, Mg and Mn were trapped as silicates or oxides [61]. In other studies, different materials such as titanium, nickel, stainless-steel and copper are used for making U-tube instead of quartz. The aim of the researchers was to obtain colder surfaces that were able to collect more volatile species. However the idea was not so successful since intermetallic compounds were formed. In addition to these cooling-heating step caused physical deformations when titanium and stainless steel were used [62, 63]. Chinese researchers developed a modified water-cooled stainless steel trap for the determination of Ag in water and found the characteristic concentration and detection limit as 0.18 ng/mL and 0.29 ng/mL, respectively [64].

To sum up, the U-tube technique which involves atom trapping and preconcentration, has some advantages that it is simple to apply, has low cost and also can be used for the analysis of various materials. Although the technique is more sensitive than slotted quartz tube, has a drawback that large volume of sample is needed due to long collection time (about 2 min for a measurement) [51].

1.5.2.5 Water Cooled U-tube Atom Trap Combined with Slotted Quartz Tube

The advantages of water cooled U-tube atom trap and slotted quartz tube were combined in a new hybrid atom trap by Roberts and Turner [60]. This new trap, which was named as slotted-tube water-cooled atom trap or STWCAT, consisting of water cooled U-tube which was placed into the slotted quartz tube. By using new hybrid trap, high sensitivity and good precision were obtained in the determination of Cd and Pb in river water. However, there was a noise in signals due to water vapor [60].

Matusiewicz and Kopras developed and used the combination of SQT and water cooled U-tube and referred to as an integrated atom trap (IAT). IAT, shown in Figure 1.5, had similar arrangement with STWCAT. It was used for the determination of Ag, Cd, Cu, Fe, In, Mn, Pb, Tl and Zn in beer. Detection limits were in the range of 0.1-10 ng/mL while using IAT technique [65].

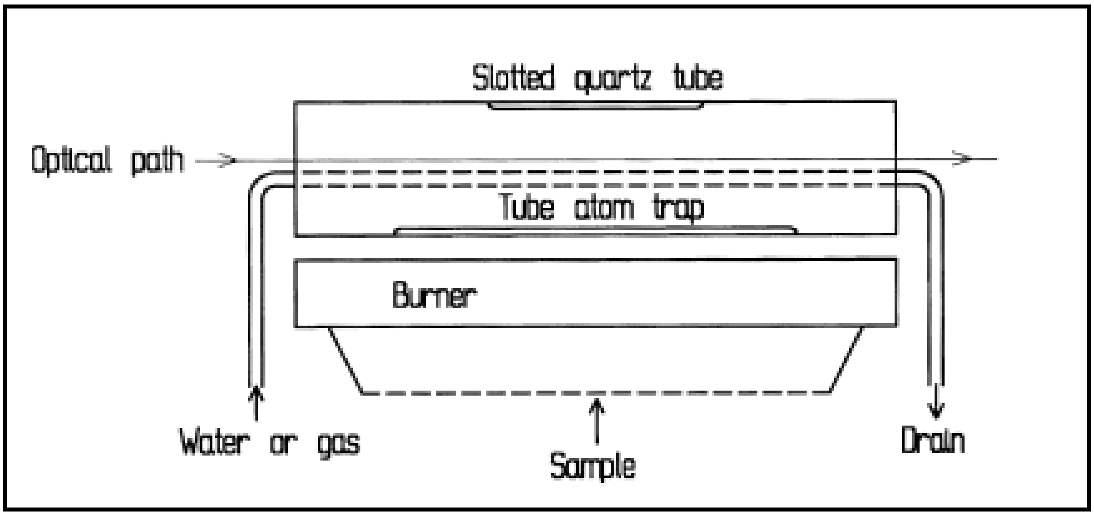

Figure 1.5 Schematic representation of integrated atom trap [51].

This atom trap technique is so simple and rapid for trace element analysis. It is also more sensitive than SQT and water cooled U-tube. Hence it can be suggested to use in the absence of ETAAS [51].

1.5.2.6 Slotted Quartz Tube Atom Trap FAAS

As mentioned in integrated atom trap system, volatile species are released from the tube after the passage of air instead of cold water. In this system, analyte species that are collected inside the SQT, are released by the organic solvent aspiration which changes the flame composition [66]. The details of the technique are given below:

(i) The SQT is placed above the flame and aligned with the optical path of the spectrometer. Sample solution is aspirated via pneumatic nebulization into the SQT and analyte species are collected on the inner surface of the SQT using optimized flame. This few minutes long step is called *collection*.

(ii) After collection step, a small volume (10-50 μL) organic solvent is aspirated to the flame and alters the flame composition momentarily. This momently change releases analyte atoms from the trapping medium so called *revolatilization* step. IBMK (isobutyl methyl ketone) is the most commonly used organic solvent in revolatilization step.

(iii) Finally rapid atomization takes place and a transient signal is obtained.

SQT-AT-FAAS technique has several advantages. One of them is the SQT is easily aligned with respect to the optical path that signal-to-noise ratio is similar with simple FAAS technique. Secondly, revolatilization step takes only few seconds and sharp signals are obtained. Also a significant increase is observed in sensitivity, therefore sample solutions could be diluted and this leads a decrease in interferences. In addition to these, this technique is simple and has low cost and few milliliters of sample are sufficient for the analysis [27].

There are several parameters that should be optimized before the sample analysis. Flame composition is one of them. Typically fuel-lean or stoichiometric flame is used in collection step; however fuel content of flame must be separately optimized for each element.Another parameter is the height of the SQT from the burner head which should be as close as possible to the burner. The reason is the efficient introduction of sample into the tube and then better trapping efficiency of analyte species. Sample suction rate is also optimized. In case of lower suction rate, nebulization efficiency and so trapping efficiency are better. Therefore, mass sensitivity is higher for lower rates. To select proper organic solvent and find the optimum volume for this solvent are another important processes throughout optimizations. IBMK is commonly used as an organic solvent since it provides rapid and complete atomization of analyte atoms. Finally the effect of trapping period which is also known as collection period should be optimized in trap studies. The sensitivity increases with the increasing trapping period as a result of increasing analyte concentration in trap medium. However, rapidity of the technique is also importantto compete with other techniques such as ETAAS [27].

In literature there are several studies regarding SQT-AT-FAAS technique. Demirtaş has studied the determination of Pb by Ta-coated SQT-AT-FAAS technique and she obtained 1650 fold enhancement in sensitivity with respect to FAAS technique [67]. In another application; Bi, Au and Mn determination by using the combination of water-cooled U-tube and uncoated SQT atom traps was studied and sensitivity improvements as compared to FAAS technique are 94, 180 and 6.6 fold respectively [68].

Apart from these; by using slotted silica tube atom trap, interference effects of some salts on Bi, Cd, In, Pb and Sb signals were studied. It was observed that there was a devitrification problem because of salts [69]. In another study, revotilization mechanisms were investigated using Bi, Au, Mn, Cd and Pb as an analytes [50].

1.6 Re-volatilization Techniques in SQT-AT-FAAS

Two techniques are suggested regarding re-volatilization:

1.6.1 Flame Alteration Technique

In flame alteration technique, fuel content of flame is increased after the collection step to revolatilize the analyte species [50].

The acetylene flow was divided into two streams which are controlled by further flow meters. In collection step, acetylene from one stream was sent to the waste and the other one was sent to the flame via valve. At the end of the collection, the stream sending to the waste was adjusted to send to the flame also. Since all acetylene streams were sent to the flame, it became stoichiometric or fuel-rich. Hence the flame composition was altered, analyte atoms were rapidly reatomized and a sharp signal was obtained [70].

1.6.2 Organic Solvent Aspiration Technique

In this technique, trapped analyte species were revolatilized with the aspiration of small volume of organic solvent [70].

With the application of this technique, the effect of temperature on revolatilization was investigated [50]. For this purpose water cooled U-shaped silica trap was used. All conditions were kept constant and the air temperature inside the tube was measured with the thermocouple. Different organic solvents were aspirated to the flame and temperature changes were monitored. It was observed that when organic solvent is aspirated to the flame, the flame temperature is either decreased or increased at insignificant level and revolatilization took place in either case.Therefore, the results showed that the revolatilization process by organic solvent aspiration technique is not thermal [50].

Momentarily increase of fuel in flame gases is followed by revolatilization of analyte species by either flame alteration technique or organic solvent aspiration technique [27]. In the previous experiment it was found thatthe revolatilization is not directly related with an increase in flame temperature [50]. Therefore, another experiment was performed to verify whether a contact between flame gases and quartz surface was necessary for revolatilization [50]. This time analyte species were collected on the inner surface of slotted silica tube and revolatilization was tried after rotating the tube around its long axis by 90°. The revolatilization was attempted by either organic solvent aspiration or flame alteration. However no signal was obtained at this position of slotted tube. When the tube was rotated 90° (back to its original position), the revolatilization was successful by either technique and there was a peak shaped signal. This experiment showed that there should be a physical contact between flame gases and silica surface for revolatilization process [50].

Several experiments showed that the sensitivities of both revolatilization techniques were comparable [70]. However, organic solvent aspiration technique is easy to apply since there is no need for extra gas [66].

1.7 Surface Studies

To improve the sensitivity and also to prevent the devitrification of SQT, inner surface of SQT may be coated with some elements such as W, Ta, Ir, Au, Os, Mo, Zr, Ti and Pd. While deciding the coating element, the critical point is that the melting point of the coating element should be significantly higher than the boiling point of the element of interest. In other words, it is desired that the coating element will not be lost before the revolatilization of analyte.

Nature of analyte species collected on the SQT surface was investigated by X-ray photoelectron spectroscopy (XPS), which is also known as electron spectroscopy for chemical analysis (ESCA), is a technique used for the measurement of the elemental composition, empirical formula, chemical state and electronic state of the elements [71]. Elements produce characteristic XPS peaks at particular binding energies. By using XPS spectra, it is possible to identify the element of interest and also its oxidation states on the surface. These peaks correspond to the electron configuration of the analyte species.

1.8 Aim of the Study

Silver is the least expensive of the precious metals which are valued for their beauty and relative scarcity in the Earth’s crust, and their superior properties. The determination of trace levels of silver plays an important role because of the widespread usage of silver especially in industrial applications.

The main purpose of this study is to develop a sensitive analytical technique for the determination of trace levels of silver. High sensitivity alone is not sufficient for a technique; simplicity and low cost are also important. ICP-MS is a good example for this criterion; although the technique provides sensitive measurements, its cost is too high for most laboratories. On the other hand, ETAAS suffers both from high cost and interferences. FAAS technique has low sensitivity without preconcentration for trace analysis.

Therefore, in this study; SQT-AT-FAAS techniques are used for the determination of silver. At the beginning, FAAS and SQT-FAAS techniques both will be used for silver determination. Also all parameters are to be optimized regarding these techniques. After that, an uncoated SQT with two slots having an angle of 90°, 120° or 180° with respect to each other will be used for sensitivity improvement in SQT-AT-FAAS technique. Then; coating of the SQT with W and Zr will be performed and experiments will be carried out with these configurations. All parameters are to be optimized for both uncoated and coated SQT-AT-FAAS techniques. Interference effects of several elements will also be studied. Finally, characterization of analyte species will be performed by using XPS spectroscopy.

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus and Materials

Three types of slotted quartz tubes were used with respect to position of two slots. The slots were positioned at 90°, 120° and 180°; the length of the lower slot was 102 mm and upper slot was 52 mm. The slotted tube was 15 cm long; its inner and outer diameters were 16 mm and 20 mm, respectively. The slotted tubes were prepared by Hazer Cam in Altındağ, Ankara.

To prepare the standard solutions, adjustable 100-1000 µL and 500-5000 µL Eppendorf micropipettes were used. The solutions were prepared in glass containers and then stored in polyethylene containers (100 mL capacity) in refrigerator.

In revolatilization step, the organic solvent was aspirated into flame by using 1.0 mL plastic cups and an adjustable micropipette.

2.2 Reagents

All reagents used in this study were of analytical grade or higher purity. The analyte solutions were prepared by 1000 mg/L High-Purity Standards silver stock solution. The working solutions were prepared daily and obtained after successive dilutions. For the dilutions, 18MΩ•cmdeionized water obtained from a Millipore (Molsheim, France) Milli-Q water purification system which was fed using the water produced by Millipore Elix 5 electro deionization system was used. All standard solutions were prepared in 1.0 M HNO_3, using analytical grade 65% (v/v) HNO_3 (Merck).

During interference study, 3 different solutions were prepared. In all solutions, Ag concentration was kept constant at 50.0 ng/mL, and interferent element concentrations were 1, 10 and 100 fold of the analyte concentration. Au (High Purity Standards), Cu (Merck), Ni (High Purity Standards), Pt (Merck), Cd (High Purity Standards), Zn (High Purity Standards), Co (Merck), Fe (High Purity Standards), Mn (Merck), As (Ultra Scientific), Se (High Purity Standards), Sb (Ultra Scientific), Bi (High Purity Standards), Hg (Merck), Sn (Merck), Pb (High Purity Standards), Tl (Ultra Scientific), In (High Purity Standards) were prepared from 1000 mg/L stock solution in 1.0 M HNO_3.

Throughout this study, all glassware and (polyethylene) plastics were stored in acid bath which is 10% (v/v) HNO_3 solution in a plastic container; the acid solution was prepared by diluting (1+9) the concentrated nitric acid reagent using water.The materials were immersed in acid bath at least 24 hours and washed with deionized water before use.

2.3 Atomic Absorption Spectrometer

In this study, ATI Unicam 929AA single beam spectrometer, equipped with a Deuterium (D_2) background correction system, was used for the absorbance measurements. Air-acetylene flame was used with a 10.0 cm burner head. The signals and results were saved by the help of SOLAAR AA software. VWR Scientific Ag hollow cathode lamp was used as a radiation source. Due to the mechanical restrictions, the sample suction rate could not be changed; it was 6.25 mL/min in the whole study. Summary of operating conditions are given in Table 2.1.

Table 2.1 Operating conditions of AA spectrometer

Parameter	**Value**
Wavelength of Ag, nm	328.1
Hollow Cathode Lamp Current, mA	4.0
Spectral Bandpass, nm	0.5
Flame Type	Air-Acetylene
Air Flow Rate, L/min	1.2

2.4 Coating Procedure for the SQT

The coating procedure was applied for the SQT having two slots positioned at 180° with respect to each other. 100 mL of 1000 mg/L standard solutions of Zr, W, Ti, Mo, Ta and Au were aspirated into the SQT in the presence of a fuel-lean flame for coating the SQT. The suction rate was 6.25 mL/min. After using the SQT 50-100 times, recoating was required since the sensitivity of the system decreased.Before recoating, the SQT was immersed in 10% (v/v) HF solution (concentrated reagent diluted 1+9 by water) for an hour to remove residuals, and then with the same procedure it was coated.

2.5 Surface Studies

Ag coated quartz surface was investigated by X-ray photoelectron spectroscopy (XPS) to identify the chemical nature of Ag. For XPS study, three 1.0 mm thick quartz pieces with the width of 1.0 cm and the length of 1.0 cm were used. These quartz pieces were carefully placed into the inner surface of the SQT. Then 150 mL of 10 mg/L Ag solution was aspirated into the SQT in the presence of fuel-lean flame for trapping Ag on quartz pieces. During coating, the suction rate was 6.25 mL/min.

PHI VersaProbe 5000-XPS instrument with Al dual mode was used for surface analysis in Middle East Technical University Central Laboratory. The instrument has a high pressure (up to 20 atm) reactor and also temperature capabilities (from -100 °C to 650 °C) in low and high pressures. The vacuum pumping of the instrument is too high (10^{-11} atm). In addition to these, the mass analyzer is functional up to 200 amu. Monochromatic Al Kα radiation was used as a X-ray source and for excitation of Ag on quartz 49.7 W energy was used. The quartz piece was irradiated with mono-energetic x-rays and then the photoelectrons were emitted from the surface of the quartz. The binding energy of these emitted photoelectrons was determined by an electron energy analyzer. By using the binding energies of photoelectrons; the elemental identity and chemical state of an element are determined. The binding energy of C 1s (284.5 eV) was used as an internal calibrant in order to estimate the chemical nature of Ag.

CHAPTER 3

RESULTS AND DISCUSSION

In this study, there are five main techniques handled for the determination of silver;

i. Firstly, simple FAAS technique was used for the determination of silver.

ii. SQT-FAAS was the second technique which improves sensitivity with the use of SQT. In the presence of SQT the flame speed is slow, therefore the residence time of analyte atoms in the measurement zoneincreases.In addition, due to the size restriction and partial elimination of oxidizing species in air, the chemical environment inside the absorption path is more stable. Only 180° angled SQT was used in this part.

iii. Thirdly, SQT-AT-FAAS technique was applied. In this case, the SQT is used as a trap medium for preconcentration. Sample solution is aspirated into the flame and analyte species are trapped on the inner surface ofthe SQT for a few minutes, then analyte atoms are revolatilizedby organic solvent aspiration. The technique was applied with 90°, 120° and 180° angled uncoated SQT to compare their efficiencies. 180°configuration of SQT was used in the rest of study. After optimum conditions were found, uncoated SQT-AT-FAAS technique was performed for the determination of silver.

iv. SQT-AT-FAAS technique was applied by coating the SQT with different elements for further sensitivity improvements. In this part, for the determination of silver W-coated SQT-AT-FAAS technique was used.

v. In the previous part, different coating elements were used and two of them gave sensitive results; W and Zr. For this reason, Zr coated SQT-AT-FAAS technique was also applied for the determination of silver.

The main point here is the evaluation of the sensitivity improvements of different techniques. Forcalculation of analytical figures of merit, the peak height values were used for signals. The standard deviation (s) values were calculated using the lowest analyte concentration. Characteristic concentration (C_0) which is the concentration that corresponds to 0.00436 absorbance (1% absorption); $C_0 = 0.00436 \times (\text{analyte concentration}/\text{absorbance})$ and limit of detection (LOD), found as $3s/m$, are the important figures of merit. In addition, limit of quantitation (LOQ), found as $10s/m$, is used in sensitivity comparison. Among them, since LOD is dependent on the instrument conditions, especially the source beam; it is better to consider the enhancement factor, E, obtained by taking the ratio of characteristic concentration values of the systems with and without atom trap. E is also known as ratio of calibration sensitivities (slopes). To compare the ratio of LOD values and E values is also useful; however, the figures of merit obtained for comparison may be different since LOD is dependent on both signal and reproducibility.

The critical part is the comparison of atom trap techniques, since different sample volumes or sampling periods render the comparisons difficult. In trap studies, sensitivity is directly related with the trapped analyte mass which increases with increasing trapping period. In many cases, it is difficult to decide whether sensitivity is improved or not since sample volume and trapping period can be given randomly. To overcome this confusion, new terms were introduced by Ataman [27] considering enhancement. The first defined value was maximum enhancement factor (E_{max}), which also depends on analyte concentration and matrix composition. Then two new terms were added; E_t and E_v, which are found as *dividing E value by total time spent* *in terms of minutes* and *dividing E value by total volume spent in terms of milliliters*, respectively. In addition to characteristic concentration (C_0), characteristic mass (m_0) is also used as a figure of merit. It is the mass of analyte that produces a defined peakthat has an absorbance value of 0.00436 (or 1% absorption) and found as the *(volume of trapped analyte) x* (C_0).

3.1 FAAS Technique

In this part, simple FAAS technique was used for the determination of silver. Acetylene flow rate was optimized in order to obtain high S/N ratio. 5.0 mg/L Ag solution was aspirated into the flame throughout the optimization.

3.1.1 Optimization of Fuel Flow Rate

In the optimization, the flow rate of air was kept constant at 1.2 L/min and sample flow rate was constant at 6.25 mL/min. As can be seen in Figure 3.1, the optimum fuel flow rate was found as 0.9 L/min. In case of higher flow rates, the Ag signals were getting worse and there was not an important change in absorbance. It is found that the optimum flame for silver determination with FAAS technique requires stochiometric flame.

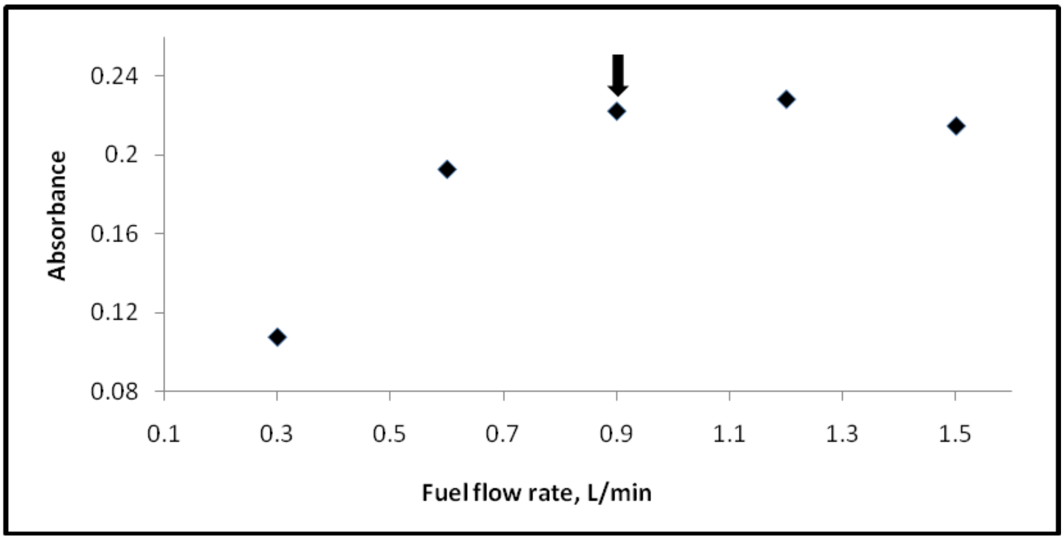

Figure 3.1 Optimization of fuel flow rate using 5.0 mg/L Ag in FAAS.
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min

3.1.2 Calibration Plots for FAAS Technique

In optimum conditions, the absorbance values of silver solutions in concentrations between 0.25-10.0 mg/L were obtained (Figure 3.2). Calibration plot is linear between 0.25-5.0 mg/L (Figure 3.3). The best line equation and correlation coefficient were, $y = 0.0449x + 0.0129$ and 0.9968, respectively, where x is the analyte concentration in mg/L.

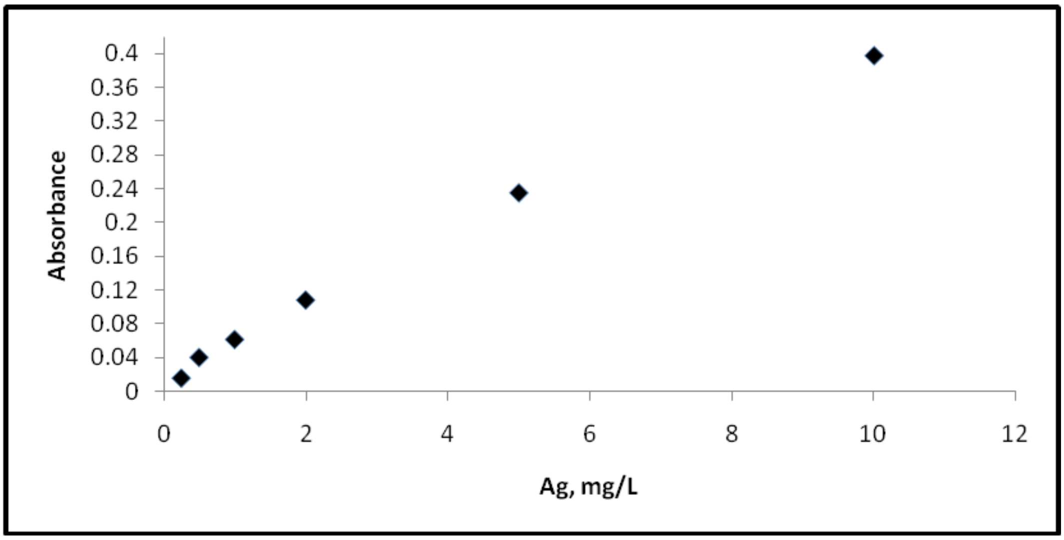

Figure 3.2 Calibration plot for FAAS technique.

Fuel flow rate: 0.9 L/min, Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

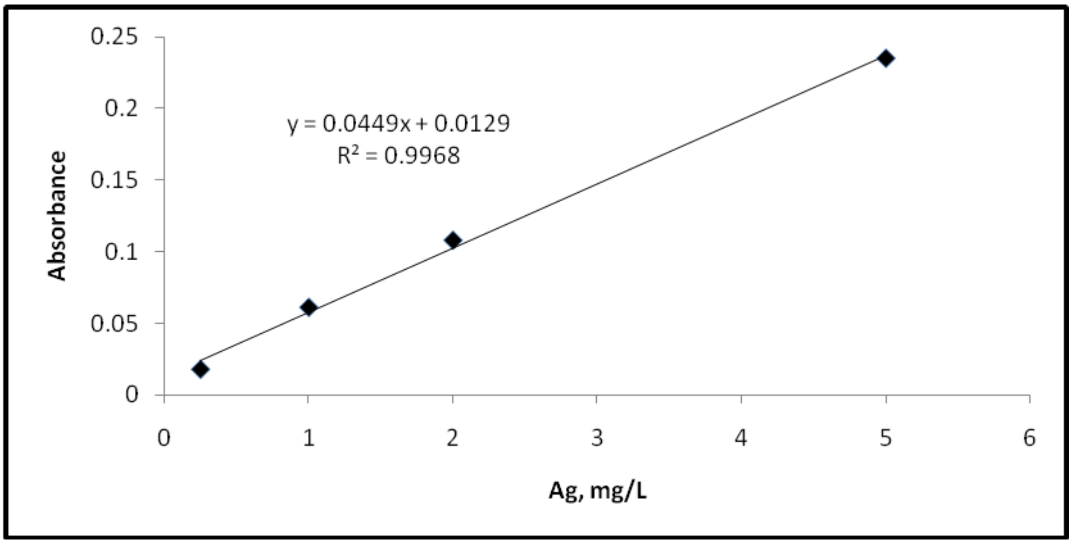

Figure 3.3 Linear calibration plot for FAAS technique.

Fuel flow rate: 0.9 L/min, Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

From the calibration plot, LOD and LOQ values were calculated as 76 ng/mL and 253 ng/mL, respectively. In order to find the values of LOD and LOQ, 11 measurements of 0.25 mg/L Ag solution were used. Characteristic concentration was found as 81 ng/mL. The calculated values can be seen in Table 3.1.

Table 3.1 Analytical figures of merit for FAAS technique.

Limit of Detection (LOD), ng/mL	76
Limit of Quantitation (LOQ), ng/mL	253
Characteristic Concentration (C_0), ng/mL	81
Linear Range, ng/mL	$2.50x10^2$-$50.0x10^2$

3.2 Slotted Quartz Tube FAAS Technique

In this technique, the SQT was used to improve the sensitivity as a result of increasing life time of analyte atoms in the measurement zone. The chemical environment inside the tube is more stable and the flame speed is slow in the presence of the SQT.The SQT is aligned with the optical path of the spectrometer and the lower slot of SQT is positioned directly above the flame. In order to improve sensitivity, fuel flow rate and height of the SQT from the burner head were optimized by using 5.0 mg/L Ag solution.

3.2.1 Optimization of Fuel Flow Rate

During optimization, the height of the SQT from the burner head was 5.0 mm. As seen in Figure 3.4, the optimum fuel flow rate was found as 1.2 L/min. The Ag signals are reproducible (%RSD, 1.45) and the absorbance values are high at this flow rate. Similar with FAAS, stochiometric flame is required for the determination of silver.

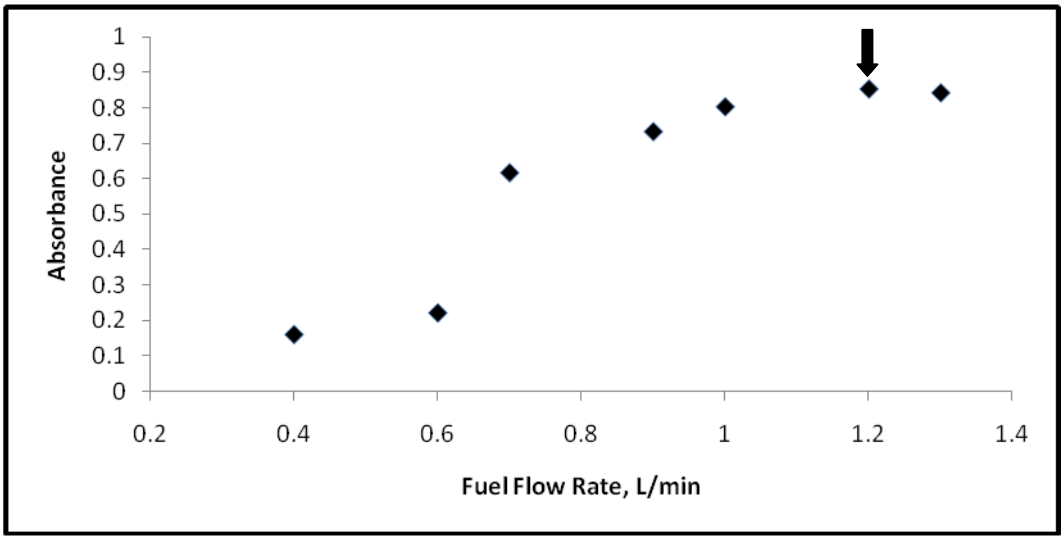

Figure 3.4 Optimization of fuel flow rate using 5.0 mg/L Ag in SQT-FAAS.
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min,
Height of SQT from the burner head: 5.0 mm.

3.2.2 Optimization of Height of the SQT from the Burner Head

Since the flame was extinguished, 5.0 mm was the lowest height that could be adjusted and it was found to be the optimum height of the SQT from the burner head, as shown in Figure 3.5. When the SQT is closer to the burner head, analyte atoms enter into the tube easily. For this reason, the sensitivity of 5.0 mm height of SQT from the burner head was higher than 8.0 mm and 11.0 mm.

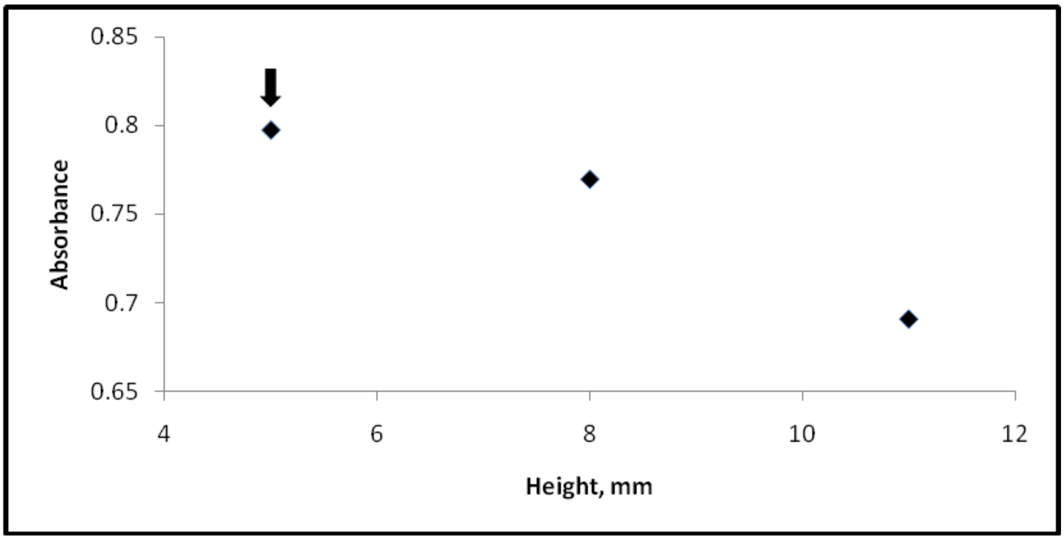

Figure 3.5 Optimization of height of SQT from the burner using 5.0 mg/L Ag in SQT-FAAS.

Fuel flow rate: 1.2 L/min, Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

3.2.3 Calibration Plots for SQT-FAAS Technique

After the optimum parameters were found, the calibration graph is drawn (Figure 3.6) with using Ag standard solutions in concentrations between 0.1-20 mg/L. Calibration plot is linear between 0.1-10 mg/L (Figure 3.7). The best line equation and correlation coefficient were, $y = 0.1213x + 0.0042$ and 0.9948, respectively, where x is the analyte concentration in mg/L.

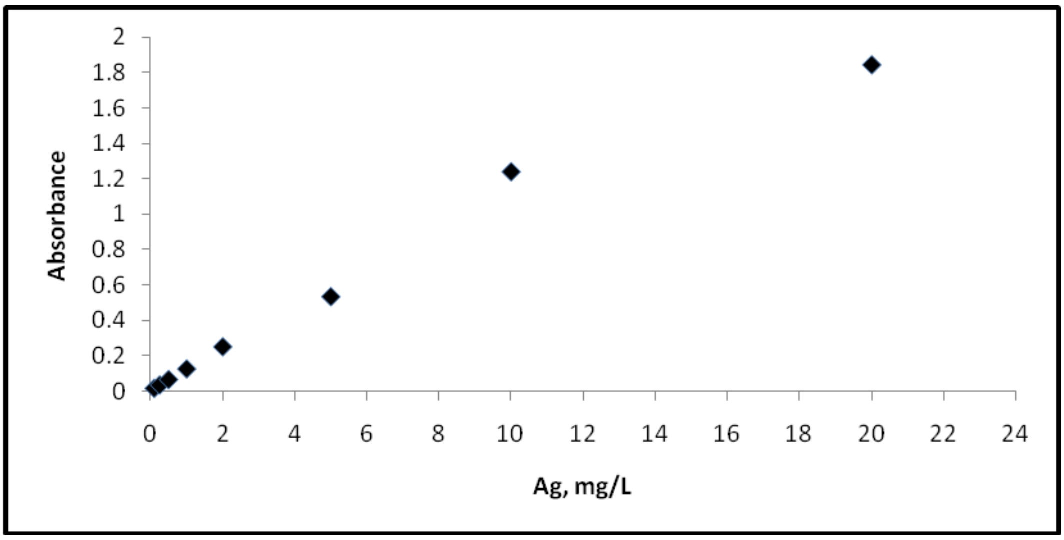

Figure 3.6 Calibration plot for SQT-FAAS technique.

Fuel flow rate: 1.2 L/min, Height of SQT from the burner head: 5.0 mm,
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

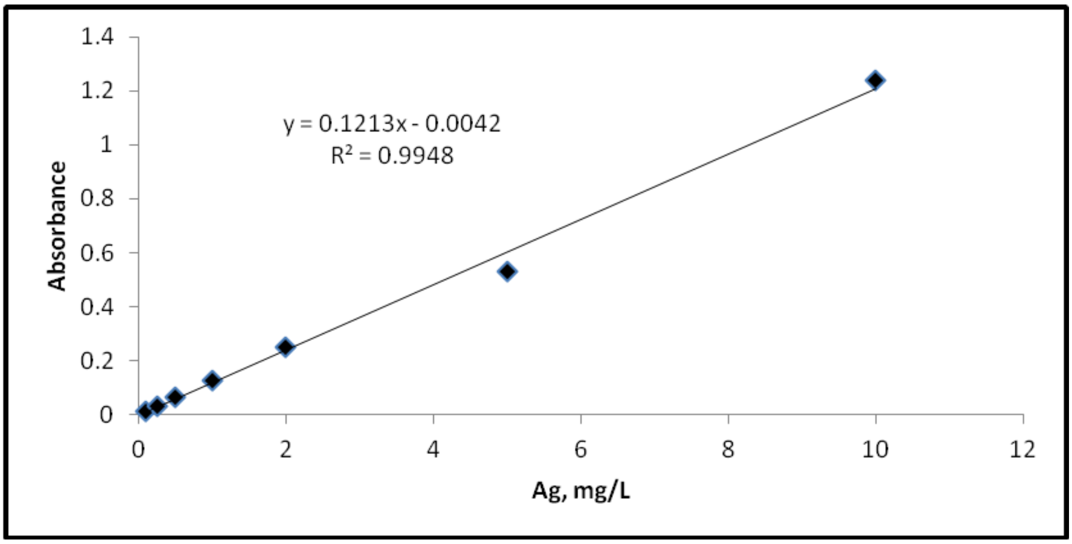

Figure 3.7 Linear calibration plot for SQT-FAAS technique.

Fuel flow rate: 1.2 L/min, Height of SQT from the burner head: 5.0 mm,
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

As seen in Table 3.2, LOD and LOQ values were calculated as 19 ng/mL and 65 ng/mL, respectively. Characteristic concentration was found as 35 ng/mL. In order to obtain LOD and LOQ values, 11 measurements of 0.25 mg/L Ag solution were used. The sensitivity enhancement was 2.31 fold with respect to FAAS technique.

Table 3.2 Analytical figures of merit for SQT-FAAS technique.

Limit of Detection (LOD), ng/mL	19
Limit of Quantitation (LOQ), ng/mL	65
Characteristic Concentration (C_0), ng/mL	35
Linear Range, ng/mL	$0.100\text{x}10^3$-$10.0\text{x}10^3$
Enhancement (E) with respect to FAAS	2.31

3.3 Slotted Quartz Tube Atom Trap FAAS Technique

At this stage, the SQT was used as a trap medium and analyte solution was aspirated into the inner surface of this medium to collect the analyte atoms for a few minutes. Then with the introduction of small volume of organic solvent, the fuel content of flame gases was momentarily increased and analyte atoms were revolatilized from the surface of the SQT. A transient signal was obtained after this rapid atomization.

At the beginning, uncoated SQT was used in the optimization studies. However, there was a memory effect which required aspirating the organic solvent more than 5 times. This excess organic solvent aspiration was time consuming. In order tosolve the memory problem, SQT was coated with Wand the revolatilization of atoms was tried again. This time memory effect was eliminated.For this reason,W-coated SQT was used throughout the optimization of atom trap parameters. Fuel flow rate, height of the SQT from the burner head, type and volume of organic solvent and trappingperiod were the important parameters that should be optimized.Finally; 90°, 120° and 180° angled SQT performance were compared and different coating elements were investigated in the optimum conditions.

3.3.1 Optimization of Fuel Flow Rate

In trap studies, fuel flow rate is an important parameter that should be carefully optimized. The optimum fuel flow rate was found as 0.27 L/min using 100.0 ng/mL Ag. This was a fuel-lean flame as usually expected in trap studies (Figure 3.8). In trap studies, a fuel-lean flame is required for the atoms to be trapped. Otherwise, the atoms may be atomized earlier and the absorption signals during releasing from the trap decrease. As seen in Figure 3.8, almost no signal was obtained at flow rates higher than 0.37 L/min.

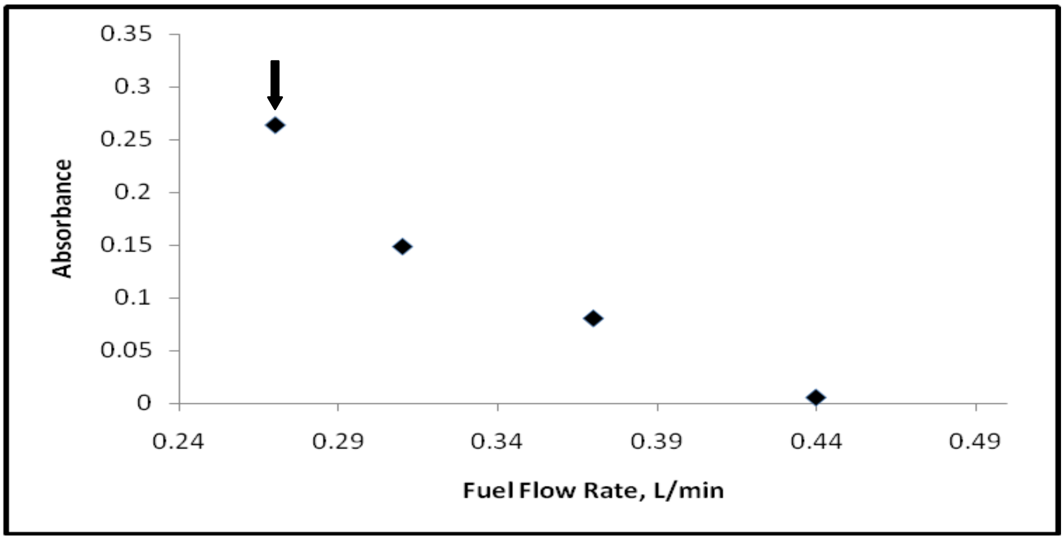

Figure 3.8 Optimization of fuel flow rate using 100.0 ng/mL Ag in SQT-AT-FAAS.

Height of SQT from the burner head: 2.0 mm, Organic solvent: IBMK
Volume of organic solvent: 25µL, Trapping period: 1.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

3.3.2 Optimization of Height of the SQT from the Burner Head

As seen in Figure 3.9, the optimum height of the SQT from the burner head was found as 2.0 mm. Similar with SQT-FAAS, increasing the height decreased the absorbance values since the sample solution could not efficiently enter the SQT. On the other hand, differently from SQT-FAAS, height could be adjusted lower than 5.0 mm since a fuel-lean flame was used. In SQT-FAAS; whenever the distance between the burner head and SQT was lower than 5.0 mm, the flame was extinguished.

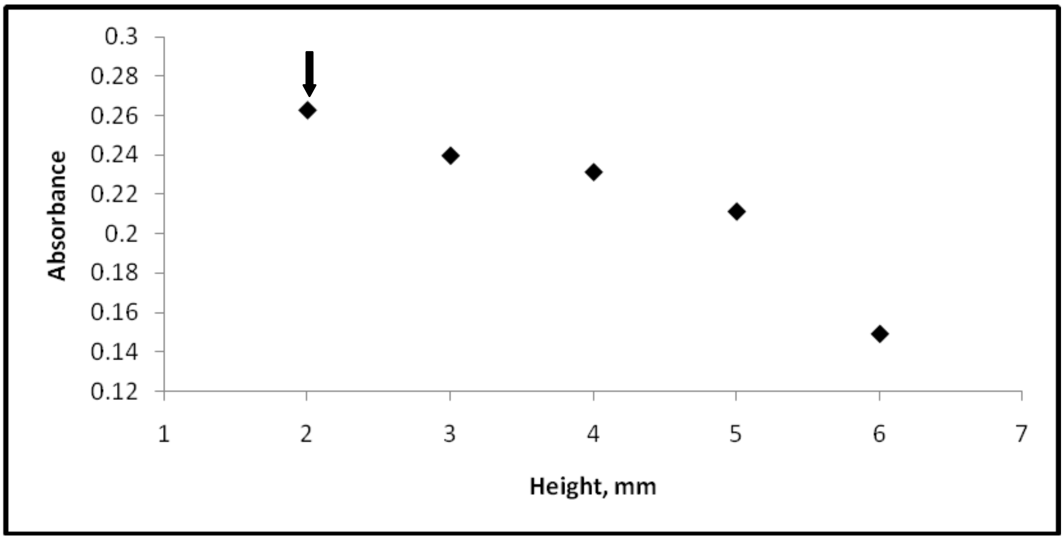

Figure 3.9 Optimization of height of SQT from the burner head using 100.0 ng/mL Ag in SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Organic solvent: IBMK
Volume of organic solvent: 25µL, Trapping period: 1.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

3.3.3 Optimization of Organic Solvent Type

In order to revolatilize the analyte atoms organic solvent aspiration technique was preferred. An optimum organic solvent should be highly flammable for rapid and complete revolatilization of analyte species. Therefore, from ketones to alcohols different types of organic solvents were tested to find the optimum one (Table 3.3). Organic solvent, having the lowest flash point at which it can vaporize to form an ignitable mixture in air, is expected to have the highest revolatilization performance. Although some have low flash points, no signal was obtained with the aspiration of ethanol, n-butanol, isopropyl alcohol, cyclopentanol and methanol. Therefore, it should be accepted that the nature of revolatilization is not known exactly. It is only estimated that the revolatilization is a complex process including radical formations. As shown in Figure 3.10, introduction of other organic solvents worked better. Acetonitrile was eliminated due to low absorbance values as compared with others. Although meaningful signals were obtained, n-Hexane was not selected since the flame was extinguished when it was introduced. The Ag signals obtained with MEK (%RSD, 9.39) and acetone (%RSD, 9.37) were not sharp and reproducible. For this reason, IBMK was found to be the proper organic solvent asthe Ag signals obtained with high absorbance value and reasonable reproducibility (%RSD, 3.44).

Table 3.3 Molecular formulas and flash points of the organic solvents used in the optimization of organic solvent type.

Organic Solvent	**Molecular Formula**	**Flash Point [72]**
Isobutyl methyl ketone (IBMK)	$C_6H_{12}O$	14 °C
Acetone	C_3H_6O	-17 °C
Methyl ethyl ketone (MEK)	C_4H_8O	-9 °C
n-Hexane	C_6H_{14}	-23 °C
Acetonitrile	C_2H_3N	2 °C
Ethanol	C_2H_6O	13 °C
n-Butanol	$C_4H_{10}O$	35 °C
Isopropyl alcohol	C_3H_8O	12 °C
Cyclopentanol	$C_5H_{10}O$	93 °C
Methanol	CH_4O	11 °C

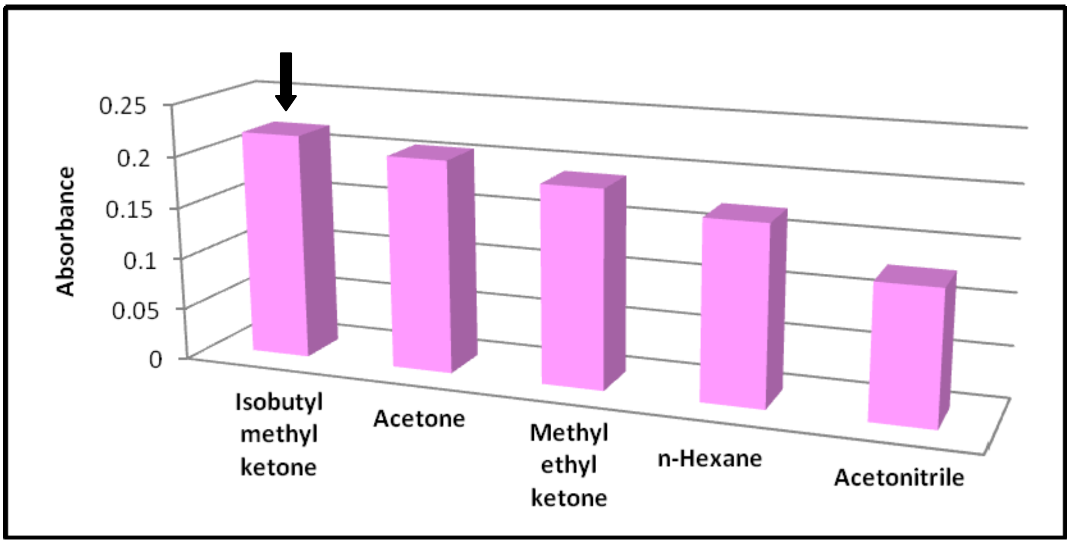

Figure 3.10 Effect of organic solvents on Ag signals using 100.0 ng/mL Ag in SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Volume of organic solvent: 25µL, Trapping period: 1.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

3.3.4 Optimization of Organic Solvent Volume

Organic solvent aspiration technique requires only a small volume of organic solvent for the revolatilization of trapped analyte atoms. For this reason, IBMK in volumes between 10-50 µL were used in order to select the optimum volume to be used. As seen in Figure 3.11, there was no significant difference between the absorbance values obtained using 25 µL and 35 µL; however, 25 µL was selected as the proper volume. The reason is that when high volumes of solvent were aspirated into the SQT, flame may tend to extend from the ends of the tube and damage the quartz windows of the instrument. In addition, the peak height of Ag signal was decreased for volumes of IBMK higher than 25 µL.

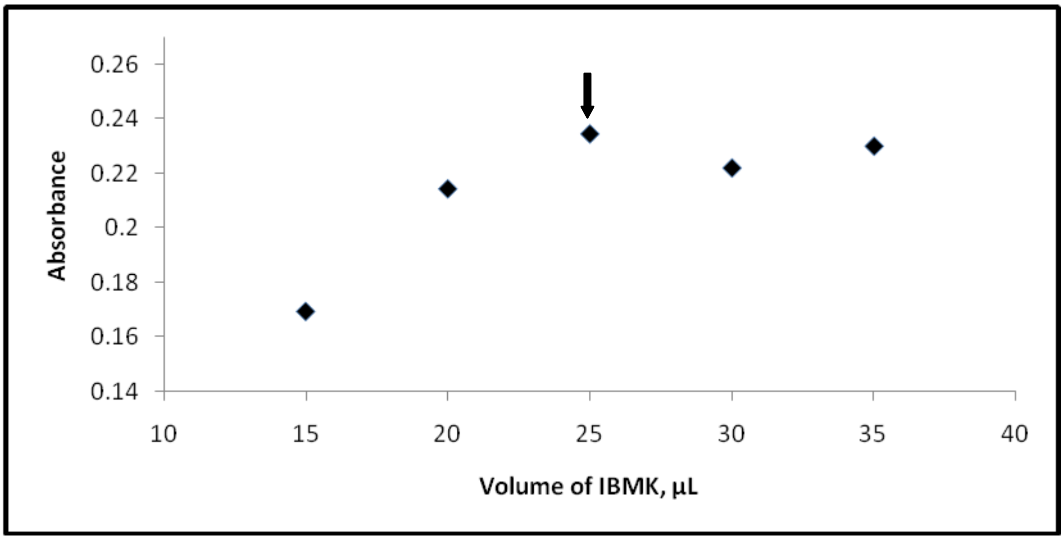

Figure 3.11 Optimization of organic solvent volume using 100 ng/mL Ag in SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Trapping period: 1.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

3.3.5 Effect of Trapping Period

In atom trap studies, increasing the collection time improves the sensitivity of the technique. However, shorter measurement time is also an important criterion to compete with other techniques. For this reason, 5.0 min was selected as an optimum trapping period (Figure 3.12). Above 5.0 min, there was not a significant increase; in addition, the curve deviated from linearity indicating a saturation effect for the SQT.

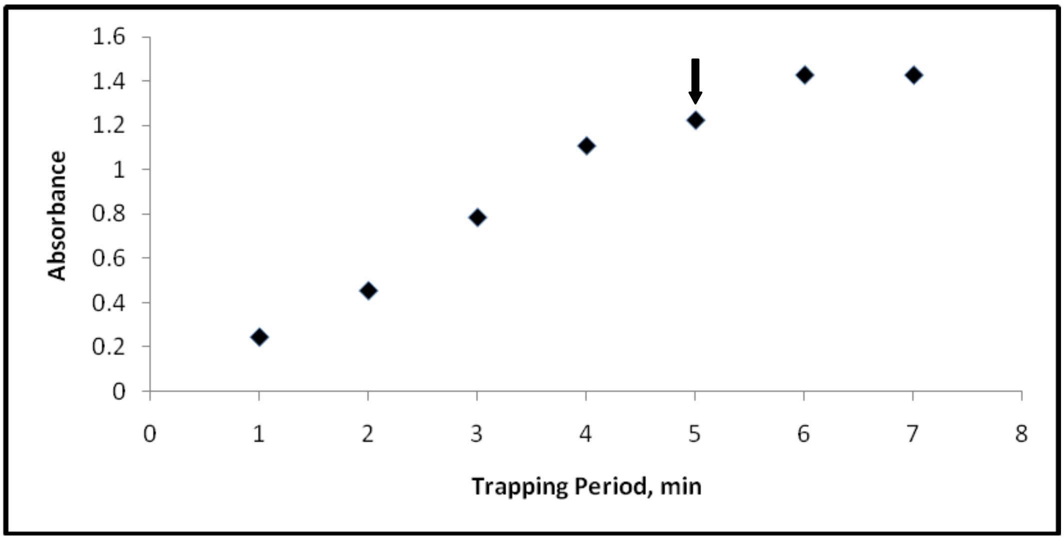

Figure 3.12 Optimization of trapping period using 100 ng/mL Ag in SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Volume of organic solvent: 25 μL
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

Table 3.4 Optimum parameters for SQT-AT-FAAS technique.

Parameter	Optimum Condition
Fuel Flow Rate, L/min	0.27
Height of SQT from the Burner Head, mm	2.0
Volume of Organic Solvent, μL	25
Organic Solvent	IBMK
Trapping Period, min	5.0

The signal of 100 ng/mL Ag, which was obtained in optimum conditions given in Table 3.4, is shown in Figure 3.13. Full width at half maximum (FWHM) of the signal was found to be 0.8 s.

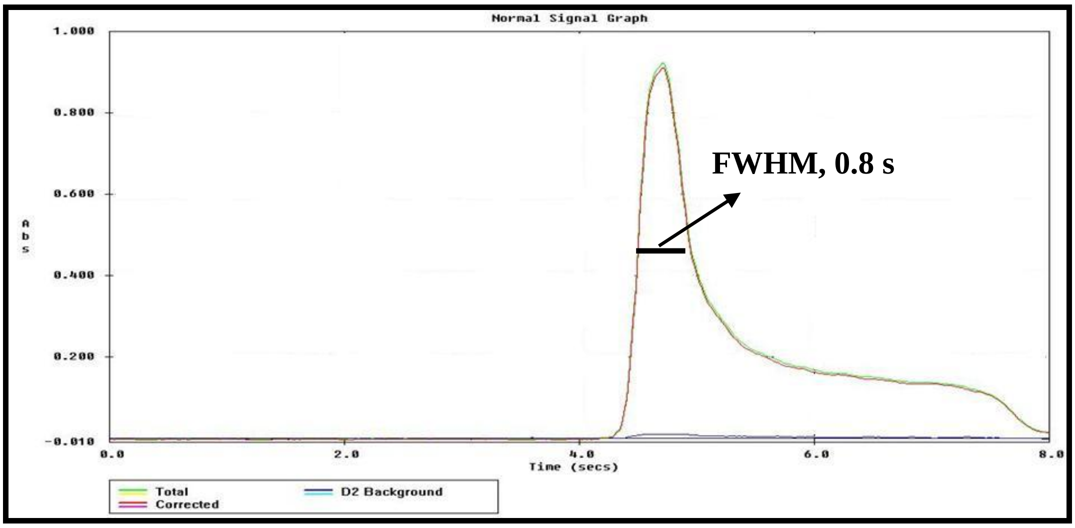

Figure 3.13 The signal of W-coated SQT-AT-FAAS for 100.0 ng/mL Ag in optimum conditions given in Table 3.4.

3.3.6 Investigation of 90°, 120° and 180° Angled SQT

The SQT atom trap optimizations were performed by using the SQT with two slots having an angle of 180°. By using the optimum conditions (Table 3.4) except the trapping period, the performance for 90°, 120° and 180° angled uncoated SQT devices were compared. As shown in Figure 3.14, the sensitivity of 180° angled SQT was higher than the others. In addition, the Ag signals for 90° and 120° angled SQT devices were broad and not reproducible. Therefore, only 180° angled SQT was used in the measurement of calibration standards.

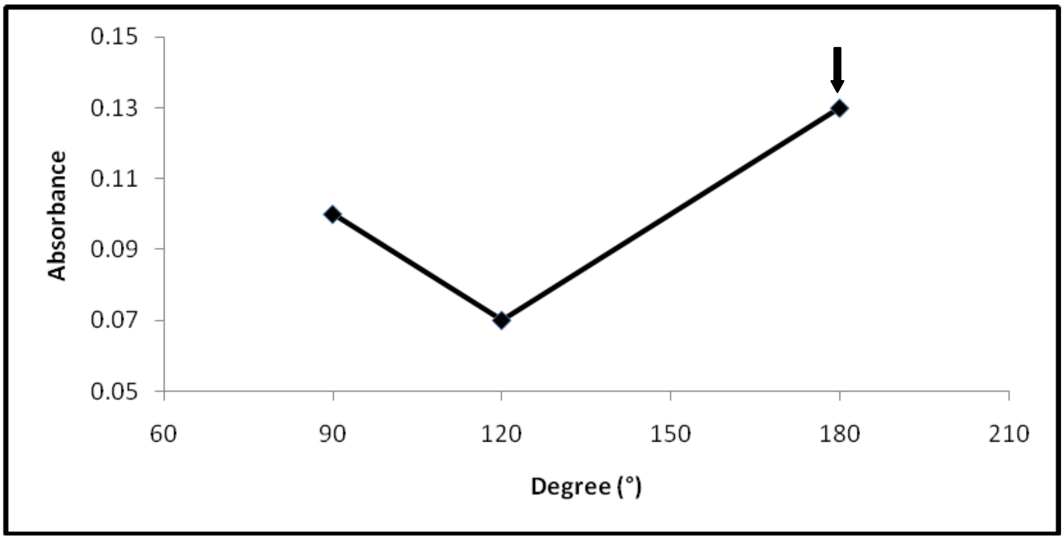

Figure 3.14 Performance of 90°, 120° and 180° angled SQT using 100 ng/mL Ag in SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Volume of organic solvent: 25 μL, Trapping period: 1.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

3.3.7 Calibration Plots for Uncoated SQT-AT-FAAS Technique

In order to obtain the calibration plots for uncoated SQT-AT-FAAS, optimum conditions (Table 3.4) were used. Ag solutions in concentrations between 5.0-100 ng/mL were used for the calibration plot which was linear between 10-100 ng/mL (Figure 3.16). %RSD was found to be 2.24. The best line equation and correlation coefficient were, $y = 0.0025x + 0.0175$ and 0.9995, respectively.

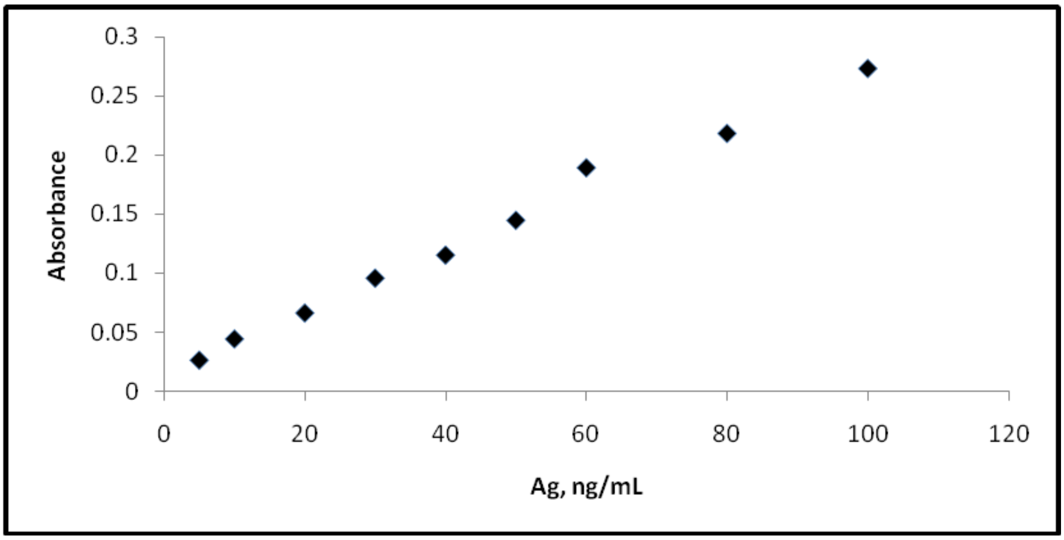

Figure 3.15 Calibration plot for uncoated SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Volume of organic solvent: 25 µL, Trapping period: 5.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

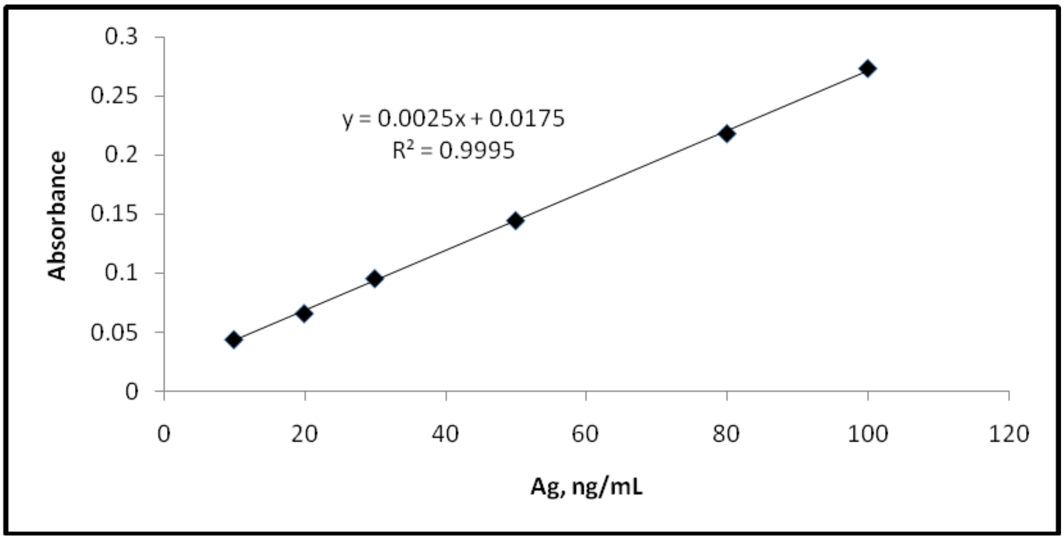

Figure 3.16 Linear calibration plot for uncoated SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Volume of organic solvent: 25 µL, Trapping period: 5.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

In Figure 3.17, the signal for 50 ng/mL Ag, whose absorbance value was used to calculate the characteristic concentration of uncoated SQT-AT-FAAS technique, is shown. The half bandwidth of the signal was found as 1.1 s.

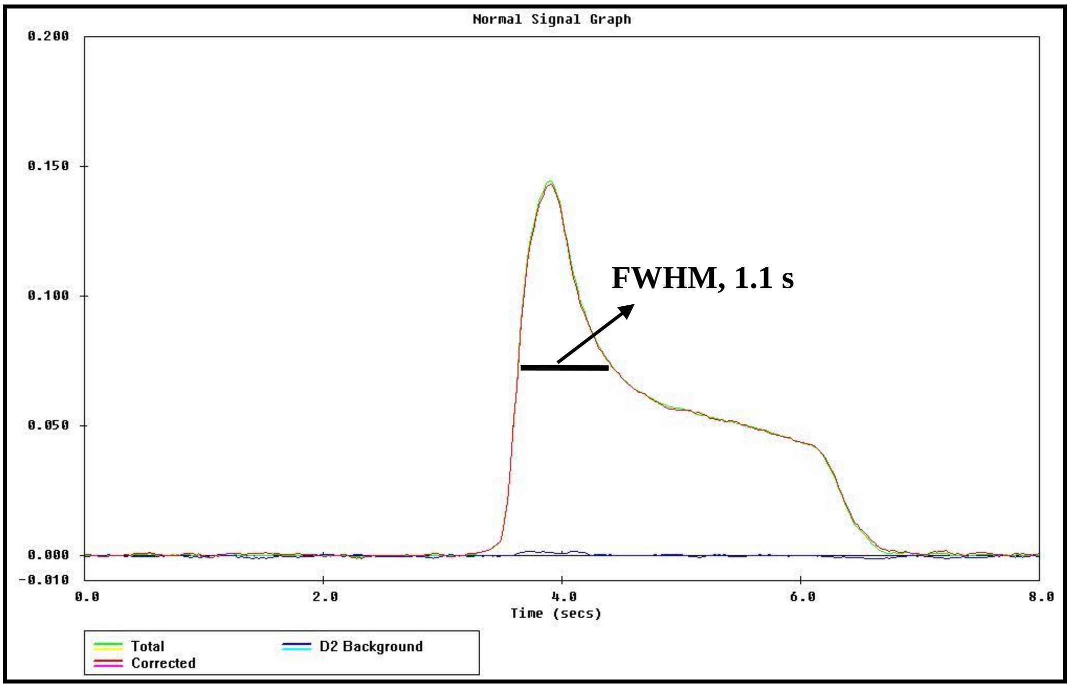

Figure 3.17 The signal of uncoated SQT-AT-FAAS for 50 ng/mL Ag in optimum conditions (Table 3.4).

3.3.8 Analytical Figures of Merit

The analytical figures of merit of uncoated SQT-AT-FAAS were calculated as seen in Table 3.5. LOD and LOQ values were calculated as 3.1 ng/mL and 10.3 ng/mL, respectively. These values were obtained with 11 measurements of 5.0 ng/mL Ag solution. Characteristic concentration was calculated as 1.5 ng/mL. The sensitivity enhancement was 54 fold with respect to FAAS technique.All these values were obtained by using a sample suction rate of 6.25 mL/min and 5.0 min sampling.

Table 3.5 Analytical figures of merit for uncoated SQT-AT-FAAS technique.

Limit of Detection (LOD), ng/mL	3.1
Limit of Quantitation (LOQ), ng/mL	10.3
Characteristic Concentration (C_0), ng/mL	1.5
Characteristic Mass (m_0), ng	47.0
Linear Range, ng/mL	10-100
Enhancement (E) with respect to FAAS	54
Enhancement (E) with respect to SQT-FAAS	23

3.4 Investigation of Coating Materials for SQT-AT-FAAS Technique

The coating procedure is important since a significant increase in sensitivity may be observed depending on the analyte element and coating element. The melting point of the coating element should be close to or significantly higher than the boiling point of the analyte element. In other words, the coating element should not leave the inner surface of SQT before the analyte element revolatilizes from the surface. As described in Section 2.4, using fuel-lean flame, 100 mL of 1000 mg/L standard solutions of Zr, W, Ti, Mo, Ta and Au were sentinto the SQT through conventional nebulization to coat the inner surface of the tube.

As seen in Figure 3.18, the absorbance values obtained for Ta and Au coated SQTs were small as compared to uncoated SQT. Although the absorbance values of Mo and Ti coated SQTs were close to the uncoated SQT, there was a splitting in Ag signals. Therefore, they were also eliminated for further studies. The absorbance values of Zr and W coated SQT devices were close to each other and both of them indicated increased sensitivity. Therefore, both Zr and W coated SQT-AT-FAAS techniques were used for the determination of silver.

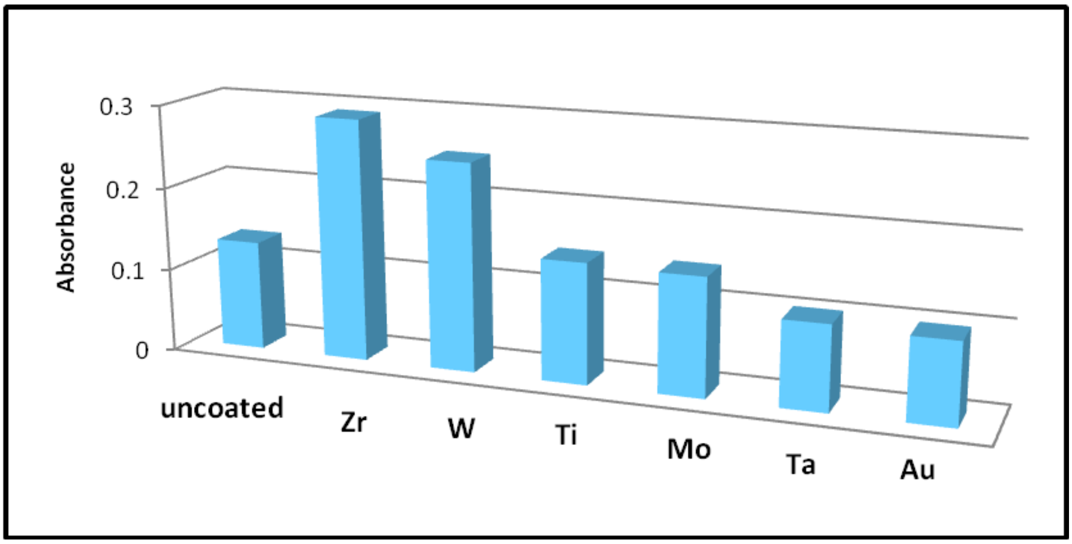

Figure 3.18 Effect of coating materials for 100 ng/mL Ag signal in SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Volume of organic solvent: 25 µL, Trapping period: 1.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

As shown in Table 3.6, the melting point of Zr is lower than the boiling point of the Ag. However, this condition did not create a serious problem because, ifthe flame temperature during revolatilization step reaches such a high value, at first quartz will melt. In addition, the revolatilization step in atom traps takes only a few seconds which is too short to remove the coating element from the surface of SQT even if the flame is too hot.Therefore; the melting point of the coating element may be lower than the boiling point of the analyte.

Table 3.6 Comparison of melting and boiling points of Ag, Zr and W.

	Ag	**Zr**	**W**	**Quartz**
Melting Point, °C	961	1855	3422	1650
Boiling Point, °C	2212	4409	5828	2230

3.5 Calibration Plots for W-coated SQT-AT-FAAS

After coating procedure, W-coated SQT-AT-FAAS technique was performed using optimum conditions that were shown in Table 3.4. In order to obtain the calibration plots, Ag solutions in concentrations between 2.5-100 ng/mL were used. The calibration plot was linear between 2.5-100 ng/mL (Figure 3.20). % RSD was found to be 4.04. The best line equation and correlation coefficient were, $y = 0.008x + 0.0029$ and 0.9995, respectively.

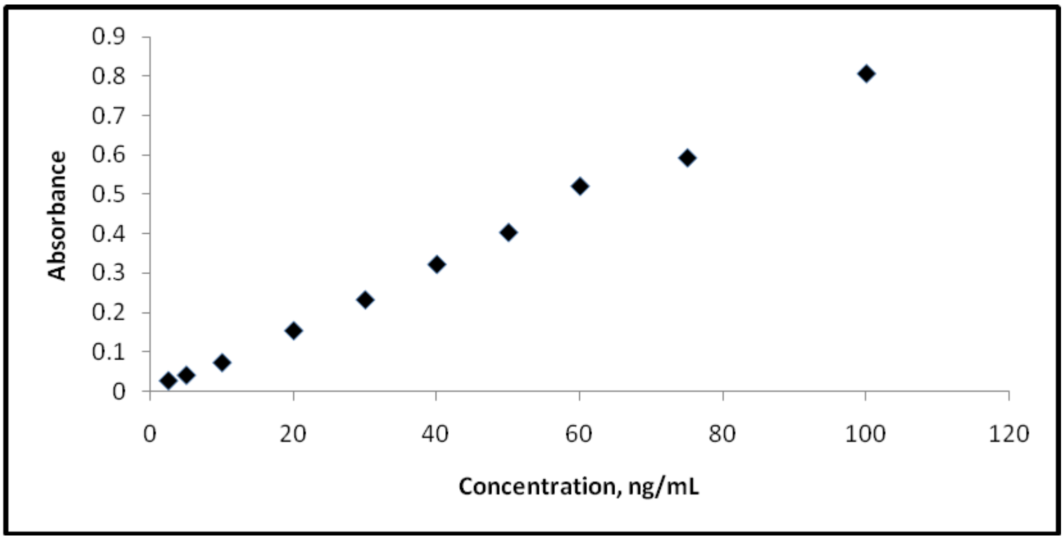

Figure 3.19 Calibration plot for W-coated SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Volume of organic solvent: 25 µL, Trapping period: 5.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

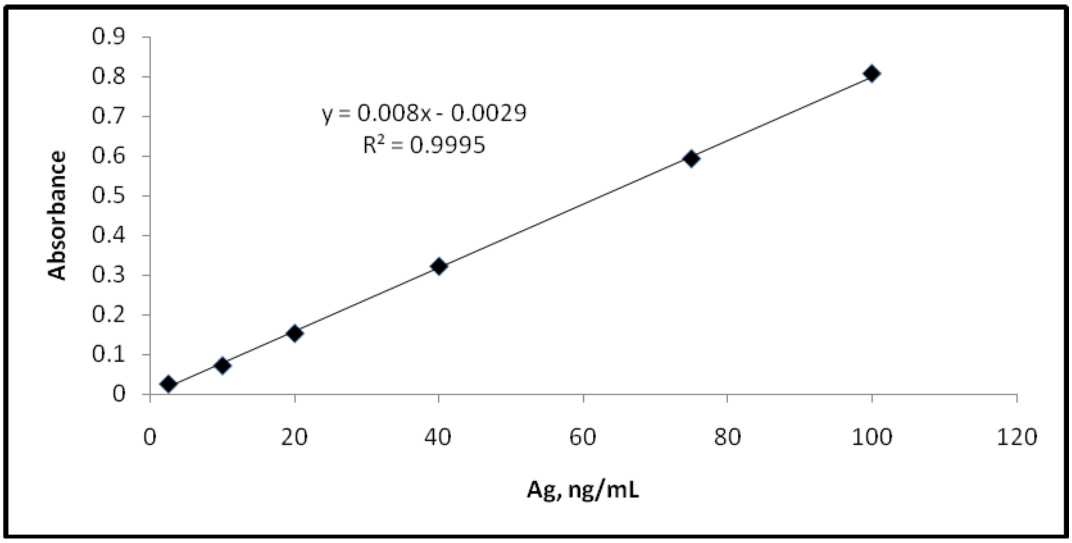

Figure 3.20 Linear calibration plot for W-coated SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Volume of organic solvent: 25 µL, Trapping period: 5.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min

The signal of W-coated SQT-AT-FAAS, whose absorbance value was used to find the characteristic concentration, is shown in Figure 3.21. The half bandwidth of the signal was found as 0.6 s.

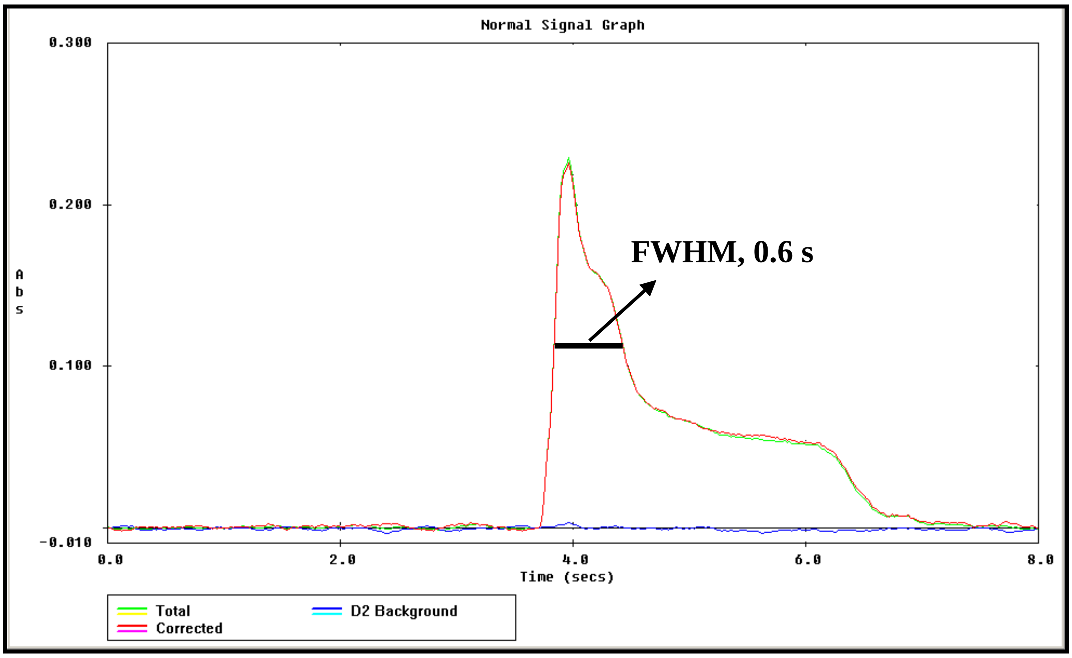

Figure 3.21 The signal of W-coated SQT-AT-FAAS for 30 ng/mL Ag in optimum conditions (Table 3.4).

3.5.1 Analytical Figures of Merit

The analytical figures of merit for W-coated SQT-AT-FAAS have been calculated as shown in Table 3.7. After 11 measurements of 2.5 ng/mL Ag solution, LOD and LOQ values were determined as 0.7ng/mL and 2.5 ng/mL, respectively. Characteristic concentration was found as 0.6 ng/mL. W-coated SQT-AT-FAAS technique was 135 fold more sensitive than the simple FAAS technique.All these values were obtained by using a sample suction rate of 6.25 mL/min and 5.0 min sampling.

Table 3.7 Analytical figures of merit for W-coated SQT-AT-FAAS technique.

Limit of Detection (LOD), ng/mL	0.7
Limit of Quantitation (LOQ), ng/mL	2.5
Characteristic Concentration (C_0), ng/mL	0.6
Characteristic Mass (m_0), ng	18.8
Linear Range, ng/mL	2.5-100
Enhancement (E) with respect to FAAS	135
Enhancement (E) with respect to SQT-FAAS	58
Enhancement (E) with respect to uncoated SQT-AT-FAAS	3

3.6 Calibration Plots for Zr-coated SQT-AT-FAAS

Using the optimum conditions given in Table 3.4, the absorbance values of Ag calibration standards in concentrations between 0.5-100 ng/mL were measured. The calibration plot was linear between 1.0-100 ng/mL (Figure 3.22). %RSD was found to be 1.21. The best line equation and correlation coefficient were, $y = 0.0136x + 0.0369$ and 0.9994, respectively.

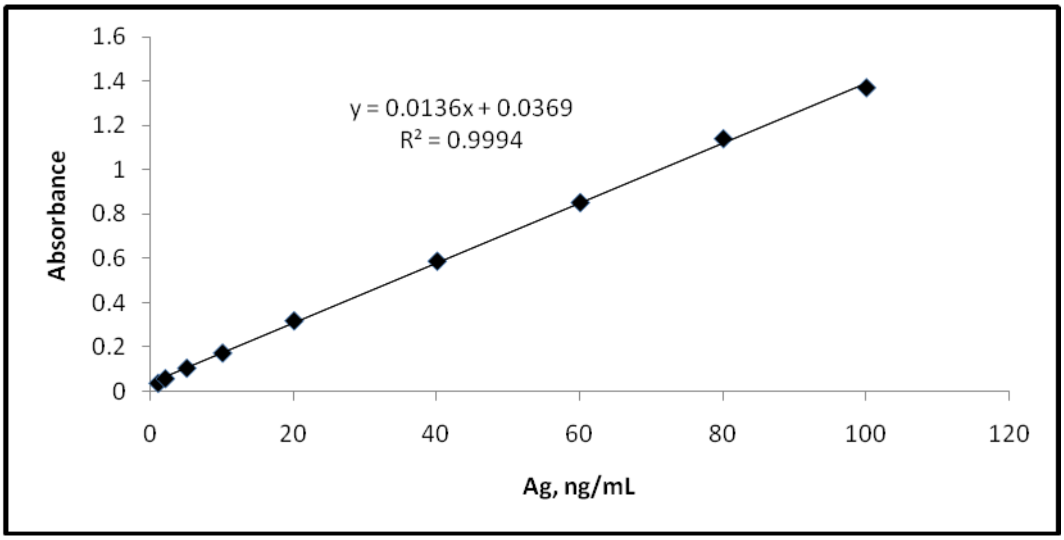

Figure 3.22 Linear calibration plot for Zr-coated SQT-AT-FAAS.

Fuel flow rate: 0.27 L/min, Height of SQT from burner head: 2.0 mm
Organic solvent: IBMK, Volume of organic solvent: 25 μL, Trapping period: 5.0 min
Flow rate of air: 1.2 L/min, Sample suction rate: 6.25 mL/min.

The absorbance value of the signal shown in Figure 3.23 was used to estimate the characteristic concentration of the Zr-coated SQT-AT-FAAS technique. The half bandwidth of the signal was found as 1.0 s.

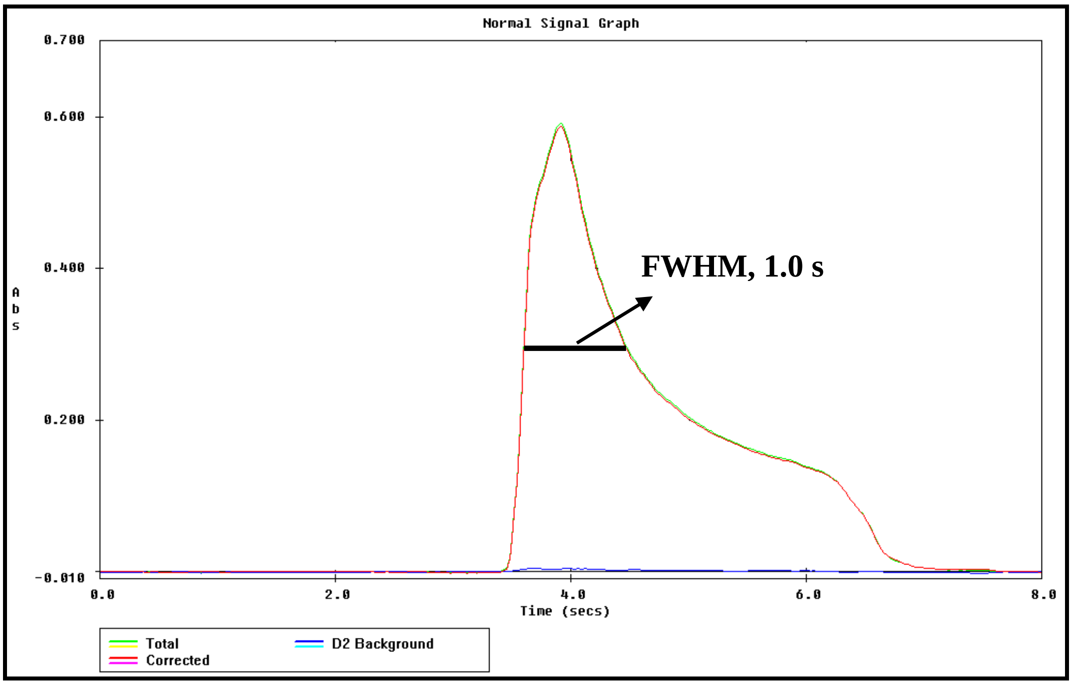

Figure 3.23 The signal of Zr-coated SQT-AT-FAAS for 40 ng/mL Ag in optimum conditions (Table 3.4).

3.6.1 Analytical Figures of Merit

Table 3.8 shows the analytical sensitivity parameters of Zr-coated SQT-AT-FAAS technique. LOD and LOQ values were calculated as 0.3ng/mL and 0.9 ng/mL, respectively. These values were obtained with 11 measurements of 0.5 ng/mL Ag solution. Characteristic concentration was calculated as 0.3 ng/mL. The enhancement of Zr-coated SQT-AT-FAAS technique was 270 fold with respect to FAAS technique.All these values were obtained by using a sample suction rate of 6.25 mL/min and 5.0 min sampling.

Table 3.8 Analytical figures of merit for Zr-coated SQT-AT-FAAS technique.

Limit of Detection (LOD), ng/mL	0.3
Limit of Quantitation (LOQ), ng/mL	0.9
Characteristic Concentration (C_0), ng/mL	0.3
Characteristic Mass (m_0), ng	9.4
Enhancement (E) with respect to FAAS	270
Enhancement (E) with respect to SQT-FAAS	117
Enhancement (E) with respect to uncoated SQT-AT-FAAS	5
Enhancement (E) with respect to W-coated SQT-AT-FAAS	2

3.7 Evaluation of System Performance

The analytical figures of merit of all techniques used in this study are summarized in Table 3.9. It seems that sensitivity improvement is required for simple FAAS technique. As seen in Table 3.9, the best sensitivity enhancement with respect to FAAS was obtained 270 fold using Zr-coated SQT-AT-FAAS technique. On the other hand, 135 fold enhancement in sensitivity was obtained using W-coated SQT-AT-FAAS technique.Zr and W both improved the sensitivity of the system. However, Zr was better as a coating element. The reason is that the analytical signals of Ag were more reproducible (%RSD, 1.21) using Zr-coated SQT.

If the SQT was not coated with any coating material, there was still an increase in sensitivity with respect to FAAS technique where the detection limit was found as 3.1 ng/mL. However, there was a memory effect without coating element.

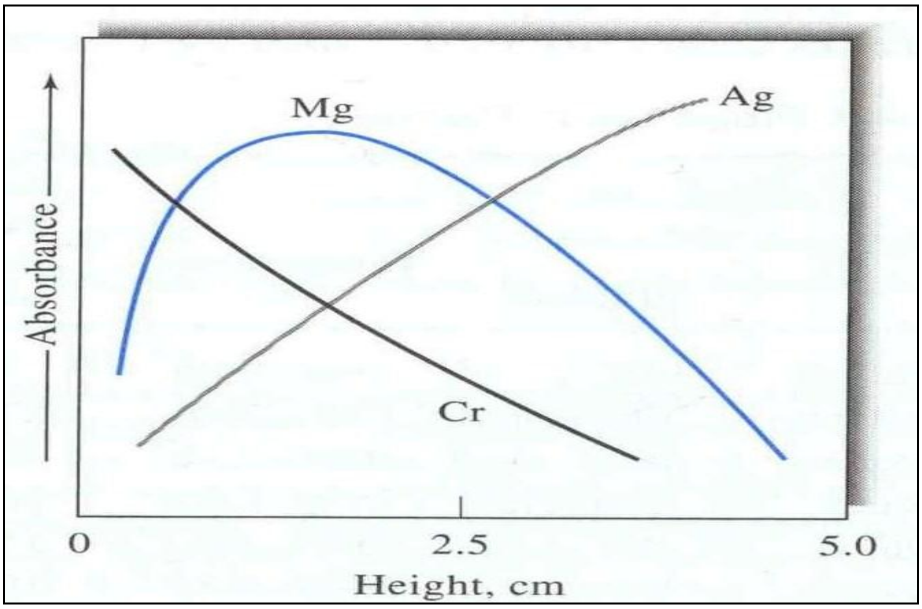

Figure 3.24 Flame absorption profiles for three elements [73].

As shown previously in Figure 3.17, Figure 3.21 and Figure 3.23 in turn there was a tailing problem in Ag signals and the problem was independent of the coating element. The tailing was observed in both coated and uncoated SQT atom trap techniques. Figure 3.24 illustrates the flame absorption profile of Ag and according to this profile Ag atoms have long life times in flame. Therefore, the atoms stay in SQT for a long time. However, since the flame conditions return back to lean flame after 1 second and the flame conditions are not optimum any more, the signal is decreased.Then a tailing is observed in the signals. It should be accepted that the reason for this undesirable behaviour in the signal may be related with the long life time of Ag atoms in flame.

Table 3.9 Comparison of Techniques in Terms of E, E_t and E_v Values.

	LOD, ng/mL	**LOQ, ng/mL**	**C_0, ng/mL**	**m_0, ng**	**E**	**E_t, min^{-1}**	**E_v, mL^{-1}**	**Slope, L/mg**
FAAS	76	253	81		1			0.0449
SQT-FAAS	19	65	35		2.31			0.1239
Uncoated SQT-AT-FAAS*	3.1	10.3	1.5	47.0	54	10.8	1.7	2.5
W-coated SQT-AT-FAAS*	0.7	2.5	0.6	18.8	135	27	4.3	8
Zr-coated SQT-AT-FAAS*	0.3	0.9	0.3	9.4	270	54	8.6	13.6

$E = C_{0\ (FAAS)}/C_{0\ (Selected\ Method)}$, $E_t = E/t_{total}$, $E_v = E/v_{total}$

* Total time (Trapping period): 5.0 min, Total volume: 31.3 mL

As seen in Table 3.10, the suggested techniques in this study are competing with the most sensitive analytical techniques such as ICP-MS, ICP-OES, CVG-AAS and ETAAS. Besides their sensitivity, the developed techniques are also simple and very inexpensive.

Table 3.10 Comparison of LOD values of different techniques with the developed atom trap techniques in this study.

Technique	LOD, ng/mL
ICP-MS	0.15 [41]
CVG-AAS	1.4 [33]
ETAAS	20 [74]
CVG-ICP-OES	50.1 [40]
Uncoated-SQT-AT-FAAS	3.1
W-coated SQT-AT-FAAS	0.7
Zr-coated SQT-AT-FAAS	0.3

3.8 Interference Studies

In order to investigate the effect of some elements on Ag signals, the interference studies were performed by using Zr-coated SQT-AT-FAAS technique. In this study; 3 different solutions were prepared for each element. In all solutions, Ag concentration was kept constant at 50.0 ng/mL, and interferent element concentrations were 1, 10 and 100 fold of the analyte concentration using the units of ng/mL. The effect of transitions and noble metals such as Cu, Zn, Au, Pt, Cd, Ni, Fe, Mn, Co and hydride forming elements such as Se, Sb, As, Hg, Sn, Bi, Tl, In, Bi were investigated in acidified solution (1.0 M HNO_3). The optimum conditions shown in Table 3.5 were used except that, the trapping period was 1.0 min instead of 5.0 min.

The effect of transition and noble metals were shown in Figure 3.25, Figure 3.26 and Figure 3.27. As seen in Figure 3.25, Zn did not have any effect on the analytical signal of Ag. 1 and 10 fold of Cu and Au also did not have a significant effect on the Ag signal. However, 100 fold of Cu and Au suppressed the Ag signal by 28% and 32%, respectively.

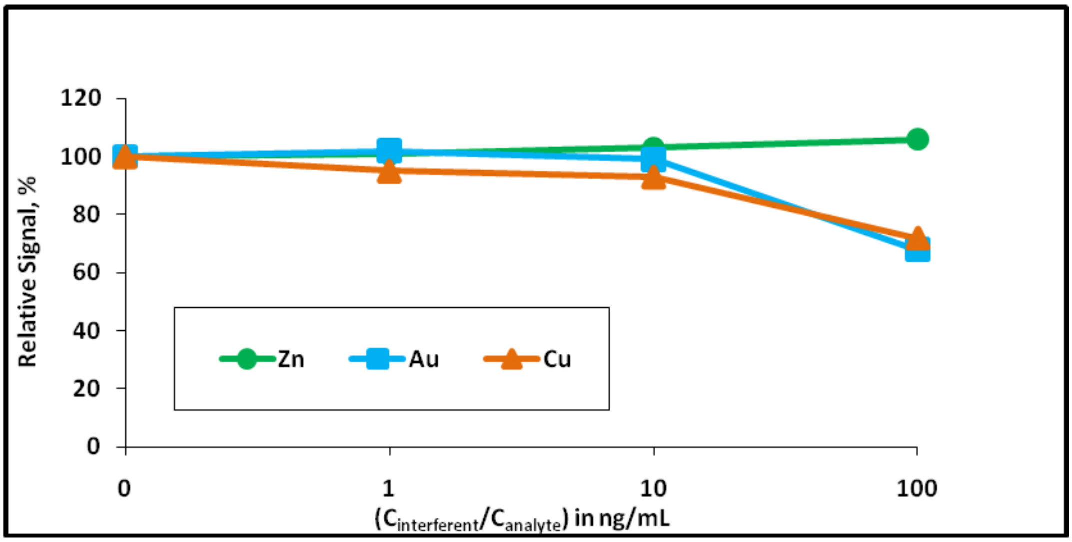

Figure 3.25 Interference effects of Cu, Zn and Au on the analytical signal of 50.0 ng/mL Ag using Zr-coated SQT-AT-FAAS.

1, 10 and 100 fold of Pt, Cd and Ni slightly altered the Ag signal, as seen in Figure 3.26. These effects were 10% or lower.

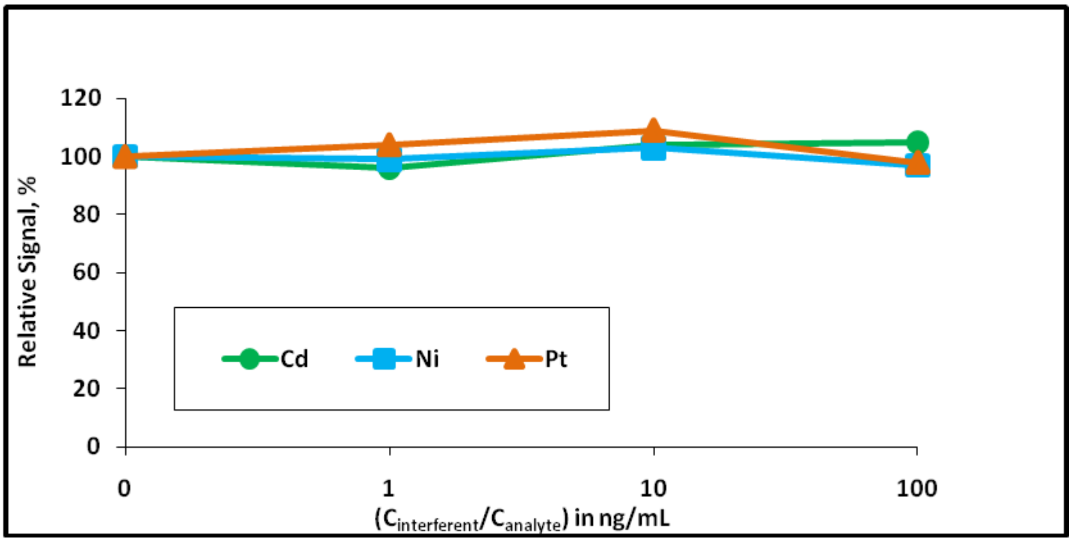

Figure 3.26 Interference effects of Pt, Cd and Ni on the analytical signal of 50.0 ng/mL Ag using Zr-coated SQT-AT-FAAS.

As shown in Figure 3.27; although 1 and 10 fold of Fe did not affect the Ag signal, 100 fold Fe increased the Ag signal by 34%. 100 fold of Mn also increased the Ag signal by 21% and only a slightly increase was observed for 1 and 10 fold of Mn. On the other hand, Ag signal was suppressed in the presence of Co. 1 and 10 fold of Co suppressed the Ag signal by 17% while 100 fold Co suppressed by 30%.

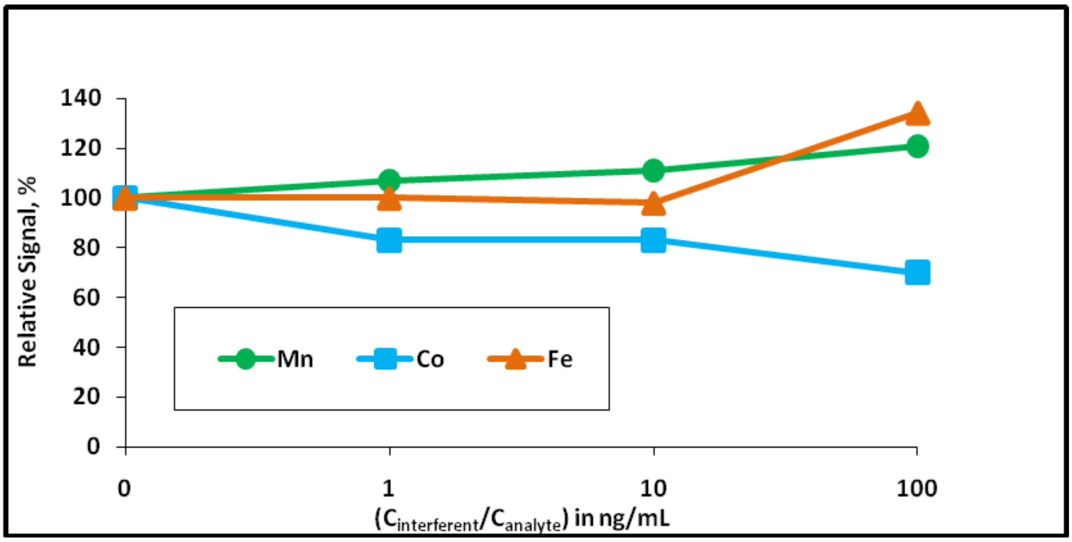

Figure 3.27 Interference effects of Fe, Mn and Co on the analytical signal of 50.0 ng/mL Ag using Zr-coated SQT-AT-FAAS.

The effects of hydride forming elements were shown in Figure 3.28, Figure 3.29 and Figure 3.30. In Figure 3.28, the effects of Se, Sb and As are shown. These three hydride forming elements did not have a significant effect on the analytical signal of Ag.

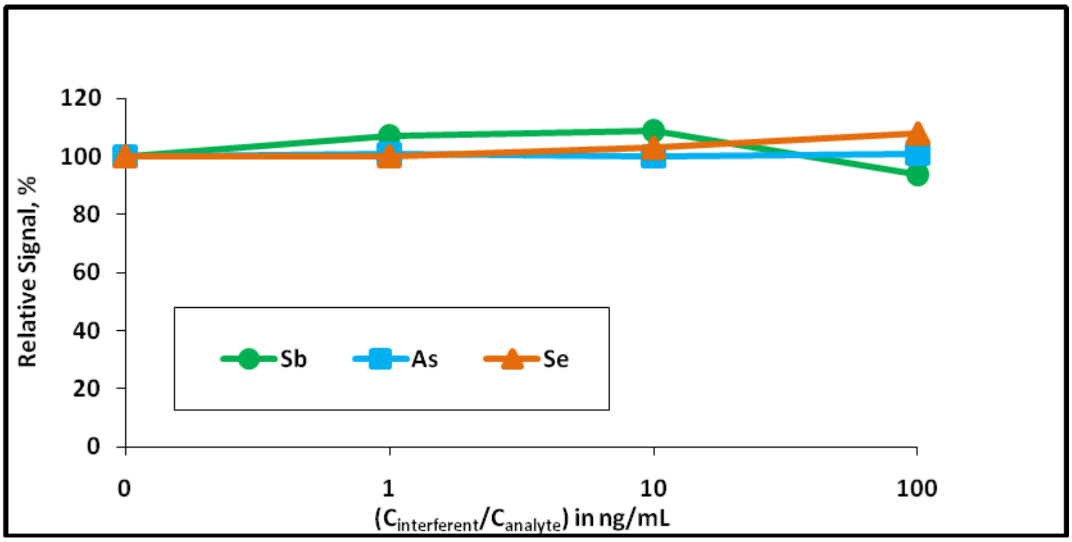

Figure 3.28 Interference effects of Se, Sb and As on the analytical signal of 50.0 ng/mL Ag using Zr-coated SQT-AT-FAAS.

As given in Figure 3.29; Sn ve Bi were having similar behaviours; 1 and 10 fold of both elements did not change the Ag signal and 100 fold of them slightly suppressed the Ag signal. While lower concentrations of Hg did not affect the Ag signal, 100 fold of Hg increased the Ag signal by 17%.

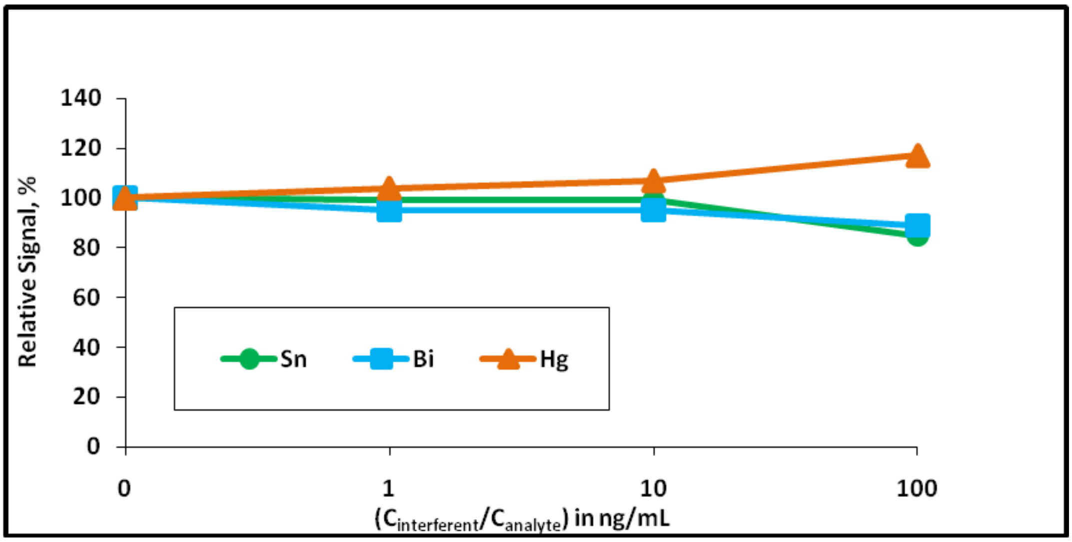

Figure 3.29 Interference effects of Hg, Sn and Bi on the analytical signal of 50.0 ng/mL Ag using Zr-coated SQT-AT-FAAS.

As shown in Figure 3.30; Tl, Pb and In did not have a significant effect on the analytical signal of Ag.

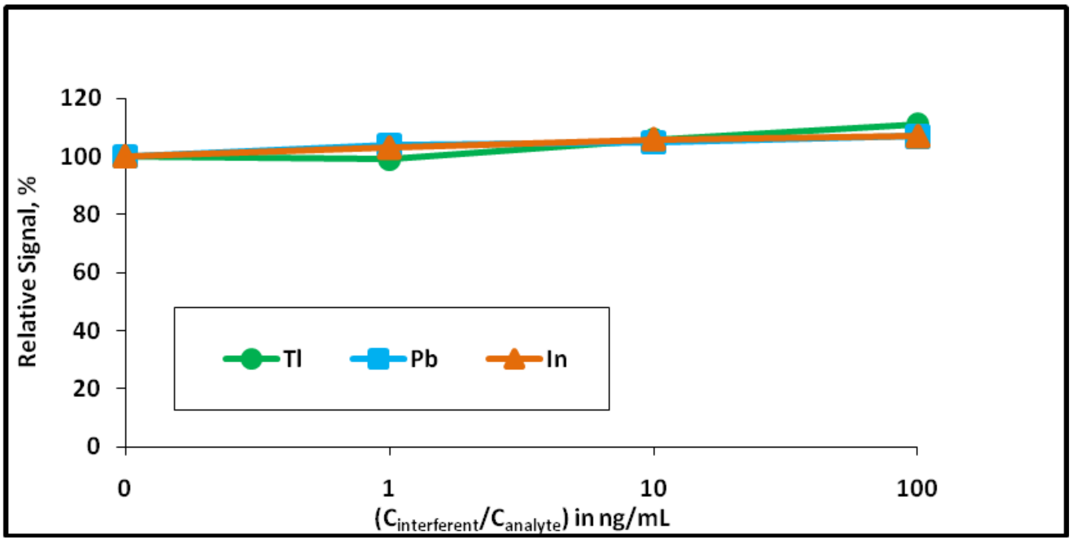

Figure 3.30 Interference effects of Tl, In and Pb on the analytical signal of 50.0 ng/mL Ag using Zr-coated SQT-AT-FAAS.

3.9 Surface Studies

X-ray Photoelectron Spectroscopy (XPS) was used for the determination of elemental identity and chemical state of analyte and trapped species collected on a relatively small quartz surface. In this way, it is easy to understand the chemical behavior of Ag throughout the trapping period. For this purpose, Ag on quartz surface was investigated by using XPS. The coating procedure for XPS study was described in section 2.5.

In XPS studies, binding energies may shift due to the physical and chemical environment. In order to estimate the real binding energies, a reference shift is required. Therefore; since C is always present as a result of hydrocarbon formation in air or vacuum, the carbon 1s line have been used to calibrate the binding-energy scale for XPS measurements; a binding energy of 284.8 eV is assumed for this purpose.

3.9.1 Chemical State of Ag on Quartz Surface

As shown in Figure 3.31; O 1s, Si 2p and C 1s were found in high percentages in XPS spectrum of Ag on quartz surface. There are also P 2p, Na 1s, Ag 3d, N 1s, Ca 2p and Ar 2p peaks in the spectrum. Ag was found as Ag 3s, Ag $3p_1$, Ag $3p_{3/2}$, Ag $3d_{5/2}$, Ag $3d_{3/2}$ and Ag 3d peaks.

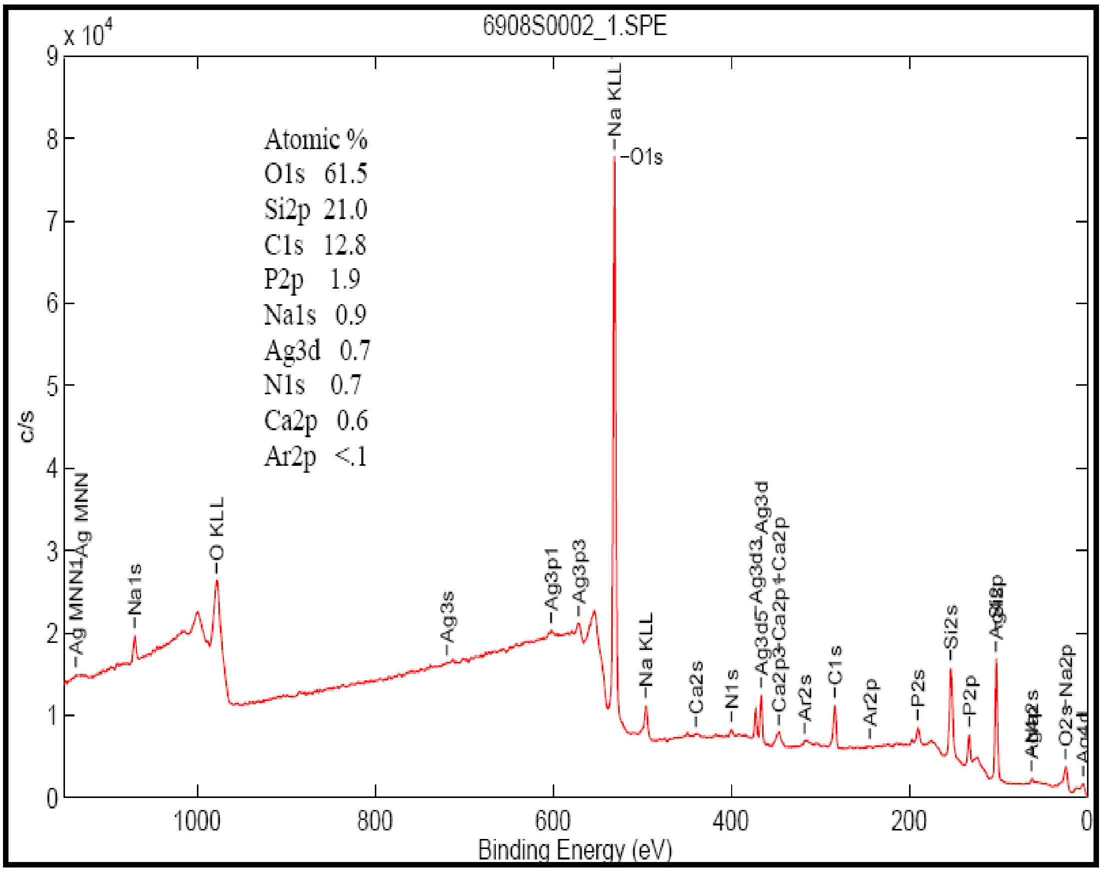

Figure 3.31 XPS spectrum of Ag on quartz surface.

The peak of C 1s is shown in detail in Figure 3.32. Theoretically, C 1s peak was assumed to be at 284.5 eV. In XPS spectrum of Ag on quartz surface, it was observed at 283.0 eV. Therefore, C shift was found as -1.5 eV.

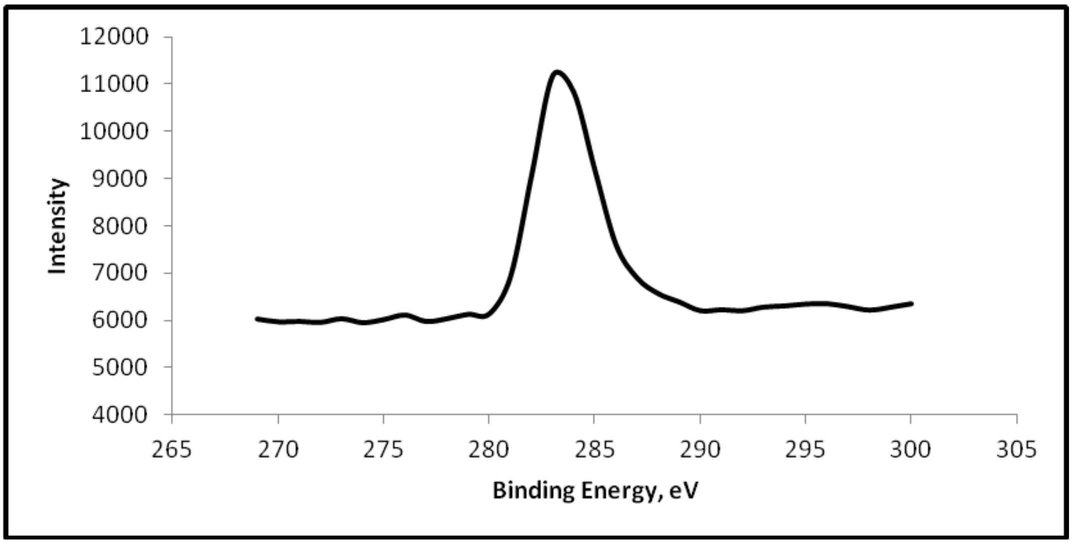

Figure 3.32 XPS spectrum of C on quartz surface.

As shown in detail in Figure 3.33, Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks were at 366.0 eV and 372.0 eV, respectively. By the substraction of C shift (-1.5 eV); the real peaks of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ were found as 367.5 eV and 373.5 eV, respectively. When we consider Ag $3d_{5/2}$ peak, Ag was found to be in its oxide form and its oxidation state was estimated as"+1" [75].

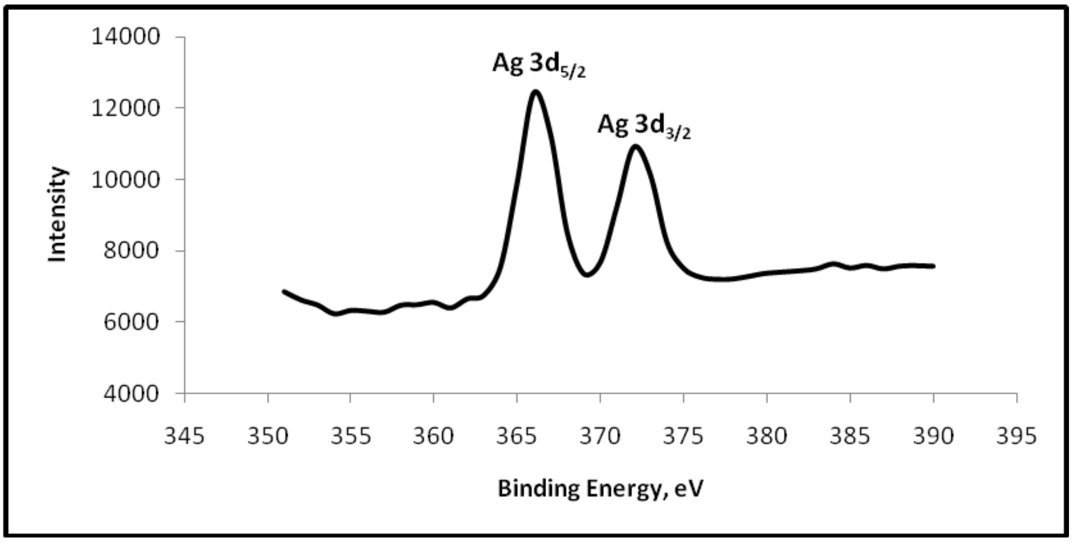

Figure 3.33 XPS spectrum of Ag $3d_{5/2}$ and Ag $3d_{3/2}$ on quartz surface.

CHAPTER 4

CONCLUSIONS

The main purpose of this study was to develop a sensitive, simple and economical technique for the determination of trace levels of silver by using slotted quartz tube.

First part of the study involves the determination of silver by simple FAAS technique. Secondly, 180° angled SQT was used to increase the residence time of analyte atoms in the measurement zone. Sensitivity was increased 2.31 fold with respect to FAAS technique when SQT was used in conjunction with stoichiometric air-acetylene flame. In this part of the studies, the height of SQT from the burner head could not be adjusted to lower than 5.0 mm since the flame was extinguished. If it were possible to adjust it lower, the sensitivity enhancement could have been higher since more analyte could reach the entrance slot which is closer to the burner head.

In the latter part, SQT device was used as an atom trap for preconcentration of analyte atoms. At the beginning, uncoated SQT was used as an atom trap. However, there was a memory effect. To overcome this problem, SQT was coated with a coating element (W) and the memory problem was eliminated. Therefore, throughout the optimization of parameters for atom trap studies; W-coated SQT was used. Afterwards, the sensitivity of 90°, 120° and 180° angled uncoated SQT devices were compared in the presence of optimum conditions. Since the sensitivity of 180° angled SQT was higher than the others, it was used for the rest of the study. To improve sensitivity further, inner surface of SQT was coated with different coating elements such as Zr, W, Ti, Mo, Ta and Au. Among them, W has been used for optimization of parameters. This time W-coated SQT-AT-FAAS technique was applied for the determination of silver where the sensitivity was increased 135 fold with respect to FAAS technique. Zr also significantly affected the sensitivity. The sensitivity enhancement was 270 fold with respect to FAAS technique when Zr-coated SQT-AT-FAAS technique was applied. Zr was better than W as a coating element. The reason is that the analytical Ag signals using Zr-coated SQT were more reproducible (%RSD, 1.21). All trap techniques were performed with 5.0 min trapping period and 31.3 mL sample volume.

To investigate the effects of some metals on Ag signals, interference studies were performed using Zr-coated SQT-AT-FAAS technique. The effect of some transitions and noble metals (Cu, Zn, Au, Pt, Cd, Ni, Fe, Mn, Co) and hydride forming elements (Se, Sb, As, Hg, Sn, Bi, Tl, In, Bi) were investigated. 100 fold of Cu, Au and Co suppressed the Ag signals approximately 30% where 100 fold of Fe increased the Ag signals in the same percentage. Others did not have any significant effect on Ag signals.

Finally, to identify the chemical state of Ag on quartz throughout the trapping period, surface studies were done by using XPS analysis. It was concluded that Ag was found in its oxide form and its oxidation state was estimated as “+1”.

As a summary, Zr-coated SQT-AT-FAAS was an analytical technique which was not only sensitive and economical but also simple and required small sample volume for the determination of silver. The technique also competed with the most sensitive analytical techniques with its low detection limit.

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