DEVELOPMENT OF SENSITIVE ANALYTICAL METHODS FOR THALLIUM DETERMINATION BY ATOMIC ABSORPTION SPECTROMETRY

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

BY

BETÜL ARI

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

APRIL 2009

Approval of the Thesis;

DEVELOPMENT OF SENSITIVE ANALYTICAL METHODS FOR THALLIUM DETERMINATION BY ATOMIC ABSORPTION SPECTROMETRY

submitted by **BETÜL ARI** in a partial fulfillment of the requirements for the degree of **Master of Science in Chemistry Department, Middle East Technical University** by

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences** ____________________

Prof. Dr. Ahmet M. Önal
Head of Department, **Chemistry** ____________________

Prof Dr. O. Yavuz Ataman
Supervisor, **Chemistry Department, METU** ____________________

Examining Committee Members:

Prof. Dr. R. Sezer Aygün
Chemistry Department, METU ____________________

Prof. Dr. O. Yavuz Ataman
Chemistry Department, METU ____________________

Prof. Dr. E. Hale Göktürk
Chemistry Department, METU ____________________

Prof. Dr. Mürvet Volkan ____________________
Chemistry Department, METU

Assoc. Prof. Dr. Gülay Ertaş ____________________
Chemistry Department, Bilkent University

Date: 14.04.2009

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Name, Last name: Betül Arı

Signature

ABSTRACT

DEVELOPMENT OF SENSITIVE ANALYTICAL METHODS FOR THALLIUM DETERMINATION BY ATOMIC ABSORPTION SPECTROMETRY

Arı, Betül

M.S., Department of Chemistry
Supervisor: Prof. Dr. O. Yavuz Ataman

April 2009, 87 pages

The use of slotted quartz tube (SQT) as an atom trap in atomic absorption spectrometry (AAS) provides a more stable chemical environment for atomization; the technique is simple and easily applicable in any laboratory. This thesis study involves application of SQT together with some other approaches to thallium determination by AAS. The first stages involve the efforts to improve nebulization efficiency of conventional flame atomic absorption spectrometry (FAAS) with and without the use of SQT. This is achieved by mixing 100 μL of propanol with 500 μL of Tl standard solution using the optimum conditions. By this method, Propanol-SQT-FAAS, 4.49 times enhancement in sensitivity has been obtained with respect to conventional FAAS, method in which the characteristic concentration was calculated as 894 ng/mL. The second stage of investigation is about the use of SQT as an atom trap, AT, preconcentration device for thallium determination. The similar technique has been successfully applied to some other analytes such as Pb, Cd, Bi and Au; detection limits at the level of ng/mL were obtained in the previous studies. In the present work, the analyte atoms are trapped on the inner surface of SQT in the presence of a lean air-acetylene flame for few minutes.

After this collection step, a volume of methyl isobutyl ketone, MIBK, amounting to 10-50 microliters is introduced via conventional nebulization; this causes a momentary alteration in the flame composition and thus results in the release of trapped analyte atoms from the quartz surface. This revolatilization step is followed by a rapid atomization and transient signal was obtained. In addition to this method, a novel approach has been investigated where the inner surface of SQT was modified by using a metal coating with low volatility. For this purpose, eight different coating materials which were tungsten, palladium, molybdenum, gold, tantalum, zirconium, titanium and osmium, have been applied to the inner surface of SQT and as osmium was found to be most appropriate one, the rest of the study was continued with Os-Coated-SQT. This modification provided a better surface than quartz alone so that analyte atoms are trapped more efficiently and also released easily. Although the working principle of the Coated-SQT-AT-FAAS method is same with SQT-AT-FAAS, the conditions for SQT-AT-FAAS and Os-Coated-SQT-AT-FAAS methods were optimized seperately. Limit of detections, 3s/m, has been found to be 38 ng/mL and 3.5 ng/mL for these cases, respectively. While the SQT-AT-FAAS method has provided 92 fold enhancement, the Os-Coated-SQT-AT-FAAS method has provided a 319 fold sensitivity improvement with respect to conventional FAAS method.

Keywords: Propanol-SQT-FAAS**,** Nebulization efficiency, SQT-AT-FAAS, Os-Coated-SQT-AT-FAAS, Preconcentration, Atomic Absorption Spectrometry, Thallium.

ÖZ

ATOMİK ABSORPSİYON SPEKTROMETRİYLE TALYUM TAYİNİ İÇİN DUYARLI ANALİTİK YÖNTEMLERİN GELİŞTİRİLMESİ

Arı, Betül

Yüksek Lisans, Kimya Bölümü

Tez Yöneticisi: Prof. Dr. O. Yavuz Ataman

Nisan 2009, 87 sayfa

Atomik absorpsiyon spektrometri (AAS) yönteminde yarıklı kuvars tüp (YKT) daha kararlı bir kimyasal ortam oluşturur; bu teknik basittir ve her laboratuvarda kolaylıkla uygulanabilir. Bu tez çalışması, YKT yaklaşımının diğer tekniklerle birlikte talyumun alevli AAS ile tayininde uygulanmasını içermektedir. Bu çalışmanın ilk aşamasında, yaygın olarak kullanılan, alevli atomik absorpsiyon spektrometri (AAAS) tekniğinde sisleştirme veriminin artırılması için bazı yarıklı kuvars tüpün kullanıldığı yada kullanılmadığı deneyler verilmektedir. Sisleştirme verimindeki artışın sağlanması için 100 μL propanol ile 500 μL Tl standart çözeltisi karıştırılarak aleve gönderilmiştir. Bu yöntem ile Propanol-YKT-AAAS, yaygın olarak kullanılan ve karakterisitk derişimi, C_0, 894 ng/mL olarak bulunan AAAS yöntemine göre 4.49 kat duyarlılık artışı sağlanmıştır. İkinci aşamada ise talyum tayini için yarıklı kuvars tüp atom tuzağı, AT, olarak önzenginleştirme amaçlı kullanılmıştır. Benzer yaklaşım, daha önceki çalışmalarda Pb, Cd, Bi ve Au gibi bazı geçiş elementlerinde başarılı ile kullanılmış, ng/mL düzeyinde gözlenebilme değerleri elde edilmiştir. Bu teknikte, analit atomlar birkaç dakika süre ile düşük asetilen akışındaki alevde YKT'nin iç yüzeyinde toplanmaktadır. Toplama basamağından sonra alev yapısında kısa bir süre için değişiklik olmasını ve analit türlerinin buharlaşmasını sağlayan 10-50 mikrolitre hacminde, metil izobutil keton, MIBK sisleştirme yoluyla aleve gönderilir. Bu basamakta tuzaklanan atomlar buharlaştıktan sonra hızlı bir atomlaşma sürecine girerler. Bu atomlaşma ile birlikte tepe şeklinde bir sinyal elde edilir. Bu çalışmaya ek olarak yeni bir araştırma gerçekleştirilmiştir; bu aşamada YKT'nin iç yüzeyi uçuculuğu az bir metalle kaplanarak değiştirilmiştir. Bu amaçla tungsten, paladyum, molibden, altın, tantalum, zirkonyum, titanyum ve osmiyum olarak sekiz farklı metal denenmiş olup; en uygun kaplama elementi osmiyum olarak bulunduğu için çalışmanın geri kalanı osmiyum kaplı YKT-AT ile tamamlanmıştır. Bu kaplama, kuvars yüzeyden daha yüksek bir verimle analit atomlarının tutulmasını ve sonraki aşamada bırakılmasını sağlamıştır. Os-Kaplı-YKT-AT-AAAS yönteminin çalışma ilkeleri YKT-AT-AAAS ile aynı olmasına karşın YKT-AT-AAAS ve Os-Kaplı-YKT-AT-AAAS yöntemleri birbirinden bağımsız olarak optimize edilmiştir. Bu yöntemler için gözlenebilme sınırları, 3s/m, YKT-AT-AAAS için 38 ng/mL olarak bulunurken, Os-Kaplı-YKT-AAAS için 3.5 ng/mL olarak hesaplanmıştır. AAAS tekniğine göre SQT-AT-FAAS metotu 92 kat duyarlılıkta artışı sağlarken, Os-Kaplı-YKT-AAAS metotu 319 kat artış sağlamıştır.

Anahtar Kelimeler: Propanol-YKT-FAAS, Sisleştirme verimliliği, YKT-AT-AAAS, Os-Kaplı-YKT-AAAS, Önzenginleştirme, Atomik Absorpsiyon Spektrometri, Talyum

To My Mother

ACKNOWLEDGEMENTS

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

My special thanks to Sezgin Bakırdere for his endless patience, guidance and contribution in each part of this study.

I am deeply grateful to thank Ahmet Yıldıran and Feriye Şenol for their endless help in my work, their valuable discussions and their warm friendship.

I also want to thank to Yasin Arslan, Necati Koç and all AtaMAn Research Group Members for their understanding, patience and the support.

Finally, my special appreciation and gratitude is devoted to my mother, my brother and my sister for their trust, patience and moral support, which makes everything possible.

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ABRREVIATIONS

Atomic Absorption Spectrometry	AAS
Atomic Fluorescence Spectrometry	AFS
Atom Trap	AT
Chemical Hydride Generation Atomic Absorption Spectrometry	CHG-AAS
Coated Slotted Quartz Tube Atom Trap Flame Atomic Absorption Spectrometry	Coated-SQT-AT-FAAS
Certified Referance Material	CRM
Cold Vapor Generation Atomic Absorption Spectrometry	CVAAS
Electrochemical Hydride Generation Atomic Absorption Spectromety	EC-HGAAS
Electrothermal Atomic Absorption Spectromety	ETAAS
Flame Alteration	FA
Flame Atomic Absorption Spectrometry	FAAS
Graphite Furnace Atomic Absorption Spectrometry	GFAAS
Hydride Generation Atomic Absorption Spectromety	HGAAS
Integrated Atom Trap	IAT

Inductively Coupled Plasma Mass Spectrometry	ICP-MS
Inductively Coupled Plasma Optical Emission Spectrometry	ICP-OES
Methyl Ethyl Ketone	MEK
Methyl Isobutyl Ketone	MIBK
Osminum-Coated-Slotted Quartz Tube Atom Trap Flame Absorption Spectrometry	Os-Coated-SQT-AT-FAAS
Propanol Flame Atomic Absorption Spectrometry	Propanol-FAAS
Propanol Slotted Quartz Tube Flame Atomic Absorption Spectrometry	Propanol-SQT-FAAS
Slotted Quartz Tube	SQT
Slotted Quartz Tube Atom Trap	SQT-AT
Slotted Quartz Tube Atom Trap Flame Atomic Absorption Spectrometry	SQT-AT-FAAS
Slotted Quartz Tube Flame Atomic Absorption Spectrometry	SQT-FAAS
Vapor Generation Atomic Absorption Spectrometry	VGAAS

CHAPTER 1

INTRODUCTION

The metals and their compounds have important physiological and toxic effects in living organisms. Some heavy metals including Hg, Cd, As, Tl, Cu and Pb show toxic effects even at very low concentrations; that is, they have the potential of adverse effects in biological systems. Therefore determination of trace and ultra trace levels of such elements in environmental, biological and metallurgical samples is very important. Since the desired detection levels for such determinations are very low, highly sensitive and precise techniques are required. In addition, the technique should be applied rapidly and easily. At present, the most commonly used analytical technique for determination of elements at trace levels which are important for human life in terms of either toxicity or essentiality is atomic absorption spectrometry (AAS). In the last two decades, the inductively coupled plasma, optical emission spectrometry (ICP-OES), the inductively coupled plasma mass spectrometry (ICPMS) and atomic fluorescence spectrometry (AFS) techniques have also become very popular. However, AAS keeps its importance in developing countries because of its simplicity and low cost; in addition, it is accessible in most analytical chemistry laboratories.

In this thesis, studies and results related to the development of sensitive AAS techniques for thallium determination is presented; use of simple flame AAS and slotted quartz tube-atom trap (SQT-AT) devices is employed.

1.1 Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is based on the absorption of electromagnetic radiation by neutral, ground state atoms produced by an atomizer. The absorption of energy by atoms follows well-known physical laws and appears to be predictable, thus providing a basis for quantitative analytical chemistry. Atomic absorption spectrometry was introduced to the world of analytical chemistry in the mid 1950s. In 1955, Walsh [1] introduced hollow cathode light sources, flame atomizers and a modulated system.

AAS techniques can be classified into several categories depending on the atomization and/or sample introduction procedures. These are flame AAS (FAAS), electrothermal AAS (ETAAS), vapor generation AAS (VGAAS) and also hyphenated techniques in which one or more of these techniques are combined.

1.2 Flame AAS

Flame AAS is relatively easy to use, commonly accessible, low cost and also a very robust technique; therefore, whenever possible it is preferred to the others. The temperature of the flame and thus the atomization efficiency depends on types of fuel and oxidant used as well as fuel to oxidant ratio. After the analyte is taken into solution, it is introduced via a nebulizer at a certain flow rate. The function of nebulization is to convert the solution to an aerosol by a pressurized air flow. In order to prevent alteration of flame temperature and atomization efficiency, the larger droplets are not allowed to reach the flame; consequently nebulization efficiency does not exceed 10 %. Therefore, relatively large sample volumes are needed for flame AAS. On the other hand, due to the high velocity of flame gases, dilution of analyte species take place; which is the other disadvantage of flame AAS.

1.3 Slotted Quartz Tube

On the pathway from simple flame AAS (FAAS) to SQT-AT devices, there are some milestones to be mentioned. A device called *long-path absorption tube* or *Fuwa's tube* could be as long as a meter. In order to improve sensitivity, the upper end of a tubular flame was directed into a silica or vycor tube through which the source beam was passed [2, 3]. Another well-known approach was *Delves' micro sampling cup technique* which consisted of a spoon-like nickel cup containing the sample that could be mechanically pushed into the flame wherein rapid atomization was obtained producing a transient signal [4]. A quartz tube having a slot at the lower surface was positioned on the top of the inserted cup to improve sensitivity. The device was introduced for determination of lead in human blood by using 10 µL of untreated sample [4]. Delves' cup was used by many laboratories before, and even a few years after the ETAAS technique became available and popular. Afterwards, *graphite furnace atomizer* [5], *tantalum sampling boats* [6], *slotted quartz tube* [7] and *Pt-loop atomizers* [8] were introduced as possible techniques for enhancing sensitivity of FAAS.

The slotted quartz tube, SQT, for sensitivity enhancement with flame AAS was first introduced to literature by Wattling [9]. The device was a simple hollow quartz tube that was positioned on the laminar flame so that the lower slot coincided with the flame; another slot was made on the tube at an angle of 120° with respect to the lower slot that accepted the analyte atoms from the flame. The improved sensitivity might be explained by partial exclusion of the entrained air which resulted in a more stable chemical environment. This tool provided a momentary improvement in sensitivity that was 2-5 folds in common for some elements such as Pb, Zn, Cd, Bi, Co, Mn, Ag, Se, As, Sb, Hg and Se [10-11] The Schematic representation of SQT is given in Figure 1.1.

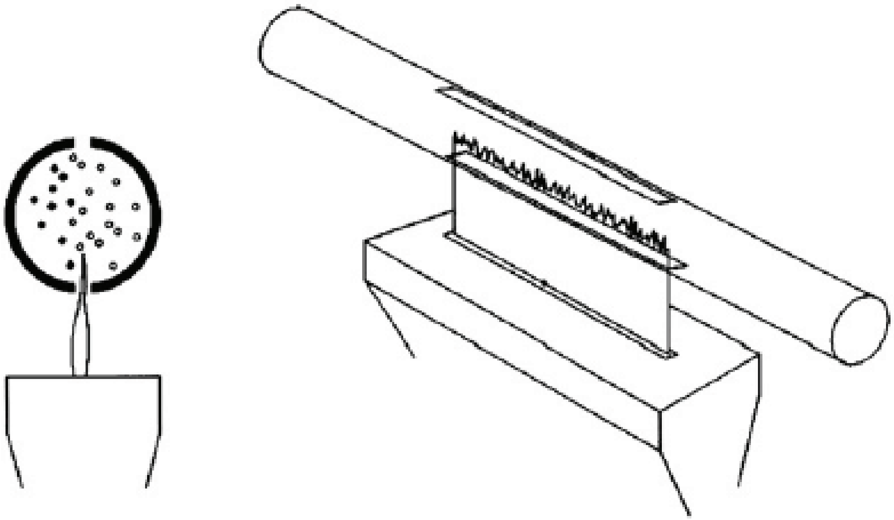


Figure 1.1 Schematic representation of 180^0 angled slotted quartz tube, SQT [7]

The elements that showed sensitivity improvements were volatile and formed compounds which decomposed thermally in the primary reaction zone of an air-acetylene flame. Afterwards, various tube designs were examined by Chimpalee and co-workers [12] in terms of different length of entrance and exit slots keeping the angle of them constant and very small differences in sensitivity also had been observed for the determination of bismuth.

Although the initial name of this technique included the term “atom trap”, it was occasionally used, mostly meaning a delay for atomic species in the measurement zone.

Apart from these kind of AAS techniques, there are several chemical preconcentration procedures to improve sensitivity of flame AAS. Moreover, atom trapping techniques are also powerful for enhancing sensitivities of flame AAS techniques.

1.4 Atom Traps for Flame Atomic Absorption Spectrometry

The sensitivity of conventional FAAS is limited by several factors; basically the residence time of analyte atoms in the light path and low nebulization efficiency. On the other hand, in flame atom trapping atomic absorption spectrometry, the main idea is *in situ* preconcentration of analyte atoms in the flame so that much higher population would be available for the AAS measurements in a discrete signal. Atom-trapping atomic absorption spectrometry is a technique that allows detection at the μg/L and ng/L level for several analytes.

In more recent versions of atom trapping, the analyte species are actually immobilized on a suitable material such as quartz or tungsten, and thus actually a preconcentration takes place in the collection period prior to a revolatilization and reatomization processes to obtain the enhanced signal [13].

1.4.1 Water Cooled U-Tube Atom Trap

The idea of this FAAS atom trap was first demonstrated by Lau et al. by use of a water cooled U-tube atom trap [14]. As seen in Figure 1.2, a 4 mm o.d. water cooled silica tube was mounted on a 10 cm long air-acetylene AAS flame immediately above the burner head slot and just below the light path of the beam from the hollow cathode lamp. The technique was based on the following steps:

I. Passage of water through the quartz U-tube in order to make its surface cooler than that of the flame.

II. Aspiration of sample via conventional nebulizer as the cooling water is passed through the U-tube. The analyte species are condensed on the relatively cool surface of the quartz tube and this stage is called as *collection step*.

III. At the end of the collection step, the cooling water was replaced manually with pressurized air. This caused rapid heating and release of the analyte species back into the flame and measurement zone where a transient absorption signal was obtained and recorded. This stage is called as *revolatilization step* [13].

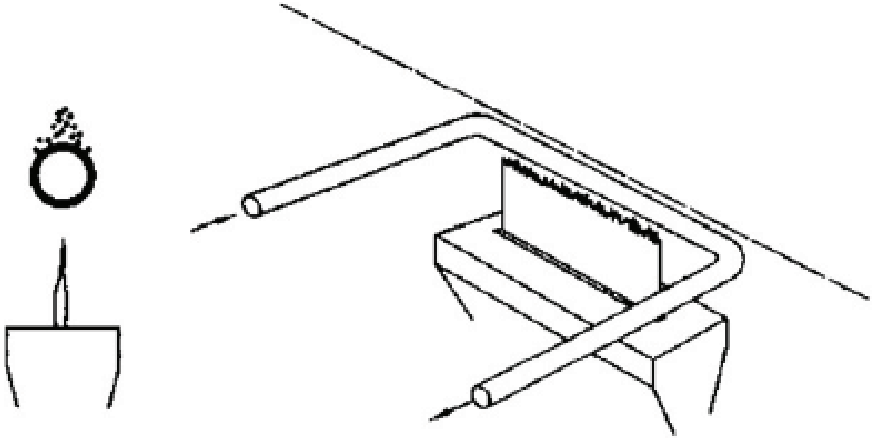


Figure 1.2 Schematic representation of water cooled U-tube atom trap [14]

The water cooled U-tube atom trap is the first example of atom trapping on quartz surface and provided a sensitivity enhancement of 1-2 orders of magnitude, depending on the element and collection period.

The atom trapping technique was re-examined by Khalighie et al. [15-17]. They investigated the effects of the acidity of the atomized solution, the nature of flame, effect of collector tube height with respect to burner, diameter of collector tube and percent obscuration of radiation by upper surface of the collector tube. The effect of the nature of the trap surface on the revaporization rate using the determination of As, Cd, Pb, Se and Zn as an example was studied [17]. On the other hand, in order to improve the reproducibility of the signals and increase the service time of trap tube, quartz trap was coated with oxides of aluminum or vanadium. Consequently, this type of trap provides an increase in the sensitivity of the determination of volatile elements approximately by a factor of 8-40 [18].

1.4.2 Integrated Atom Trap

After investigation of water cooled U tube atom trap technique for FAAS, Roberts and Turner offered to combine U-tube trap and SQT in order to combine the advantages of both techniques [19]. As mentioned by Turner et al., although higher sensitivities could be obtained than the other two trap techniques by this combined system, it suffered from much noise in the signal due to water droplets condensing on the cold silica surface producing excessive amounts of water vapor. In further investigations and improvements, the combination of the U-tube and SQT was called as *integrated atom trap, IAT*, by Matusiewicz and was used for determination of Ag, Cd, Cu, Fe, In, Mn, Pb, Zn and Tl in beer [20]. The schematic representation of integrated atom trap is given in Figure 1.3.

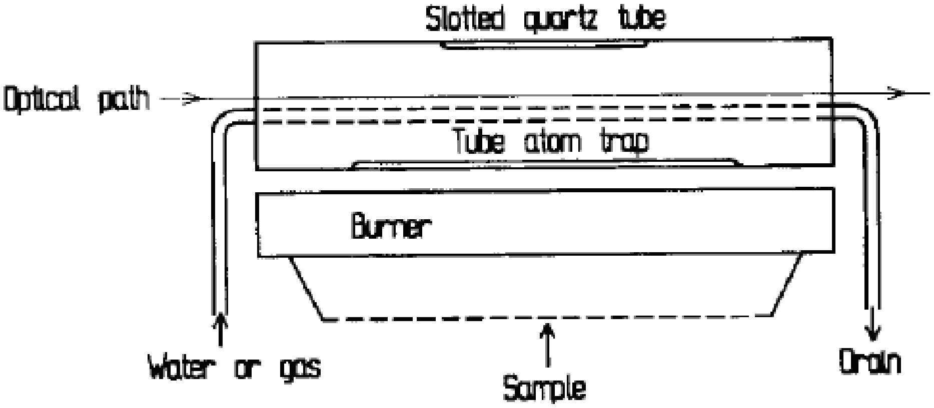


Figure 1.3 Schematic representation of integrated atom trap [20]

1.4.3 Slotted Quartz Tube Atom Trap

Slotted quartz tube has now become an atom trap, SQT-AT when used in the *in situ* preconcentration mode. Its introduction was done by two different research groups at about nearly the same time [21-23].

Although the atomization step was achieved by the stopping and the replacement of the flow of water with air in the methods of water cooled U-tube atom trap and IAT, Ertaş et al. developed alternative ways for atomization since the former one was not an easily controlled and operated technique. One of suggested atomization techniques was *flame alteration, FA*, by introducing extra fuel to momentarily change the composition of flame [24]. The other atomization technique suggested was the aspirating a micro amount of organic solvent to alter the chemical and physical environment of flame immediately following collection stage [22, 23]; this technique was termed as *organic solvent aspiration*.

Huang et al. [21] utilized the slotted quartz tube for preconcentration of the analyte atoms. At a fixed collection time the sample solution is aspirated and preconcentration is achieved. Flame conditions are altered to atomize the preconcentrated atoms by FA technique and approximately 70-270 fold increase compared to conventional FAAS was achieved for volatile elements.

From all such studies, the SQT atom trapping techniques has provided an alternative for *in situ* preconcentration of atoms for enhancement of sensitivity using FAAS.

1.4.3.1 Principles of Operation and Advantages of SQT-AT

In principle, collection and revolatilization steps are similar with the way the U-tube atom trap is used. The SQT-AT is used as follows:

I. In the presence of an optimized lean flame, sample solution is aspirated via nebulizer while the SQT is positioned above the flame. Analyte atoms are trapped on the inner surface of the SQT. This stage is called as *collection step*.

II. At the end of the collection step, 10-50 microliters amount of an organic solvent is introduced to the flame. This alters the flame composition for a very short period of time, that is sufficient to release analyte species from the quartz surface; this step is called *revolatilization*.

III. Revolatilization is followed by rapid atomization and a transient signal is obtained [13].

As Ataman mentioned in his review paper [13], the one of the most important advantages of SQT-AT apart from being a much easier technique than water cooled U-tube atom trap and IAT, is that due to the convenient design, there is no beam obscuration by the silica tube; consequently, a better S/N which is similar to that resulted in simple flame operation can be obtained. In addition to these advantages, flame alteration or organic solvent aspiration atomization techniques eliminate errors in the absorption signals faced in those previous two methods due to alteration in the zeroing which is a result from repetitive heating and cooling of the silica tube. In the suggested techniques of FA and organic solvent aspiration, flame composition is altered for such a short period that any physical change due to the higher temperatures can not be noticed.

1.5. Vapor Generation and Atom Traps

In vapor generation AAS, the analyte is converted to its volatile species by chemical or electrochemical means and then introduced to the atomizer in the gas phase. As a sample introduction method, it offers significant advantages over conventional nebulization. This is a low cost sampling method providing high sensitivity and low LOD's because of high chemical yields and high transport efficiency to the atomizer.

The principle of application of atom trap on the vapor generation techniques involves generation of volatile species, usually hydrides, trapping these species on the surface of an atom trap held at an optimized temperature and, finally, revolatilizing the analyte species by rapid heating of the trap and transporting them in a carrier gas to a heated quartz tube, as commonly used with hydride generation AAS systems. A transient signal having, in most cases, a full width at half maximum of less than 1 second is obtained [13].

Nowadays, electrochemical hydride generation atomic absorption spectrometry (EC-HGAAS) [25-26], chemical hydride generation atomic absorption spectrometry (CHG-AAS) [27-28] and cold vapor generation atomic absorption spectrometry (CVAAS) [29-30], are among the most studied and applied techniques for achieving better detection limits. All of these techniques are generally named as *vapor generation techniques*.

Hydride generation AAS is currently the most popular vapor generation method which can be applied to determination of elements which form relatively stable and volatile hydrides. Hydride generation was first introduced by Holak as a sample introduction technique in atomic spectrometry to determine arsenic in 1969 [31]. It offers a route to the trace analysis of several important elements which have specific problems when determined by FAAS. Although the number of elements is limited, As, Sb, Bi, Ge, Pb, Se, Tl, In, Te and Sn, it is a valuable technique for the determination of very low levels of these elements.

1.5.1 Quartz and Metal Atom Traps with Vapor Generation

After observation of trapping analyte on the inner surface of SQT successfully, this idea was applied to vapor generation techniques by Korkmaz et al. [32] for determination of lead. In this study, some quartz particles obtained by crushing were placed in the inlet arm of a quartz T-tube atomizer, near its connection point to the horizontal arm which is heated externally using a flame or a resistively heated wire. Ataman described the working principle of this method briefly [33];

I. Lead hydride (PbH_4) is formed by reaction of analyte in a HCl solution with $NaBH_4$ in a continuous flow system.

II. Analyte vapor separated from the liquid stream by a gas-liquid separator is directed to the quartz T-tube atomizer and passed through the trap held at an optimized collection temperature; some of the analyte hydride molecules are trapped here.

III. At the end of the *collection stage*, analyte introduction is terminated.

IV. The trap is rapidly heated to its *revolatilization* temperature; release of analyte species takes place when pumps are reactivated, transporting and mixing HCl carrier and $NaBH_4$ flows to produce H_2 gas. The resultant volatile species are transported to the quartz T-tube atomizer where the transient signal is formed and recorded as a result of analyte atomization in the measurement zone.

Afterwards, these trapping technique was also used for determination of Sb both by chemical [34,35] and electrochemical [25] HGAAS; the technique has also been applied for determination of Bi [36], As and Se [37]. The detection limits in all of these studies are at lower levels of ng/mL and pg/mL.

Moreover, after the quartz atom trap application, the use of a W-coil as a metal trap has been widely used mostly as an alternative to the graphite furnace [38]. A W-coil atom trap can be resistively heated by passing electricity directly through this device while external heating is required for the quartz trap; therefore, higher heating rates can be achieved for the former. The tungsten coil is taken from a commercial visible tungsten lamp; it can be readily and economically obtained, used and replaced when a new one is needed. Most recently, tungsten coil atom trap has been used by Cankur et al. for determination of Bi and Cd in the levels of ng/L [39, 40]. Souza and coworkers has also developed a method by using hydride generation technique combined with tungsten coil atom trap for determination of Se and As in biological and water samples [41].

The operating principles of W-coil atom trap located in the inlet arm of a conventional T-tube quartz atomizer are similar to quartz atom trap [33].

Although the most common metal atom trap is tungsten coil, there are other examples of metal atom traps in the literature. Dočekal et al. had investigated the collection of arsenic and selenium on molybdenum foil strip [42]; the same research group carried out similar studies for antimony and bismuth in 2006 [43]. Externally heated gold wire is also another example of a pure metal atom trap for determination of selenium [44].

1.5.2 Coating of W-coil Trap

In order to increase the trapping efficiency, some coating materials can be applied on W-coil so that the coated surface traps the analyte and also releases it at optimum temperatures much better than the bare W-coil.

The first coated tungsten atom trap was used by Barbosa et al. in 2002 [45]. He coated a tungsten coil with 300 µg of rhodium and determined selenium with

HGAAS technique. The detection limit with only 60 s trapping of selenium hydride species for a total sample volume of 2.5 mL was 50 ng/L. Alp et al. [46] also used iridium-coated tungsten coil for determination of antimony. Kula et al. [47] studied on selenium determination using hydride generation and gold-coated W-coil trapping AAS; in this study, a novel technique was used to make gold plating on W-coil. Ultra pure gold wire was dissolved using aqua regia to prepare a solution of 1000 mg/L; 25.0 mL of this solution was placed in a 100 mL separatory funnel; 10.0 mL of methyl isobutyl ketone (MIBK) was added and the contents were shaken for 20 s. After organic solvent was separated from water, 25.0 µL of Au-MIBK solution was injected on the surface of W-coil. The W-coil was resistively heated to 165 ^{0}C and was kept at this temperature for 2.0 s. This procedure was repeated three times for one coating. Since no water was involved in the coating procedure, corrosion of W-coil during the process has been eliminated.

1.6 Evalution of Trap Techniques

As it is known, atom trap techniques depend on total mass of analyte and also total time consumed. In some kinds of atom trap techniques, the sensitivity of methods can be improved by increasing trapping period and thus increasing total mass of trapped analyte; in the process a higher volume of sample is to be used. Therefore, a comparison of atom trap methods in terms of the period involved and sample volume used would be relevant, in addition to using characteristic concentration, C_0, values. In order to render such a comparison as objective as possible, Ataman has introduced two new terms; enhancement factors in term of unit time, E_t, and unit volume, E_v. [13]. Besides determining C_0 and LOD values, normalization is also done according to total time and total volume involved for atom trapping. Ataman names sensitivity enhancement with respect to characteristic concentration as enhancement factor (E) value. In other words, E value is the ratio of calibration sensitivities (slopes). However, in order to normalize results for different periods and sample volumes for different cases, E_t and E_v values are calculated by dividing E value by total time spent in terms of minutes and by total sample volume used in terms of mL, respectively. Higher E values indicate better sensitivity improvement.

1.7 Determination of Thallium

Thallium which has atomic number of 81 is a soft, malleable, bluish-white heavy metal. It can also be found combined with other substances such as bromine, chlorine, fluorine, and iodine. Its compounds appears colorless-to-white or yellow. In its pure form, thallium is odorless and tasteless.

Thallium is known as one of the toxic heavy metals. It has severe health effects on human health in very low concentrations and it causes both chronic and acute poisoning. It was reported that it is more toxic to mammals than some toxic elements such as Hg, Cd, Pb, Cu or Zn [48]. In the human body, Tl affects the central nervous system and it can cause hair loss and some visual disorders such as failing eyesight or total blindness [49]. In addition, it was reported that non-specific symptoms including tiredness, sleep disorders, headaches and muscle pains may appear in the case of low level environmental exposure to Tl [50]. In the natural source, thallium is mainly present in the sulfide ores of zinc, copper, lead. Average thallium concentration in earth's crust varies between 0.1 and 1.7 mg/kg. Relatively higher concentrations of Tl are found in granite and shale. In limestone, sandstone and coal, it is found in intermediate concentrations [50, 51]. It was also reported that Tl concentration is less then 1 ng/m^3 in uncontaminated air, 1 mg/L in uncontaminated water, 1 mg/kg in uncontaminated water sediments. In addition, concentration of Tl in different plants is generally lower then 0.1 mg/kg in dry mass [50].

Although the toxicity of this element is higher than other toxic elements, number of studies about thallium is much less then other elements due to low sensitivity for this element in classical analytical methods [51]. Due to the trace level concentration of thallium, determination of this element is a difficult task. Up to the present, thallium determination was achieved by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [52-53]. In addition, for Tl determination Matusiewicz et al. combined hydride generation technique and integrated atom trap system with AAS [54]; in another study, a Chinese research group combined atom trap technique with graphite furnace AAS [55] in order to increase the sensitivity for determination of thallium. Moreover, determination of thallium was done by using ICPMS for biological samples [56] or chemical hydride generation and ICPMS [57] .

1.8 Aim of the Study

The determination of thallium at trace levels is important in environmental and biological samples because of its toxic effects and critical concentration ranges. The sensitivity that is attainable by FAAS, conventional HGAAS and even ETAAS sometimes may not be enough for such analyses. On the other hand, although ICPMS systems may offer high sensitivity, they suffer from interferences due to high solid contents. Moreover, it may not be accessible in many laboratories due to its high cost. Therefore alternative sensitive methods which are applicable in any laboratory in terms of its cost and simplicity are needed for determination of thallium.

The main purpose of this study is to develop a sensitive analytical technique by using advantages of slotted quartz tube with FAAS for determination of thallium. This was achieved mainly by three different ways. The first way was increasing the nebulization efficiency by using an organic solvent apart from increasing the chemical stability of flame by using SQT. The other two techniques involved the use of uncoated and coated SQT devices as atom traps. All parameters for these three techniques were optimized and accuracy checks were performed. These three techniques can be applied in any instrumental analysis laboratory having a simple FAAS instrument, resulting in simple and low cost approaches.

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus and Materials

The slotted quartz tube (SQT) is 15 cm long; its inner and outer diameters are, 13 and 17 mm, respectively. SQT has two slots positioned at 120^0 with respect to each other; the lower one has a length of 10 cm which is equal to the length of flame length and it is positioned so that it receives the laminar flame; the other slot is 8 cm long. The slotted quartz tubes were made by Çalışkan Cam in OSTİM (Ortadoğu Sanayi ve Ticaret Merkezi), Ankara.

Polyethylene containers with a capacity of 100 mL were used to prepare and store the solutions. All standard solutions were prepared using adjustable Eppendorf micropipettes (100-1000 µL and 500-5000 µL) with polyethylene tips.

2.2 Chemicals and Reagents

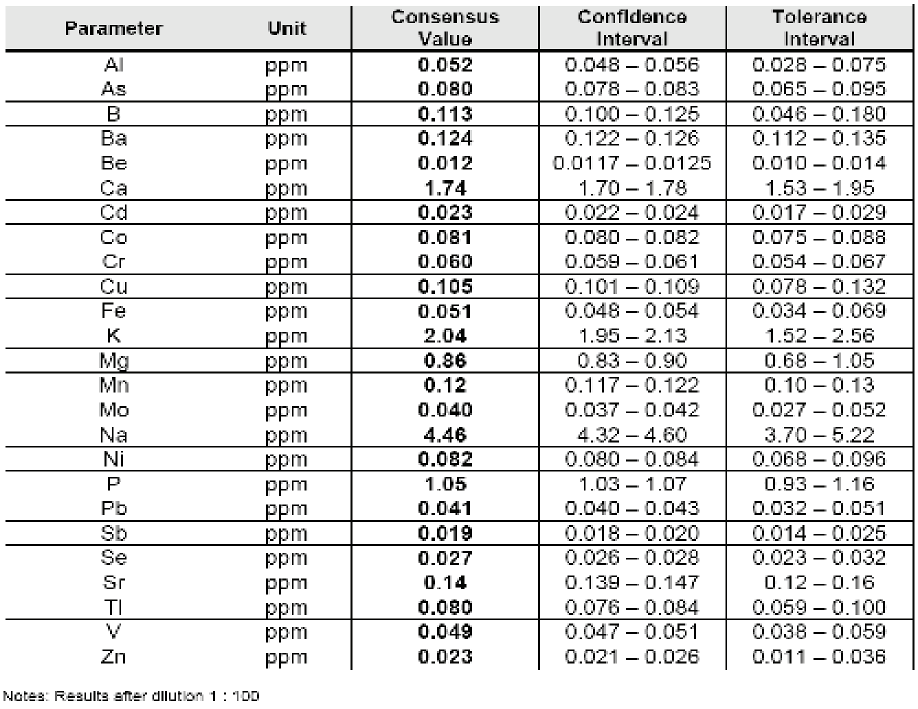
All reagents during the experiments were of analytical grade. Stock solution of thallium (1000 mg L^{1-}) was prepared by dissolving appropriate amount of $TlNO_3$ in 1.0 M HNO_3 (Merck). During the interference studies, Stock solutions (10000.0 mg/L) of interfering ions, Na, Mg, Ca, Al, Co, Mn, Fe, Cu, Cr, Zn, Ni, Cd and Pb, were prepared from their salts, using NaCl, $NaNO_3$, $Mg(NO_3)_2.6H_2O$, $Ca(NO_3)_2.4H_2O$, $Al(NO_3)_3.9H_2O$, $Co(NO_3)_2$, $MnSO_4.H_2O$, $Fe(NO_3)_3.9H_2O$,

$CuCl.2H_2O$, $Cr(NO_3)_3.9H_2O$, $Zn(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Cd(NO_3)_2.4H_2O$ and $Pb(NO_3)_2$. The standard solutions were prepared by appropriate dilutions of the stock solutions (10000 mg/L) by using de-ionized water. Dilutions were made using 18 MΩ·cm deionized water obtained from a Millipore (Molsheim, France) Milli-Q water purification system which was fed using the water produced by Millipore Elix 5 electrodeionization system. For the acidification of analyte solutions, analytical grade 65% (w/w) HNO_3 (Merck) was used.

All the glass and plastic apparatus were kept permanently in 2.0 M $HNO_3$when not in use, to remove the all kind of metal contaminations.

SCP SCIENCE EnviroMAT Waste Water, Low (EU-L-2) was used as the certified reference material, CRM, in able to perform accuracy check test for developed methods. Its content is given in Table 2.1

Table 2.1 Certified of Analyses of SCP SCIENCE EnviroMAT Waste Water, Low (EU-L-2)



Parameter	Unit	Consensus Value	Confidence Interval	Tolerance Interval
Al	ppm	**0.052**	0.048 – 0.056	0.028 – 0.075
As	ppm	**0.080**	0.078 – 0.083	0.065 – 0.095
B	ppm	**0.113**	0.100 – 0.125	0.046 – 0.180
Ba	ppm	**0.124**	0.122 – 0.126	0.112 – 0.135
Be	ppm	**0.012**	0.0117 – 0.0125	0.010 – 0.014
Ca	ppm	**1.74**	1.70 – 1.78	1.53 – 1.95
Cd	ppm	**0.023**	0.022 – 0.024	0.017 – 0.029
Co	ppm	**0.081**	0.080 – 0.082	0.075 – 0.088
Cr	ppm	**0.060**	0.059 – 0.061	0.054 – 0.067
Cu	ppm	**0.105**	0.101 – 0.109	0.078 – 0.132
Fe	ppm	**0.051**	0.048 – 0.054	0.034 – 0.069
K	ppm	**2.04**	1.95 – 2.13	1.52 – 2.56
Mg	ppm	**0.86**	0.83 – 0.90	0.68 – 1.05
Mn	ppm	**0.12**	0.117 – 0.122	0.10 – 0.13
Mo	ppm	**0.040**	0.037 – 0.042	0.027 – 0.052
Na	ppm	**4.46**	4.32 – 4.60	3.70 – 5.22
Ni	ppm	**0.082**	0.080 – 0.084	0.068 – 0.096
P	ppm	**1.05**	1.03 – 1.07	0.93 – 1.16
Pb	ppm	**0.041**	0.040 – 0.043	0.032 – 0.051
Sb	ppm	**0.019**	0.018 – 0.020	0.014 – 0.025
Se	ppm	**0.027**	0.026 – 0.028	0.023 – 0.032
Sr	ppm	**0.14**	0.139 – 0.147	0.12 – 0.16
Tl	ppm	**0.080**	0.076 – 0.084	0.059 – 0.100
V	ppm	**0.049**	0.047 – 0.051	0.038 – 0.059
Zn	ppm	**0.023**	0.021 – 0.026	0.011 – 0.036

Notes: Results after dilution 1 : 100

2.3 Atomic Absorption Spectrometer

A Perkin-Elmer 305B atomic absorption spectrophotometer equipped with deuterium background correction system was used as an instrument for absorbance measurements throughout this study. A Varian Tl coded hollow cathode lamp was used as the light source; it was operated at 7.5 mA and a wavelength of 276.8 nm was selected in the measurements; the spectral bandwidth of the measurements was 0.5 nm. Air-acetylene flame with a 100 mm burner slot was used. The signal was monitored using a Kipp & Zonnen single channel Model BD 111 flatbed recorder operated at 5 mV.

2.4 Coating Procedure of Slotted Quartz Tube

For the method of Coated-SQT-AT-FAAS, coating of slotted quartz tube was done by aspiration of 100 mL of 1000 mg/L coating element with 2.0 mL/min suction rate into the slotted quartz tube via conventional nebulizer in the presence of a lean flame. Recoating procedure was also done by the aspiration of 25 mL of 1000 mg/L of coating element under the same conditions.

CHAPTER 3

RESULTS AND DISCUSSION

In order to develop a method for determination of thallium, five alternative approaches were investigated.

i. First one is to increase the nebulization efficiency using a partially organic solvent; the technique will be named as Propanol-FAAS.

ii. The other way is to use a SQT to improve sensitivity also to create more stable chemical environmental since the air diffusion to flame is partly eliminated. The acronym used is SQT-FAAS.

iii. Third way is the combination of advantages of first two techniques above, using propanol in the sample solution and also an SQT device. This approach will be named as Propanol-SQT-FAAS.

iv. In order to obtain much better limits of detection, SQT were also used as an atom trap system in the uncoated configuration, this technique will be named as SQT-AT-FAAS.

v. As an additional approach, several coatings were tried on the surface of SQT to improve sensitivity; the technique will be called as Coated SQT-AT-FAAS.

Peak heights were used for the discrete signals throughout the studies. Sensitivity enhancements were calculated with respect to characteristic concentration, C_0, which is the concentration that corresponds to 0.00436 absorbance (1% absorption); $C_0 = 0.00436x(analyte\ concentration/absorbance)$. In addition to characteristic concentration, limit of detection, *3s/m*, and limit of quantitation, *10s/m*, were also calculated for each method. Furthermore, analysis of a certified references material was performed for accuracy test by use of SCP SCIENCE EnviroMAT Waste Water, Low (EU-L-2). Finally, the effects of interfering elements were also investigated for SQT-FAAS, Propanol-SQT-FAAS, SQT-AT-FAAS and Os-Coated-SQT-AT-FAAS methods.

PART I

As mentioned above, the first aim is to minimize the loss of sensitivity which results from low nebulization efficiency of conventional FAAS and also to increase the chemical stability of flame by use of SQT. The nebulization efficiency of conventional nebulizer was improved by mixing of aqueous solution with organic solvents. The reason for the increase in nebulization efficiency could be partly due to the decrease in surface tension of solution.

In this experiment, miscibility of the organic solvents with aqueous solution is also crucial since homogeneity of sample is important for analyses. While ethanol, propanol, acetonitrile and isopropanol are completely soluble in water; methyl isobutyl ketone, methyl ethyl ketone and cyclopentanol are slightly soluble.

3.1 Optimization of FAAS Method

Thallium is determined by FAAS method. For this method, two parameters, flow rate of acetylene and suction rate of thallium solution were optimized. Optimizations were done by using 20.0 mg/L Tl in 1.0 M HNO_3 standard solution. The optimum sample suction rate and acetylene flow rate were found as 6.0 mL/min and 2.8 L/min.

3.1.1 Effect of Flame Conditions

Throughout the study, flame conditions were investigated by varying the acetylene flow rate while the flow rate of air was kept constant at 25 L/min. For conventional FAAS method, a stoichiometric flame was used since variations in acetylene flow rate from stoichiometric to fuel rich flame did not have any significant effect on the signal; an acetylene flow rate of 2.8 L/min was used.

3.1.2 Optimization of Suction Rate of Sample Solution

The importance of sample suction rate for conventional FAAS method is that it affects nebulization efficiency. Nebulization efficiency becomes better as suction rate decreases. On the other hand, since population of analyte atoms per unit time in flame decreases, absorbance signals of Tl shows a decreasing trend for lower suction rates. The optimization of sample suction rate was done by using 20.0 mg/L Tl in 1.0 M HNO_3 solution and its effect was investigated in the range of 2.5-10.0 mL/min. As seen in Figure 3.1, the optimum value was found as 6.0 mL/min.

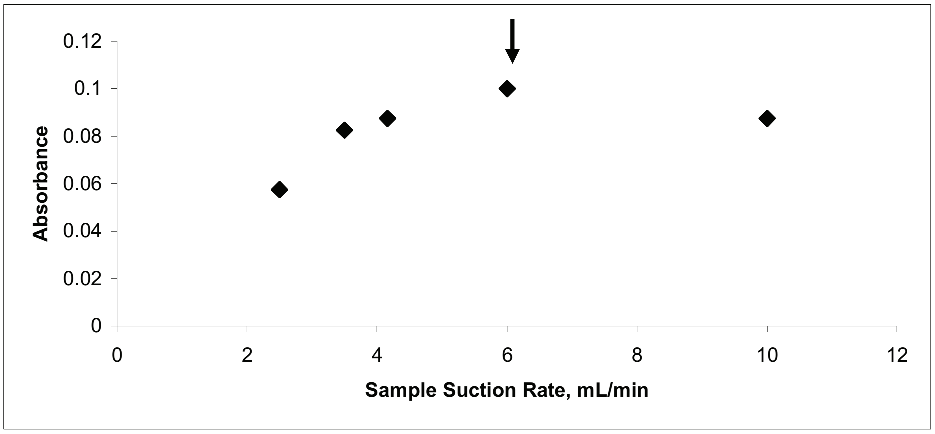


Figure 3.1 Optimization of suction rate with use of 20.0 mg/L Tl in FAAS. Acetylene flow rate: 2.8 L/min, Flow rate of air: 25 L/min

3.2 Optimization of Organic Solvent-FAAS Method

In this method, thallium aqueous solution was partially mixed with a certain organic solvent just before aspirating into flame in order to increase nebulization efficiency of conventional FAAS. In addition to optimized parameters of FAAS, type and amount of the organic solvent were also optimized. All the optimization studies were performed by using 10.0 mg/L Tl in 1.0 M HNO_3 standard solution.

3.2.1 Effects of Type of Organic Solvent

Since the purpose of using an organic solvent is to increase the nebulization efficiency of FAAS, type of used organic solvent gains importance. For this purpose, the effects of methanol, ethanol, methyl isobutyl ketone, methyl ethyl ketone, acetonitrile, isopropanol, propanol and cyclopentanol were investigated. Optimization was done by adding 100 µL of the selected organic solvent to 500 µL of Tl solution. It was found that enhancement effects of cyclopentanol and propanol on Tl signal were clearly higher than the other solvents (Table 3.1). Although the effects of cylopentanol and propanol were the same, propanol was selected as the best one since it is totally soluble in water but the other solvent has a poor miscibility with aqueous solutions.

Table 3.1 Effect of Organic Solvent on the 10.0 mg/L Tl Signal for Organic Solvent-FAAS Method*

Added Organic Solvent**	Absorbance***	Enhancement Factor****
–None	0.05	1.00
MeOH	0.061	1.22
EtOH	0.056	1.12
MIBK	0.0650	1.30
MEK	0.063	1.26
Acetonitrile	0.0613	1.22
Isopropanol	0.065	1.30
Propanol	0.0725	1.46
Cyclopentanol	0.0725	1.46

*Conditions are: Acetylene flow rate, 2.8 L/min; Flow rate of air, 25 L/min; Sample suction rate, 6.0 mL/min; Volume of organic solvent, 100 µL; 500 µL of 10.0 mg/L Tl.

**100 µL of organic solvent were added to 500 µL of aqueous solution

***Maximum observed RSD is 6.6 % (n=5)

****$\mathrm{Abs}_{\mathrm{org.}}/\mathrm{Abs}_{\mathrm{FAAS}}$

3.2.2 Optimization of Volume of Organic Solvent

Amount of organic solvent was another optimization parameter. As seen in Figure 3.2; while the absorbance signals show a decreasing trend when the dilutions were done with water, the signals of diluted 500 µL of 10.0 mg/L Tl with propanol solution show a different behavior. Since the sensitivity loss due to dilution factors were compensated by the increase in nebulization efficiency, after a certain point Tl absorbance signals stayed constant. In order to study in plateau region, 100 µL of propanol was preferred to be added to 500 µL of 10.0 mg/L Tl solution in the further experiments.

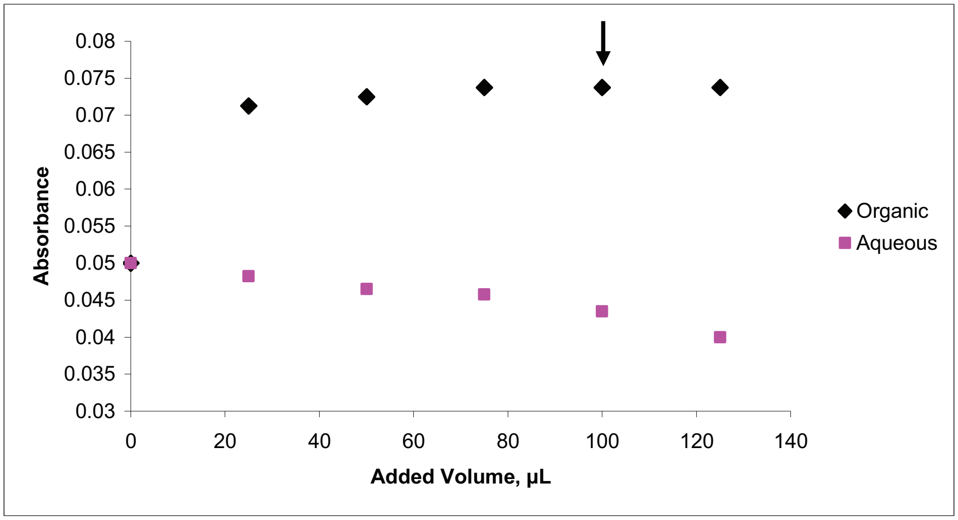


Figure 3.2 Optimization of volume of organic solvent using 10.0 mg/L Tl in Organic Solvent-FAAS.

Acetylene flow rate: 2.8 L/min, Flow rate of air: 25 L/min,

Sample Suction rate: 6.0 mL/min, Type of organic solvent: Propanol, 500 µL Tl

3.3 Optimization of SQT-FAAS Method

In this method, SQT described in the experimental part was positioned on the flame. The light beam passed through it with no beam obscuration and the sample solution was aspirated continuously. All parameters were optimized again since the method was completely different than the previous ones. Suction rate of thallium solution, flow rate of acetylene and height of SQT from burner head were optimized. All optimizations were done by using 10 mg/L Tl in 1.0 M HNO_3 solution. Using this method, 3.89 fold enhancement in sensitivity with respect to FAAS method was achieved.

3.3.1 Optimization of Flame Conditions

As seen in the Figure 3.3, the optimum flow rate of acetylene was found to be 2.8 L/min. for SQT. The Tl signals showed a decreasing behavior at lower acetylene flow rates because analyte atoms started to be trapped in the inner surface of the SQT instead of being atomized in the flame zone that is SQT starts to work as atom trap.

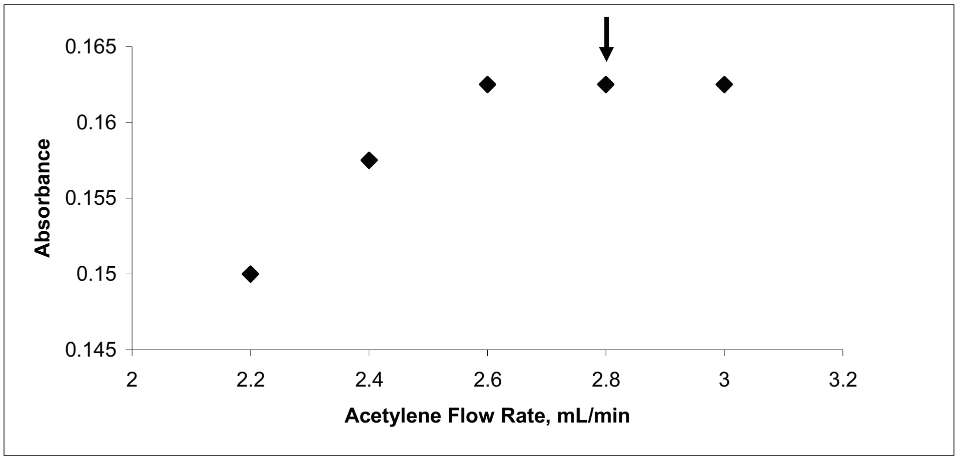


Figure 3.3 Optimization of flow rate of acetylene using 10.0 mg/L Tl in SQT-FAAS.
Sample suction rate: 6.0 mL/min, Flow rate of air: 25 L/min,
Height of SQT from the burner head: 2.0 mm.

3.3.2 Optimization of Sample Suction Rate

As it is seen in the Figure 3.4, the optimum suction rate of Tl solution in SQT-FAAS method was determined as 7.5 mL/min.

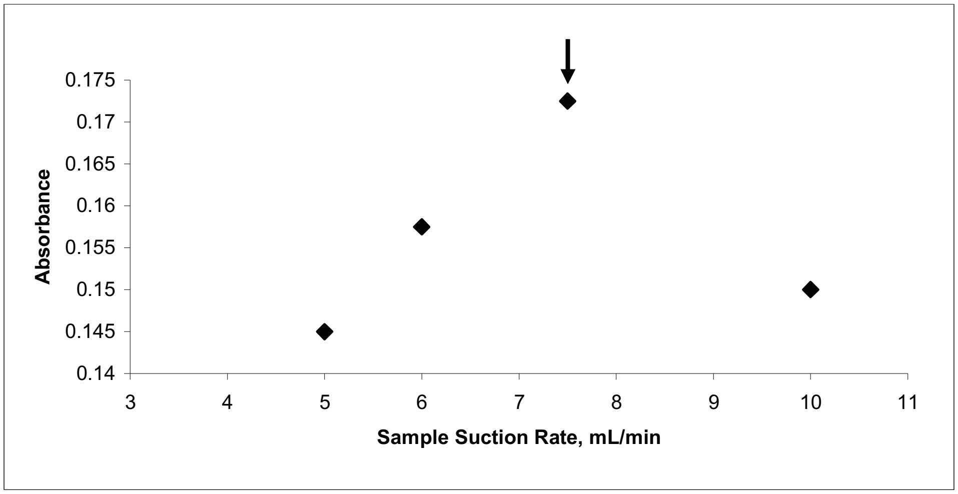


Figure 3.4 Optimization of sample suction rate using 10.0 mg/L Tl in SQT-FAAS.
Flow rate of acetylene: 2.8 L/min, Flow rate of air: 25 L/min,
Height of SQT from the burner head: 2.0 mm

3.3.3 Optimization of Height of the SQT from the Burner Head

One of the crucial parameters for SQT-FAAS method was the height of the SQT from the burner head; this parameter was varied between the values of 1.0 mm to 4.0 mm. The optimum height was found as 3.0 mm (Figure 3.5).

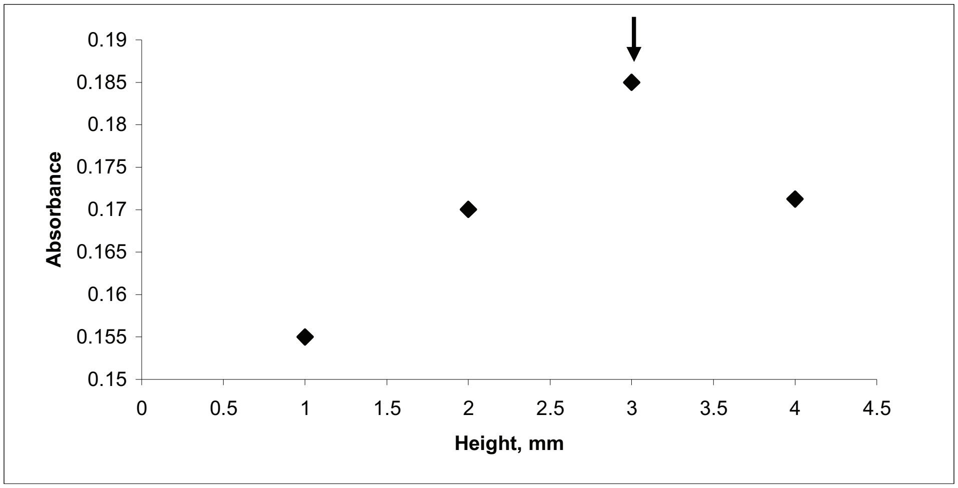


Figure 3.5 Optimization of flame height from the burner head using 10.0 mg/L Tl in SQT-FAAS.

Flow rate of acetylene: 2.8 L/min, Flow rate of air: 25 L/min, Suction rate of sample solution: 7.5 mL/min

3.4 Optimization of Organic Solvent-SQT-FAAS Method

In this method, thallium solution was mixed with a certain amount of an organic solvent just before aspiration into SQT. In addition to the optimized parameters of suction rate of Tl solution, flow rate of acetylene and SQT height from burner head, the type and volume of organic solvent were optimized. Throughout the optimization, 5.0 mg/L Tl in 1.0 M HNO_3 standard solution was used.

3.4.1 Effect of Type of Organic Solvent

Propanol, isopropanol, cyclopentanol, ethanol, methanol, acetonitrile, methyl ethyl ketone and methyl isobutyl ketone were investigated as organic solvents. Optimization was done with an addition of 100 µL of the selected organic solvent to

500 μL of 5.0 mg/L Tl standard solution. As seen in Table 3.2, the enhancement factor of propanol on Tl signal was clearly higher than other solvents.

Table 3.2 Effect of Organic Solvent Types on 5.0 mg/L Tl Signal for Organic Solvent-SQT-FAAS Method*

Added Organic Solvent**	Absorbance***	Enhancement Factor****
None	0.094	1.00
Cyclopentanol	0.114	1.21
EtOH	0.114	1.21
Isopropanol	0.123	1.31
Acetonitrile	0.104	1.11
MEK	0.110	1.17
MIBK	0.118	1.26
→ Propanol	0.125	1.33

*Conditions are: Flow rate of acetylene: 2.8 L/min, Flow rate of air: 25 L/min, Suction rate of sample solution: 7.5 mL/min, Height of SQT from burner head: 3.0 mm, Volume of organic solvent: 100 μL, Volume of 5.0 mg/L Tl: 500 μL

**100 μL of organic solvent were added to 500 μL of aqueous solution

***Maximum observed RSD is 3.4 % (n=5)

****$Abs_{org.}$/ $Abs_{SQT\text{-}FAAS}$

3.4.2 Optimization of Volume of Organic Solvent

As seen in the Figure 3.6, thallium signals did not show significant increase or decrease after a certain amount of propanol. Therefore, 100 μL of propanol were chosen as the optimum volume for mixing with 500 μL of 5.0 mg/L Tl solution.

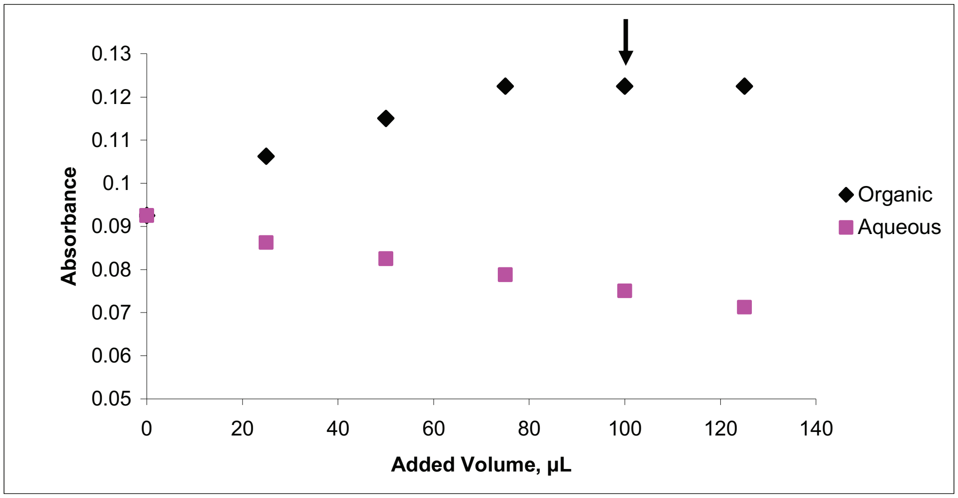


Figure 3.6 Optimization of volume of organic solvent using 5.0 mg/L Tl in Organic Solvent-SQT-FAAS.

Flow rate of acetylene: 2.8 mL/min, Flow rate of air: 25 L/min, Suction rate of sample solution: 7.5 mL/min, Height of SQT from burner head: 3.0 mm, Type of organic solvent: Propanol, Volume of 5.0 mg/L Tl: 500 µL

Table 3.3 Optimized Conditions for FAAS, Propanol-FAAS, SQT-FAAS and Propanol-SQT-FAAS Methods.

	FAAS	**Propanol-FAAS**	**SQT-FAAS**	**Propanol-SQT-FAAS**
Suction rate, *mL/min*	6.0	6.0	7.5	7.5
Flow Rate of Acetylene *L/min*	2.8	2.8	2.8	2.8
Height of SQT, mm	-	-	3.0	3.0
Type of Organic Solvent	-	Propanol	-	Propanol
Volume of organic Solvent, µL, to be added to 500 µL of aqueous solution	-	100	-	100

The signals of FAAS, Propanol-FAAS, SQT-FAAS and Propanol-SQT-FAAS methods are given in Figures 3.7 and 3.8.

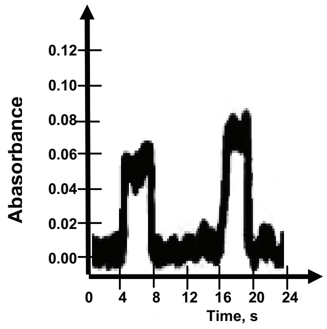


Figure 3.7 The signals of FAAS and Propanol-FAAS for 10.0 mg/L Tl solution, respectively.

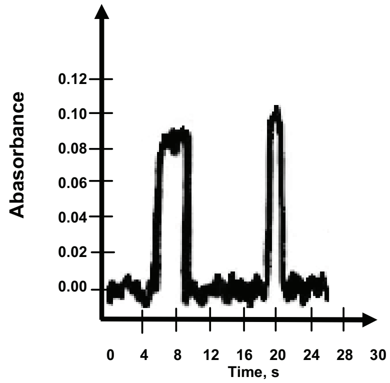


Figure 3.8 The signals of SQT-FAAS and Propanol-SQT-FAAS for 5.0 mg/L Tl solution, respectively.

3.5 Analytical Figure of Merits

For the four methods investigated, the optimized conditions are given in the Table 3.3; calibration plots were obtained under optimum conditions. Detection limits, 3s/m, limits of quantitation, 10s/m, and the characteristic concentrations were calculated. In all the methods, enhancements in sensitivities in terms of characteristic concentrations were calculated with respect to FAAS method.

3.5.1 Calibration Plots for FAAS Method

The calibration plot was linear between 2.0-25 mg/L (Figures 3.9 - 3.10). The best line equation and the correlation coefficient were, $y = 0.0047x + 0.0028$ and 0.9968, respectively. LOD and LOQ were calculated as 1.3×10^3 ng/mL and 4.2×10^3 ng/mL, respectively.

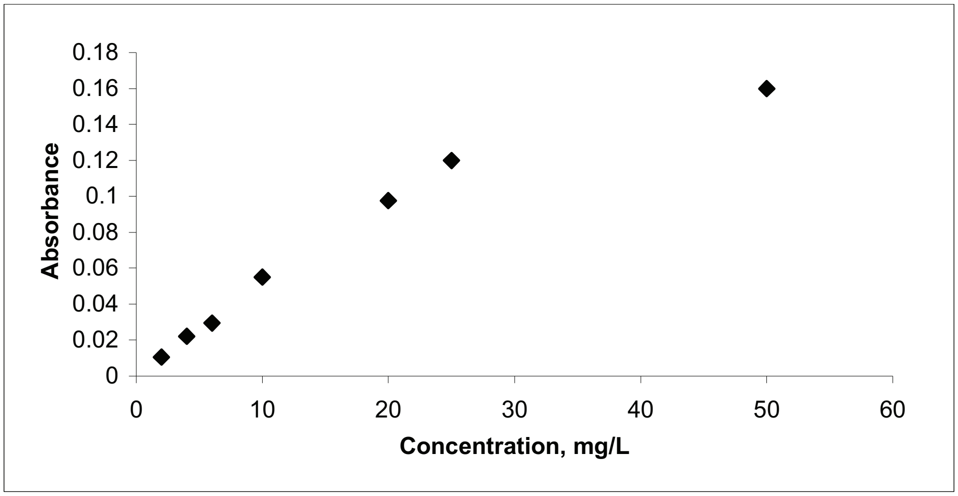


Figure 3.9 Calibration plot for FAAS method

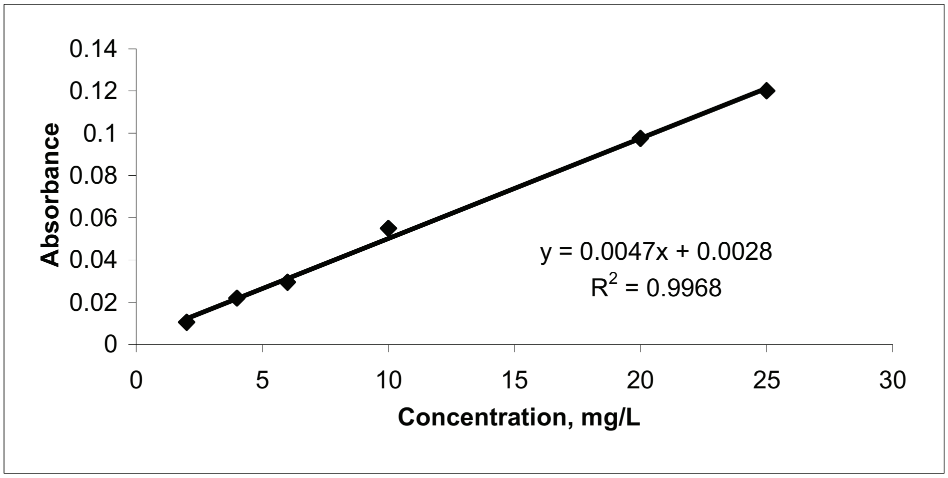


Figure 3.10 Linear calibration plot for FAAS method

3.5.2 Calibration Plots for Propanol-FAAS Method

As seen in the Figures 3.11 and 3.12, the calibration plot for Propanol-FAAS method was linear between 2.0-50 mg/L. The best line equation and correlation coefficient were, $y = 0.0066x + 0.0031$ and 0.9996, respectively. LOD and LOQ were found as 9.5×10^2 ng/mL and 3.2×10^3 ng/mL, respectively.

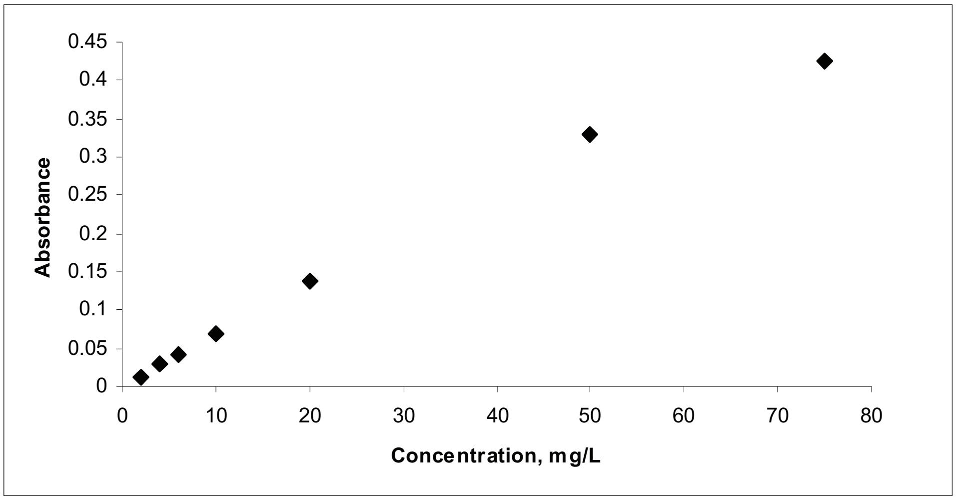


Figure 3.11 Calibration plot for Propanol - FAAS method

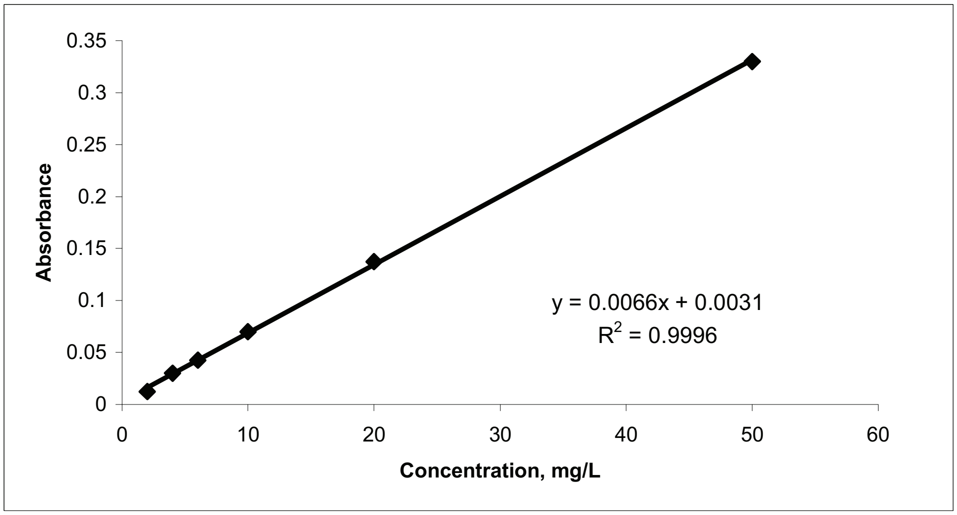


Figure 3.12 Linear calibration plot for Propanol - FAAS method

3.5.3 Calibration Plots for SQT-FAAS Method

As seen in the Figures 3.13 and 3.14 the calibration plot for SQT-FAAS was linear between 1.0-10.0 mg/L. The best line equation and correlation coefficient were, $y = 0.0184x + 0.0019$ and 0.9999, respectively. LOD and LOQ were found as 3.4×10^2 ng/mL and 1.1×10^3 ng/mL, respectively.

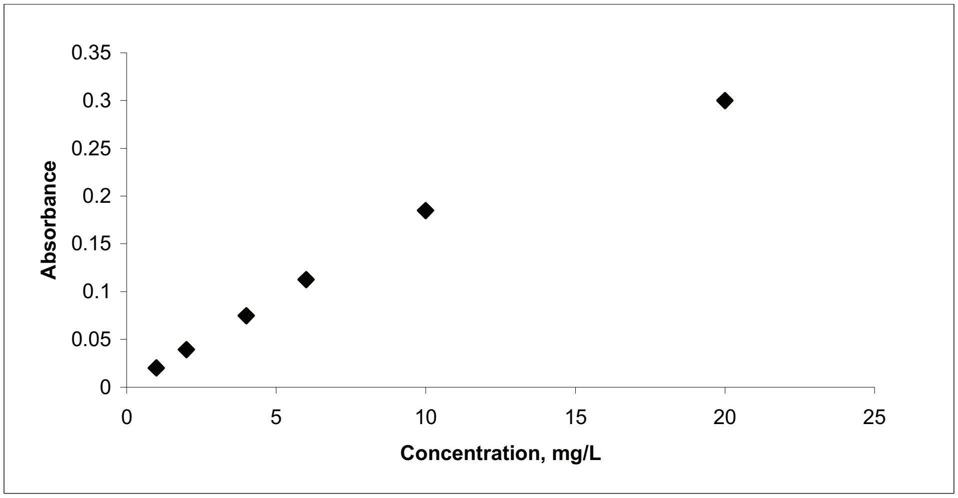


Figure 3.13 Calibration plot for SQT-FAAS method

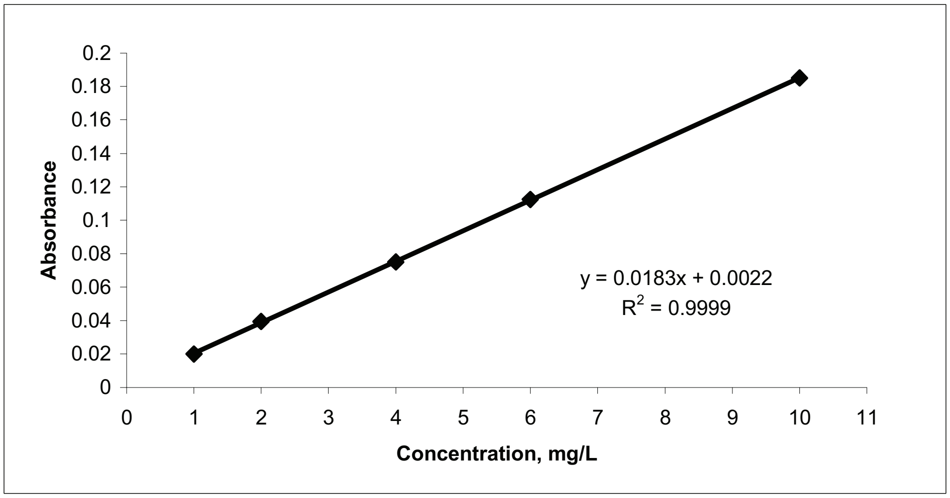


Figure 3.14 Linear calibration plot for SQT-FAAS method

3.5.4 Calibration Plots for Propanol-SQT-FAAS Method

It was found that the calibration plot for Propanol-SQT-FAAS was linear between 1.0-20.0 mg/L (Figures 3.15 and 3.16). The best line equation and correlation coefficient were, y = 0.0213x+0.0053 and 0.9998, respectively. LOD and LOQ were found as 140 ng/mL and 470 ng/mL, respectively.

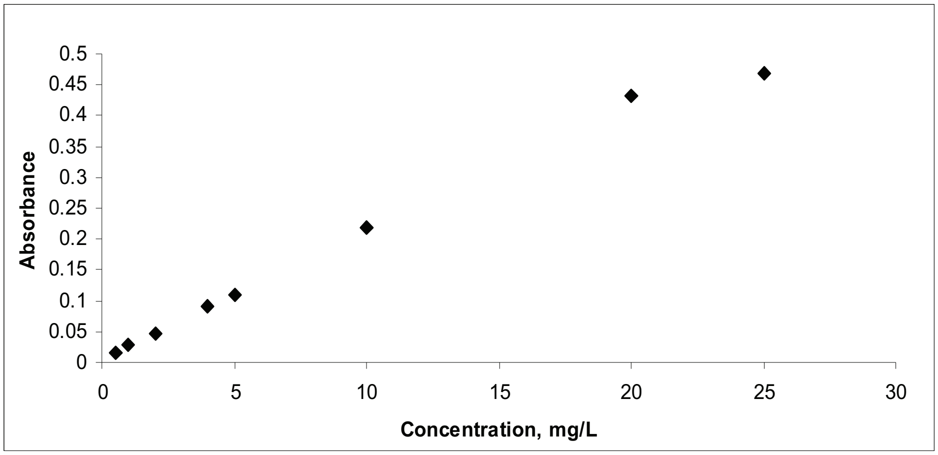


Figure 3.15 Calibration plot for Propanol-SQT-FAAS method

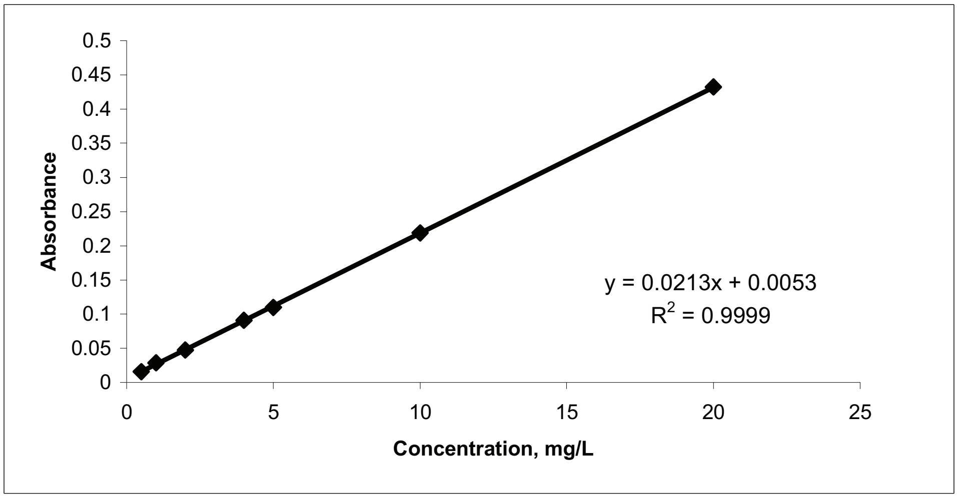


Figure 3.16 Linear calibration plot for Propanol-SQT-FAAS method

As it is seen in the Table 3.4, Propanol–FAAS technique is 1.41 times more sensitive than the FAAS method. The reason of this enhancement is due to the positive effect of propanol on nebulization efficiency and thus the improved transport efficiency. In addition, SQT-FAAS method is 3.89 times more sensitive than the FAAS method. This enhancement was the result of more stable chemical environment than the FAAS method. Propanol-SQT-FAAS method is a combination of Propanol-FAAS and SQT-FAAS methods. Using Propanol-SQT-FAAS method, 4.49 fold of sensitivity enhancement in terms of characteristic concentration was achieved. This is due to not only improvement in nebulization efficiency using propanol but also using the advantages of SQT over conventional flame AAS. The detection limit and characteristic concentration of this method were 140 ng/mL and 199 ng/mL, respectively.

Table 3.4 Analytical Figures of Merit

	Limit of Detection LOD, *ng/mL*	**Limit of Quantitation** LOQ, *ng/mL*	**Characteristic Concentration** C_o, *ng/mL*	**Enhancement in Sensitivity***	**Dynamic Ranges** *mg/L*
FAAS	$1.3x10^3$	$4.2x10^3$	894	1.00	2.0-25
Propanol-FAAS	$9.5x10^2$	$3.2x10^3$	634	1.41	2.0 -50
SQT-FAAS	$3.4x10^2$	$1.1x10^3$	230	3.89	1.0-10.0
Propanol-SQT-FAAS	$1.4x10^2$	$4.7x10^2$	199	4.49	1.0 – 20

* $C_{0(FAAS)} / C_{0(Selected\ method)}$

3.6. Interference Studies for SQT-FAAS and Propanol-SQT-FAAS Method

Interference free measurements are very important in analytical chemistry. Interferences in atomic absorption spectrometers can be categorized as *spectral* and *nonspectral* interferences. Radiation absorbed by species other than free atoms of the analyte causes spectral interferences. Nonspectral ones are caused by influence of sample constituents on the analyte signal. The most frequently studied interference is matrix interferences caused by inorganic compounds. Ionic types of analyte may react with other possible ionic interferants present in sample.

Throughout the interference studies, the interfering elements were catogarized into two groups. In the first group, some major elements like Ca, Al, Na and Mg in the environment were selected. As a second group, some transition elements, such as Pb, Co, Mn, Fe, Cu, Cr, Zn and Ni were studied. In addition to these interference studies, in order to investigate the effect of anions in the medium, such as effects of Cl^- and NO_3^- ions were also investigated by comparing the results obtained NaCl and $NaNO_3$.

Throughout the interference studies of SQT-FAAS and Propanol-SQT-FAAS methods, since the enhancement factors between these methods is very close to unity, the interference studies were done with the same analyte concentration which was 5.0 mg/L Tl in 1.0 M HNO_3 under the optimum conditions of the methods. The interferent concentrations were 1, 10 and 100 folds of the analyte concentration. The summary of interference studies for SQT-FAAS and Propanol-SQT-FAAS methods is given in Table 3.5.

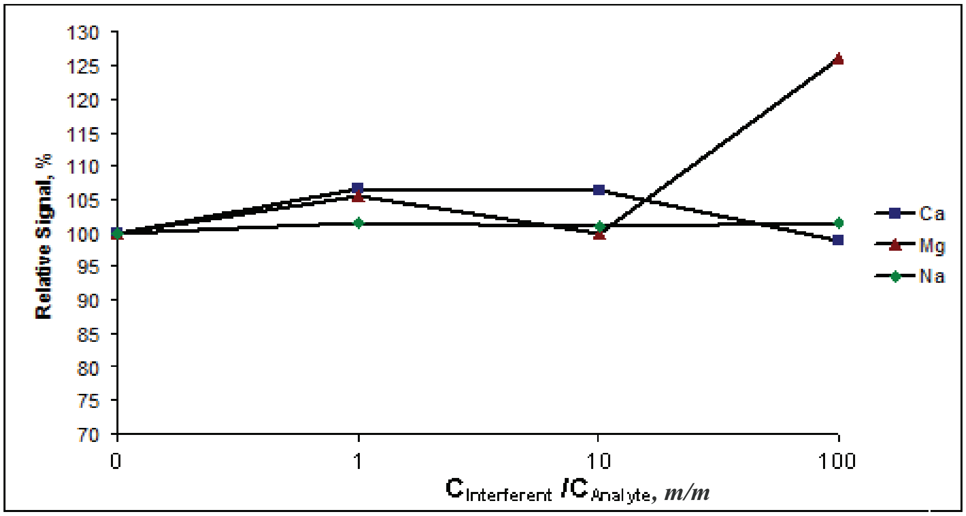


Figure 3.17 Interference effects of Ca, Mg and Na on 5.0 mg/L Tl signal by use of SQT-FAAS method

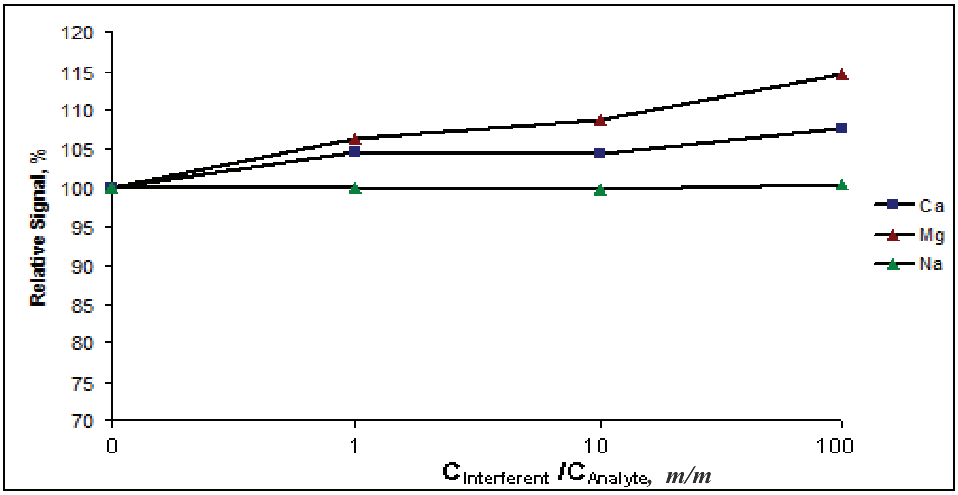


Figure 3.18 Interference effects of Ca, Mg and Na on 5.0 mg/L Tl signal by use of Propanol SQT-FAAS method

As seen in Figures 3.17 and Figure 3.18 any concentrations of Ca and Na did not have any serious interference effect on Tl determination for the both techniques. However, the presence of 100 folds Mg enhanced the signal using SQT-FAAS method by 26 %. By using Propanol-SQT-FAAS method, this enhancement was decreased to %15.

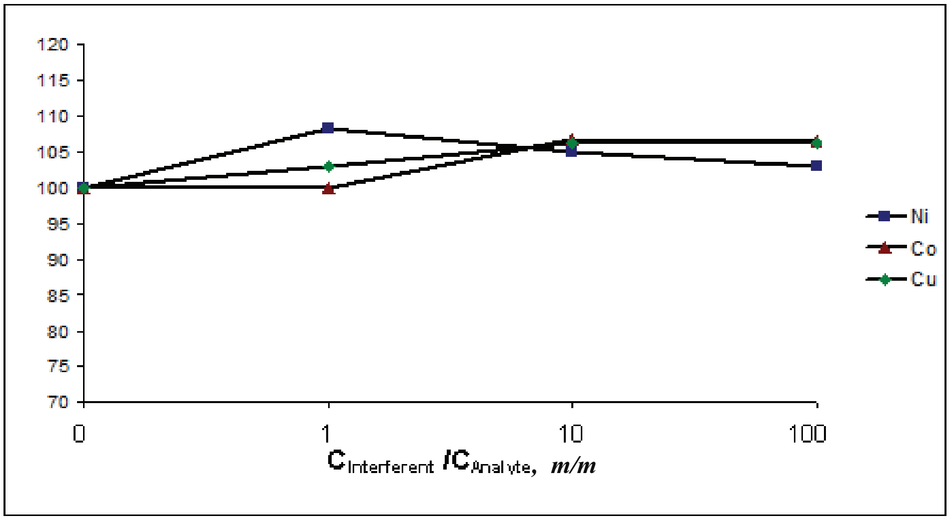


Figure 3.19 Interference effects of Co, Ni and Cu on 5.0 mg/L on Tl signal by use of SQT-FAAS method

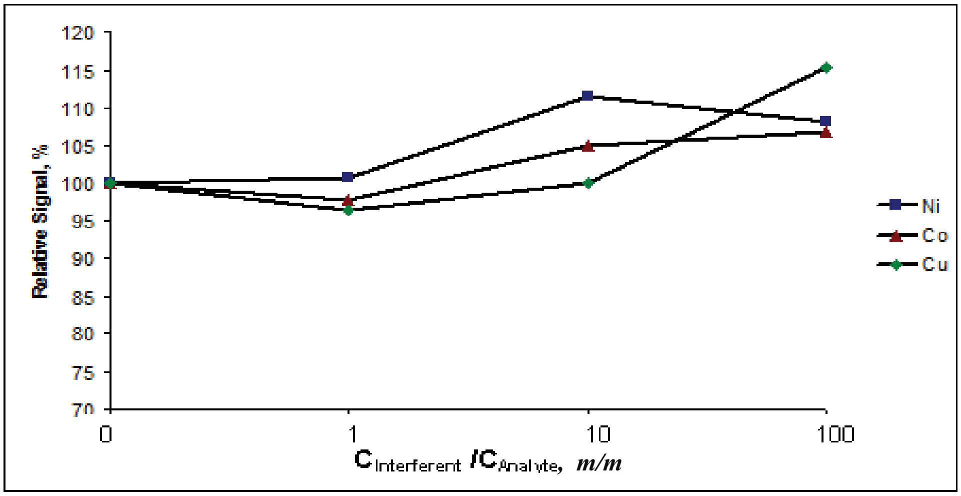


Figure 3.20 Interference effects of Ni, Co and Cu on 5.0 mg/L Tl signal by use of Propanol SQT-FAAS method

As seen in Figure 3.19 and Figure 3.20; while one fold of Ni gave rise to enhancement effect on Tl signal, there were no serious interference effects of Ni, Co and Cu for SQT-FAAS method at elevated concentrations. However, ten folds Ni and 100 folds Cu showed 12% and 15% enhancement effect on thallium determination by Propanol-SQT-FAAS method, respectively.

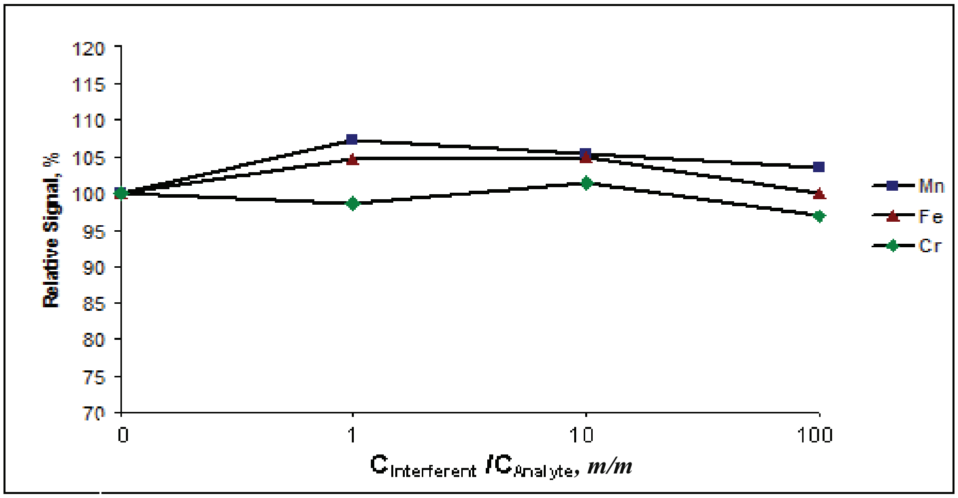


Figure 3.21 Interference effects of Mn, Fe and Cr on 5.0 mg/L Tl signal by use of SQT-FAAS method

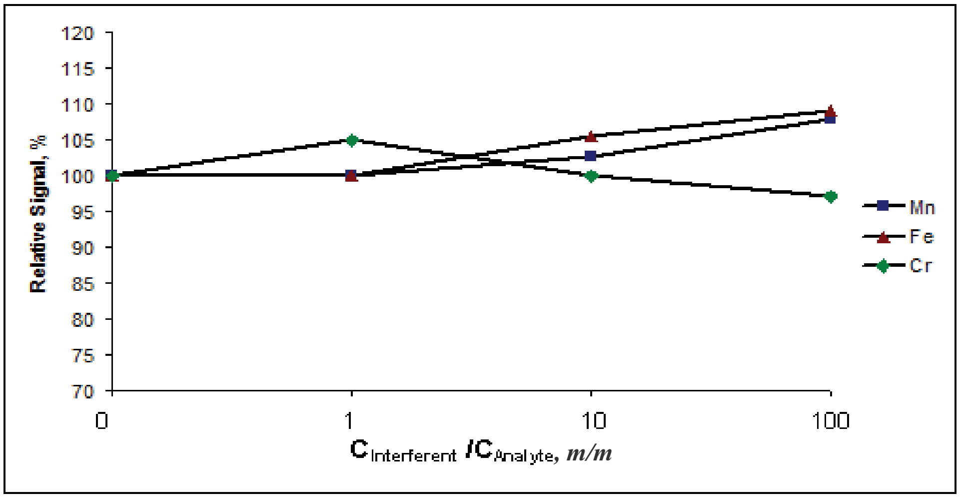


Figure 3.22 Interference effects of Mn, Fe and Cr on 5.0 mg/L Tl signal by use of Propanol-SQT-FAAS method

As it is seen in Figure 3.21, there were no significant interference effects of Mn, Fe and Cr in used concentrations for SQT-FAAS method. However, only 100 folds of Mn and Fe resulted in 9 % enhancement by using Propanol-SQT-FAAS method (Figure 3.22)

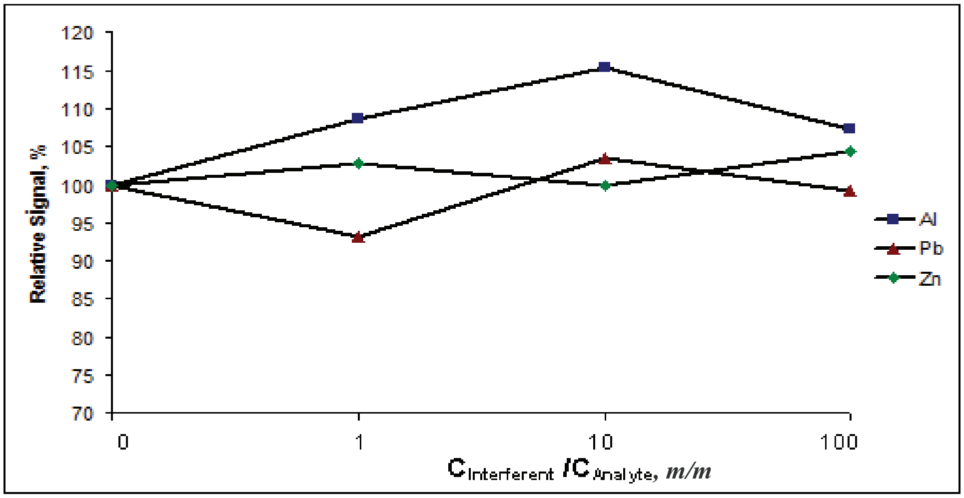


Figure 3.23 Interference effects of Al, Zn and Pb on 5.0 mg/L Tl signal use of SQT-FAAS method

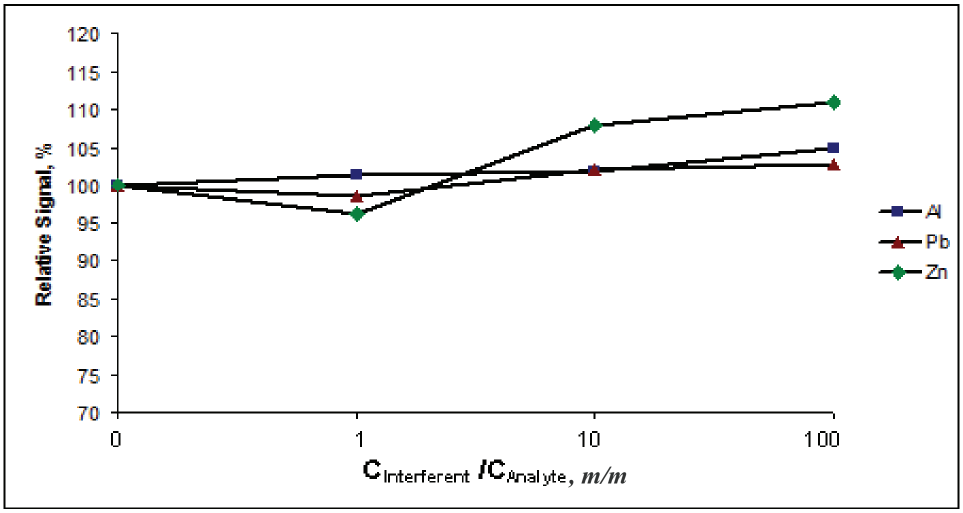


Figure 3.24 Interference effects of Al, Pb and Zn on 5.0 mg/L Tl signal by use of Propanol SQT-FAAS method

As it is seen in the Figure 3.23, there was no significant interference effects of Zn and Pb on Tl determination by SQT-FAAS method. By using the same method, Al had generally an enhancement effect on Tl determination. On the other hand, while Propanol-SQT-FAAS method eliminated these interference effects, 10 and 100 folds of zinc resulted in approximately 10% enhancement on Tl signal (Figure 3.24).

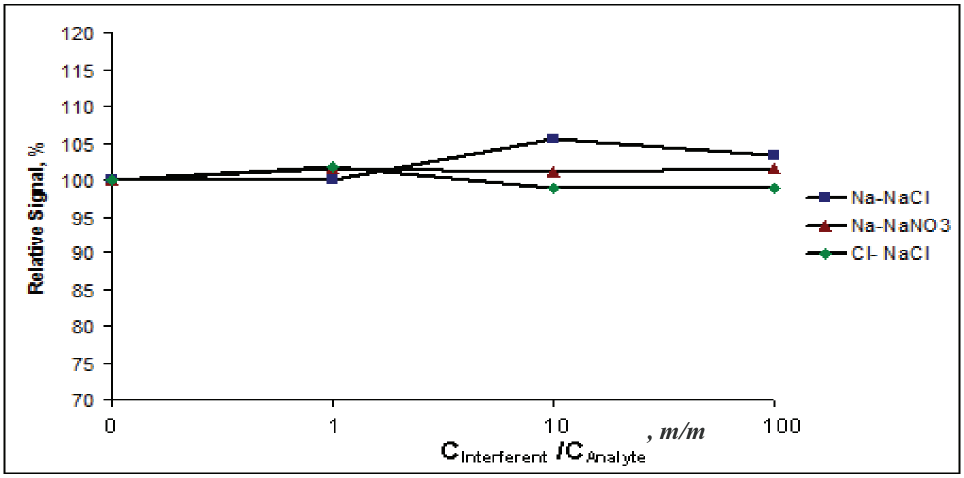


Figure 3.25 Interference effects of Cl^- and NO_3^- as counter ions on 5.0 mg/L Tl signal use of SQT-FAAS method

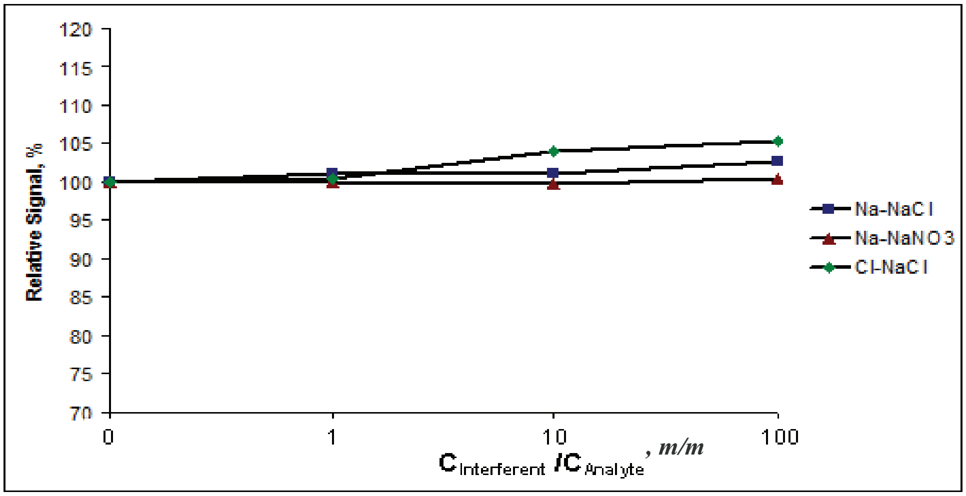


Figure 3.26 Interference effects of Cl^- and NO_3^- as counter ions on 5.0 mg/L Tl signal by use of Propanol SQT-FAAS method

It can be claimed that there were no interference effects of Cl^- and NO_3^- anions on Tl determination by using both methods with in the concentration range used (Figure 3.25, Figure 3.26).

Table 3.5 Summary of Interference Studies for SQT-FAAS and Propanol-SQT-FAAS Methods

Method Elements	Folds of Interferent	SQT-FAAS	Propanol-SQT-FAAS
		Relative Signal	Relative Signal
Na ($NaNO_3$)	1	102	100
	10	101	100
	100	102	101
Mg	1	106	106
	10	100	109
	100	126	115
Ca	1	105	105
	10	105	104
	100	99	106
Ni	1	108	101
	10	105	112
	100	103	108
Co	1	100	98
	10	107	105
	100	106	107
Cu	1	103	96
	10	106	100
	100	106	115
Mn	1	106	100
	10	105	103
	100	103	109
Fe	1	105	100
	10	105	105
	100	100	109
Cr	1	99	105
	10	101	100
	100	97	97
Al	1	109	101
	10	116	102
	100	107	105
Pb	1	93	99
	10	103	102
	100	99	103
Zn	1	103	96
	10	100	109
	100	104	111
Na (NaCl)	1	100	101
	10	105	101
	100	103	103
Cl (NaCl)	1	102	101
	10	99	104
	100	99	105

3.7 Accuracy Check for SQT-FAAS and Propanol-SQT-FAAS Methods

The CRM, SCP SCIENCE EnviroMAT-Waste Water, Low (EU-L-2), was used for the accuracy testing of SQT-FAAS and Propanol-SQT-FAAS methods. The direct calibration plot was employed and three replicate measurements were done under optimum conditions. The results were in good agreement with the certified value in the 95% confidence level for SQT-FAAS and Propanol-SQT-FAAS as shown in the Table 3.6.

Table 3.6 The Results of Accuracy Testing for SQT-FAAS and Propanol SQT-FAAS Methods, using CRM, SCP SCIENCE EnviroMAT-Waste Water Low (EU-L-2)

Certified Value, *mg/L*	**SQT-FAAS** Experimental Result, *mg/L*	**Propanol- SQT-FAAS** Experimental Result, *mg/L*
8.0 ± 0.4	8.3 ± 0.3	8.4 ± 0.1

PART II

In the second part of the study, slotted quartz tube has been used as atom trap apparatus in uncoated and coated forms. The use of Coated-SQT-AT-FAAS is a novel technique for the literature.

3.8 Optimization of Slotted Quartz Tube Atom Trap Flame AAS Method, SQT-AT-FAAS, Conditions for Determination of Thallium

As mentioned in the introduction part, thallium solution was aspirated for a certain time in the presence of lean flame through the slotted quartz tube having entrance and exit slots angled at 120^0 with respect to each other, with lengths of 100 and 80 mm, respectively. After collecting of analyte on the inner surface of SQT, aspiration of sample solution was terminated and certain amount of organic solvent at microliters level was aspirated into flame. As a result of organic solvent aspiration, atoms released from inner surface of SQT give a transient signal. All parameters for this method were optimized by changing one variable at a time while the others were kept constant.

The crucial optimization parameters are the height of entrance slot of SQT with respect to the burner head, flame conditions, trapping period of the analyte, type and volume of organic solvent, and suction rate of the nebulizer. All optimizations were done by using 1000 ng/mL or 250 ng/mL Tl as indicated.

3.8.1 Optimization of Flow Rate of Acetylene

One of the most important parameters was the flow rate of acetylene. Since air flow rate kept constant at 25 L/min, as the flow rate of acetylene increased trapping temperature also increased and as seen in the Figure 3.27 trapping efficiency decreases. Therefore, the possible leanest fuel in which flow rate of acetylene 1.6 L/min was selected as the optimum flame condition for SQT-AT-FAAS. Using a fuel flow rate lower than than 1.6 mL/min results in an extinguished flame.

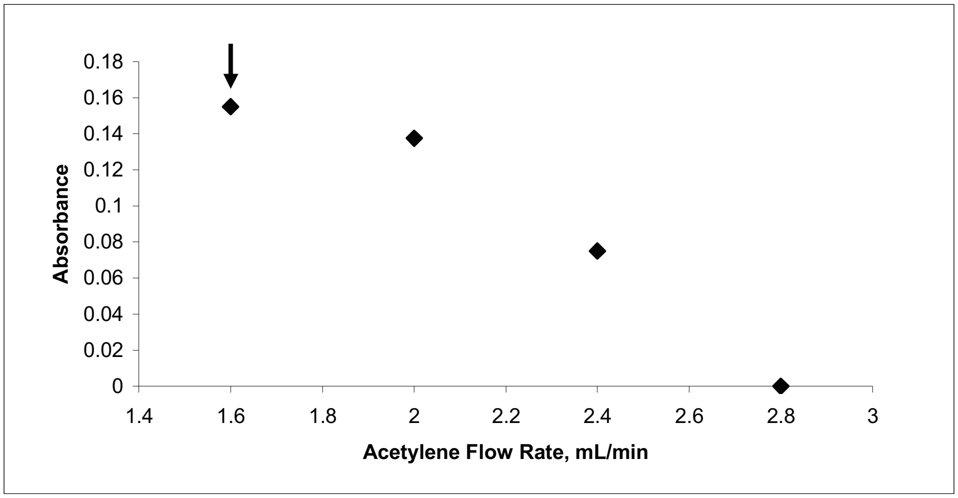


Figure 3.27 Optimization of acetylene flow rate using 1000 ng/mL Tl in SQT-AT-FAAS

60 µL of MIBK as organic solvent:, Suction rate of sample solution: 6.0 mL/min,
Flow rate of air: 25 L/min Trapping Period: 2.0 min,
Height of SQT from the burner head: 1.0 mm

3.8.2 Optimization of Suction Rate of Sample Solution

For atom trapping techniques, suction rate of sample solution is one of the crucial parameters when the sample introduction is done with conventional nebulizers. There are two reasons that makes suction rate important. One of them is that as the suction rate increases; mass of analyte solution aspirated in unit time also increases but nebulization efficiency decreases. Therefore; as suction rate of sample solution is decreased, better nebulization efficiency results in higher trapping efficiency up to a certain point but starts to decrease due to the decrease in total mass of analyte. The other reason is that same suction rate is also used for aspirating the organic solvent which alters the flame condition momentarily for the revolatilization step. It was optimized by keeping the collection period constant. As a result of investigation, the optimum suction rate of sample solution was determined as 3.5 mL/min (Figure 3.28).

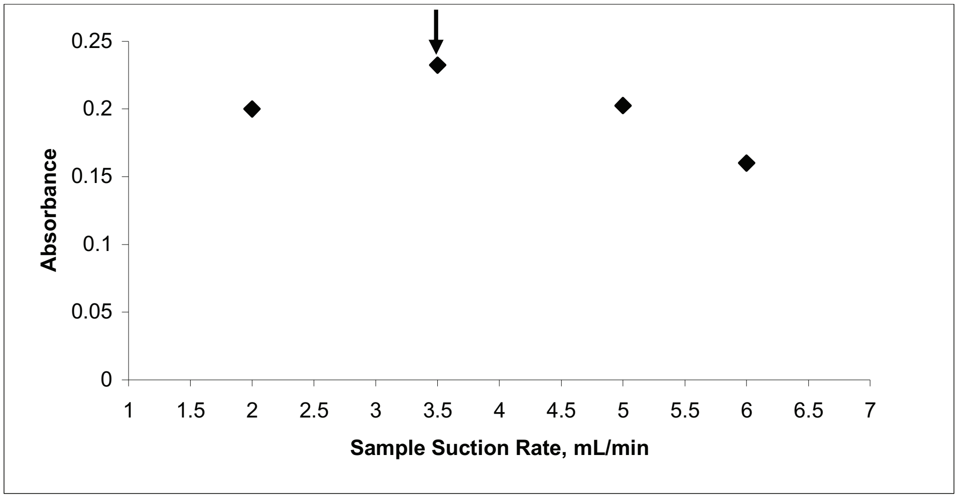


Figure 3.28 Optimization of sample suction rate using 1000 ng/mL Tl in SQT-AT-FAAS

60 µL of MIBK as organic solvent, Flow rate of acetylene: 1.6 L/min,
Flow rate of air: 25 L/min, Trapping period: 2.0 min,
Height of SQT from burner head: 1.0 mm.

3.8.3 Effect of Organic Solvent

In SQT-AT-FAAS technique, aspiration of organic solvent result in momentary alteration of flame conditions which cause revolatilization of trapped atoms on the inner surface of the SQT. Therefore, in order to find the optimum flame condition for revolatilization, several kinds of organic solvent such as methyl isobutyl ketone, methyl ethyl ketone, isopropanol, ethanol and acetonitrile were investigated. As seen in the Table 3.7, although MEK and acetonitrile were also successful for the revolatilization step, the best performance regarding complete atomization was obtained by use of MIBK.

Table 3.7 Effect of Organic Solvents on Tl Signals for SQT-AT-FAAS Method*

Type of Organic Solvent	Absorbance	Enhancement Factor**
	0.020	1.00
⟶ MIBK	0.184	9.20
MEK	0.173	8.65
Isopropanol	No signal	0.00
EtOH	No signal	0.00
Acetonitrile	0.145	7.25

*Conditions are: Volume of organic solvent: 60 µL, Sample suction rate: 3.5 mL/min, Flow rate of acetylene: 1.6 L/min, Flow rate of air: 25 L/min, Trapping period: 1.0 min, Height of SQT from burner head: 1.0 mm, 1000 ng/mL Tl

** $\text{Abs}_{\text{Org.}}/\text{Abs}_{\text{SQT-FAAS.}}$

3.8.4 Optimization of Volume of Organic Solvent

Amount of organic solvent should be enough for the complete revolatilization of trapped atoms so that the highest signals could be obtained. Otherwise, since not all the trapped atoms could be released, signals show a decreasing trend as the amount of organic solvent decrease. As seen in the Figure 3.29, as the amount of organic solvent was increased, the Tl signal also increased and stayed constant after a certain volume aspirated MIBK. Therefore, 60 µL of MIBK was used for the rest of the study.

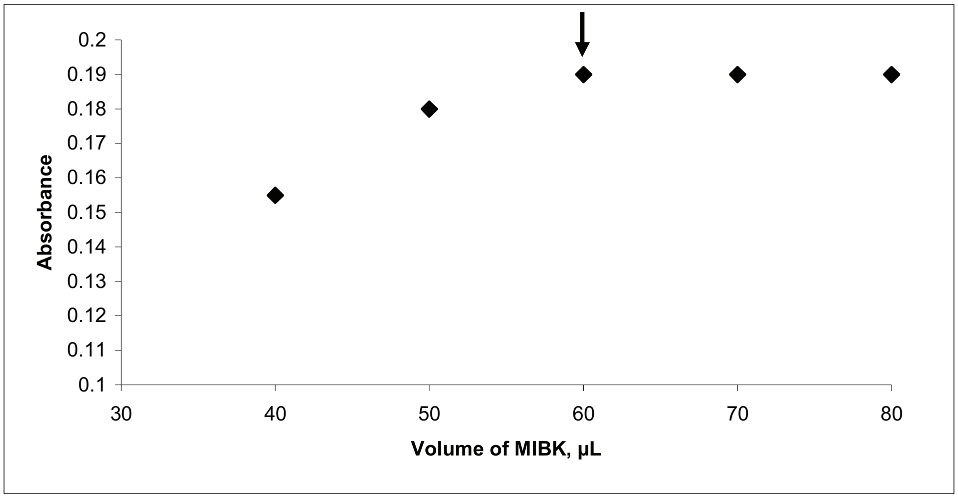


Figure 3.29 Optimization of volume of organic solvent using 1000 ng/mL Tl in SQT-AT-FAAS

MIBK as organic solvent, Suction rate of sample solution: 3.5 mL/min,
Flow rate of acetylene: 1.6 L/min, Flow rate of air: 25 L/min,
Trapping period: 1.0 min, Height of SQT from burner head: 1.0 mm.

3.8.5 Optimization of Height of the SQT from the Burner Head

Another crucial parameter for the optimization of SQT-AT-FAAS method is the position of SQT on the head of the burner. After a certain height, since the entrance of atoms into the SQT becomes difficult and there may be a also temperature difference in the flame zone, the absorbance signals shows sharp decreasing behavior. As seen in the Figure 3.30, optimum height of the SQT from the burner head was observed as 3.0 mm.

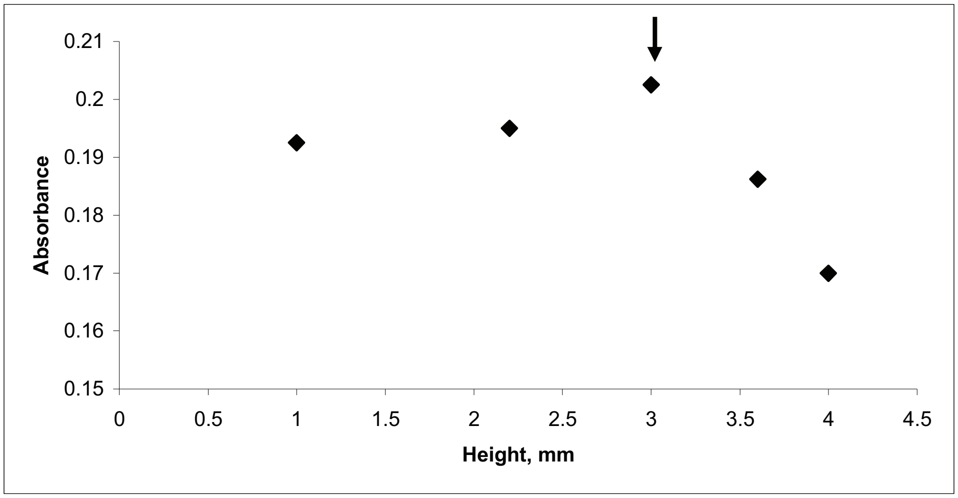


Figure 3.30 Optimization of height of the SQT from the burner head using 1000 ng/mL Tl in SQT-AT-FAAS

60 µL of MIBK as organic solvent, Suction rate of sample solution: 3.5 mL/min, Flow rate of acetylene: 1.6 L/min, Flow rate of air: 25 L/min, Trapping Period: 1.0 min.

3.8.6 Investigation of Trapping Period

Collection period was investigated between 60-600 seconds. As the trapping time increases, the absorbance signal of Tl also increases (Figure 3.31). However, in order to have a procedure comparable with that of graphite furnace, the time involved should not be more than few minutes. In other words, although sensitivity could be increased by using longer trapping periods, it would not be so practical if the technique is to compete with graphite furnace. As a result, a period of 300 seconds was chosen as the optimum value for trapping.

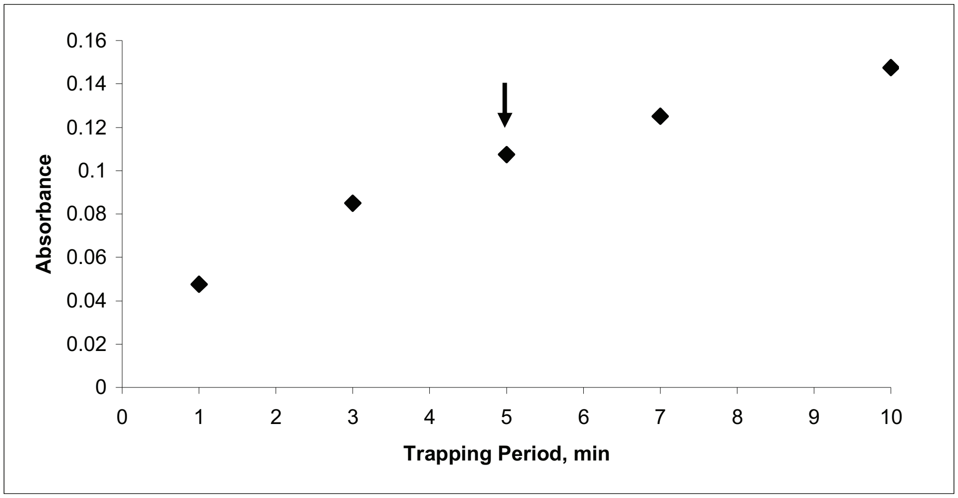


Figure 3.31 Effect of trapping period using 250 ng/mL Tl in SQT-AT-FAAS
60 µL of MIBK as organic solvent, Suction rate of sample solution: 3.5 mL/min,
Flow rate of acetylene: 1.6 L/min, Flow rate of air: 25 L/min,
Height of SQT from burner head: 3.0 mm.

Table 3.8 Optimized Conditions for SQT-AT-FAAS Method

Parameters	**Optimized Conditions**
Type of Organic Solvent	MIBK
Sample Suction Rate	3.5 mL/min
Volume of Organic Solvent	60 µL
Trapping Period	5.0 min
Height of The SQT from the head of the burner	3.0 mm
Flow Rate of Acetylene	1.6 L/min

The signal for 200 ng/mL Tl solution is given in Figure 3.32; the optimized conditions given in Table 3.8 were used. The half bandwidth of this signal was found to be 0.6 s.

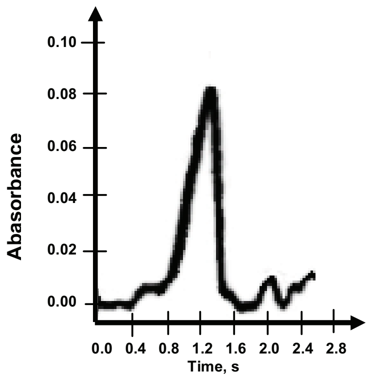


Figure 3.32 The signal of SQT-AT-FAAS for 200 ng/mL Tl solution.

3.9 Analytical Figures of Merit

For the SQT-AT-FAAS method calibration plot was obtained using the optimum conditions. Limit of detection as 3s/m, limit of quantitation as 10s/m and characteristic concentration were calculated. Enhancement in sensitivity was calculated by the comparison of characteristic concentrations for FAAS and SQT-AT-FAAS methods.

3.9.1 Calibration Plots for SQT-AT-FAAS Technique

As seen in the Figures 3.33 and 3.34, the calibration plot was linear between 50 - 300 ng/mL. The best line equation and correlation coefficient were $y = 0.0004x + 0.002$ and 0.9992, respectively. While limit of detection was found as 38 ng/mL and limit of quantitation was calculated as 130 ng/mL, characteristic concentration was 9.7 ng/mL.

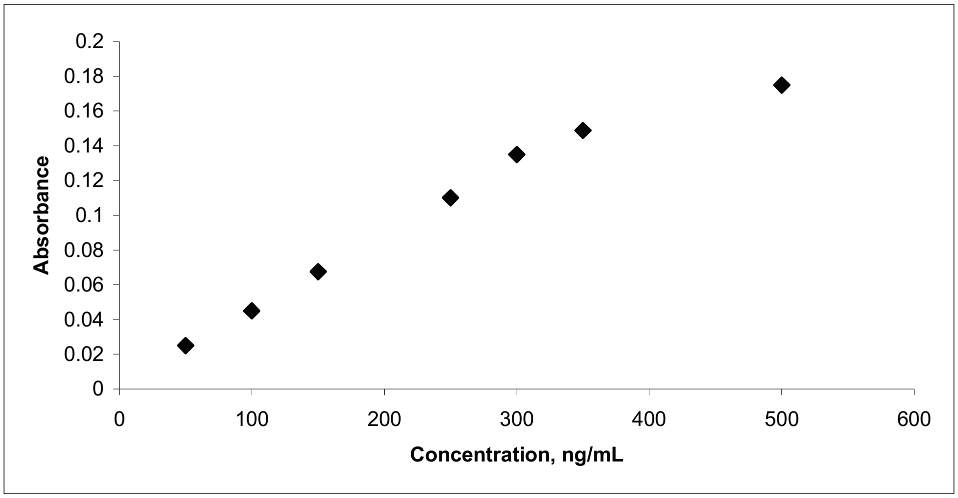


Figure 3.33 Calibration plot for SQT-AT-FAAS method

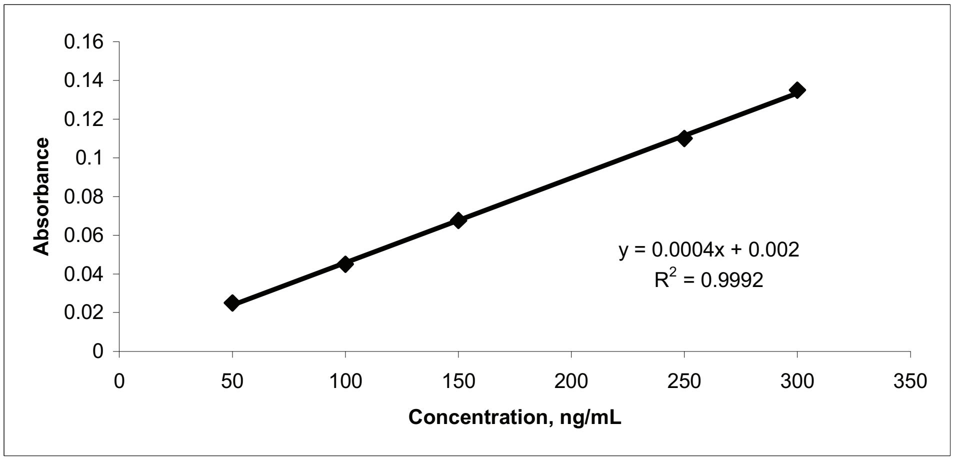


Figure 3.34 Linear calibration plot for SQT-AT-FAAS method

In this method, considerable enhancements in sensitivity and detection limit were obtained as compared to conventional FAAS. As seen in the Table 3.9, compared to FAAS, 92 folds enhancement has been obtained. This sensitivity has been achieved by trapping thallium atoms on the inner surface of the slotted quartz tube and then revolatilizing by aspiration of microliter amounts of MIBK.

Table 3.9 Analytical Figures of Merit

	Limit of Detection, LOD, 3s/m *(N=6)* ng/mL,	**Limit of Quantitation**, LOQ, 10s/m *(N=6)* ng/mL,	**Characteristic Concentration**, C_0 ng/mL	**Enhancement Factor***	**Dynamic Ranges,** ng/mL
FAAS	$1.3x10^3$	$4.2x10^3$	894	1.00	$2x10^3$-$25x10^3$
SQT-FAAS	$3.4x10^2$	$1.1x10^3$	230	3.89	$1x10^3$-$10x10^3$
SQT-AT-FAAS	38	$1.3x10^2$	9.7	92	50-300

* $C_{0(FAAS)} / C_{0(selected\ method)}$

3.10 Interference Studies for SQT-AT-FAAS Method

The aim of this study was to make interference studies for thallium determination in 1.0 M HNO_3 medium using SQT-AT-FAAS method. Some major elements, transition elements and also anions were tested as interferents

During the interference studies, standards at concentrations of 200 ng/mL Tl in 1.0 M HNO_3 were used together with interferents. The interferent concentrations were 1, 10 and 100 folds of the analyte concentration.

Figures between 3.35 and 3.38 are graphical representations of the interferences of Na, Ca, Mg, Co, Cu, Ni, Cr, Mn, Fe, Pb, Al and Zn on the absorbance signals of Tl. In addition to these elemental interference effects of Cl^- and NO_3^- ions as counter ions were also investigated (Figure 3.39).

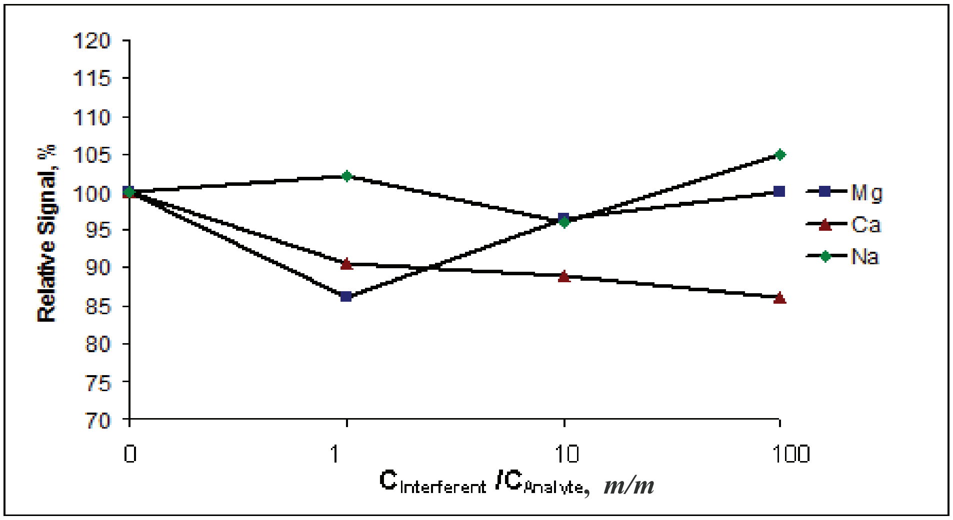


Figure 3.35 Interference effects of Ca, Mg and Na on 200 ng/mL Tl signal by use of SQT-AT-FAAS method

As it can be seen from the Figure 3.35, one fold of Mg affects Tl signal in a negative way, while the elevated concentrations of Mg did not significantly interfere with thallium. On the other hand, the presence of 200 ng/mL and 2000 ng/mL Ca depressed Tl signal about 10 % and when Ca concentration was 100 folds of Tl concentration, it resulted in 16 % depression. The presence of Na in any concentration used did not affect the Tl signal.

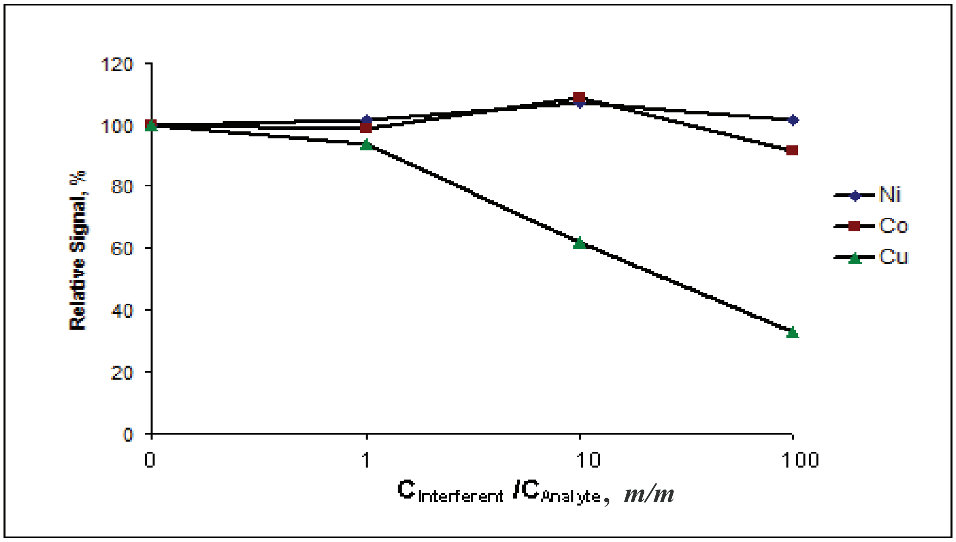


Figure 3.36 Interference effects of Co, Ni and Cu on 200 ng/mL Tl signal by use of SQT-AT-FAAS method

As it is seen in the Figure 3.36, the presence of 200 ng/mL Ni and Co did not interfere with Tl. When the concentration of them was 10 folds of Tl concentration, they both caused 8 % enhancement of Tl signal. On the other hand, while Tl signal was suppressed by 10 % in the presence of 20.0 mg/L Co, it was not affected by the same concentration of Ni. Copper was one of the most strongly interfering elements. Although the presence of 200 ng/mL Cu did not interfere with Tl, the presence of 10 and 100 folds copper had 38 % and 68 % suppressing effect on Tl signal, respectively. It was observed that the interference effect of copper was permanent and the surface of the slotted quartz tube had to be cleaned prior to further use. For this purpose, SQT was kept in 20 % HF solution for three minutes, then rinsed with distilled water and dried.

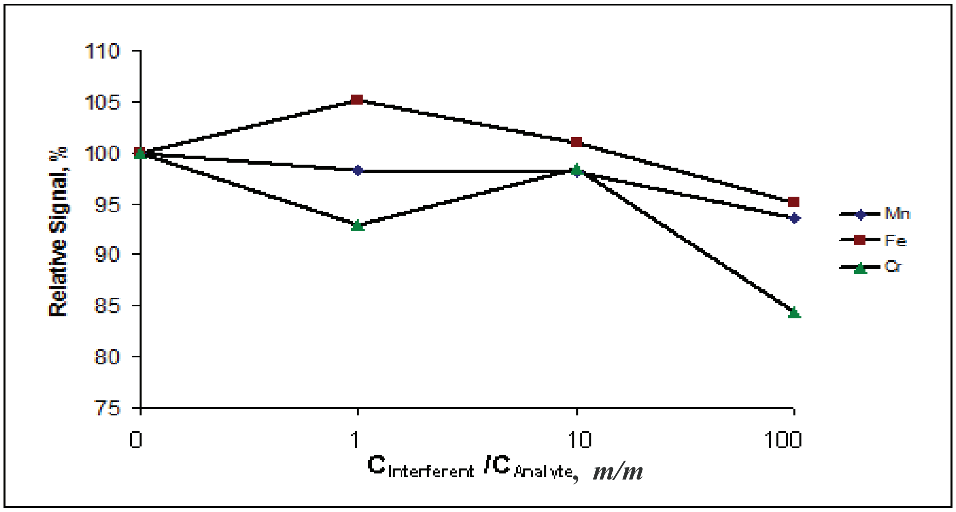


Figure 3.37 Interference effects of Mn, Fe and Cr on 200 ng/mL Tl signal by use of SQT-AT-FAAS method

As it is seen the Figure 3.37, the presence of Mn and Fe in any concentration did not give rise to any significant interference effect. On the other hand, although 1 and 10 folds chromium did not interfere with Tl, 100 folds chromium resulted in decrease on Tl signal by 16 %.

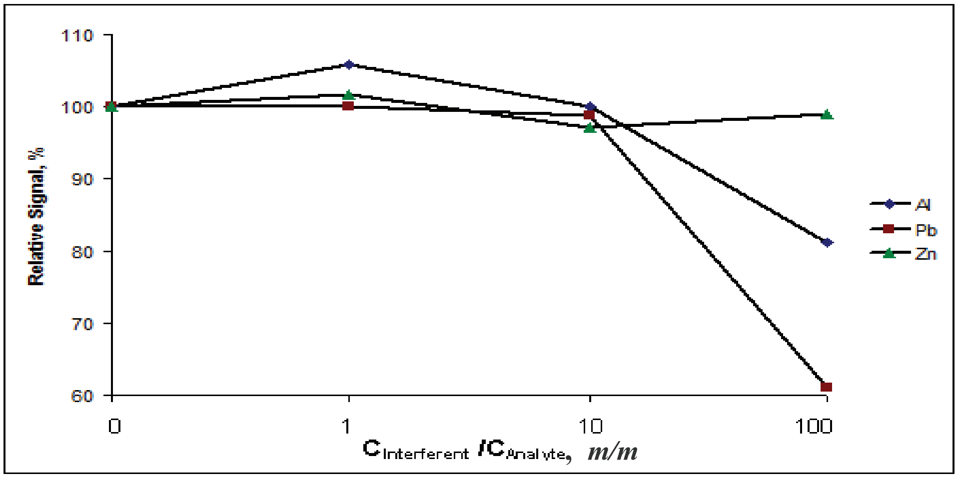


Figure 3.38 Interference effects of Al, Zn and Pb on 200 ng/mL Tl signal by use of SQT-AT-FAAS method

As seen from the Figure 3.38, no interference effect of Zn wasobserved on Tl signal. While 100 folds of Al and Pb showed 19% and 39%, respectively, suppressing effect for Tl determination, the other ratios of them did not cause any interference effect.

In addition to these elemental interference effects for Tl determination by SQT-AT-FAAS method, counter ion effects were also investigated. In order to verify the effects of Cl^- and NO_3^- anions; NaCl and $NaNO_3$, were tested separately in 1 M HNO_3.

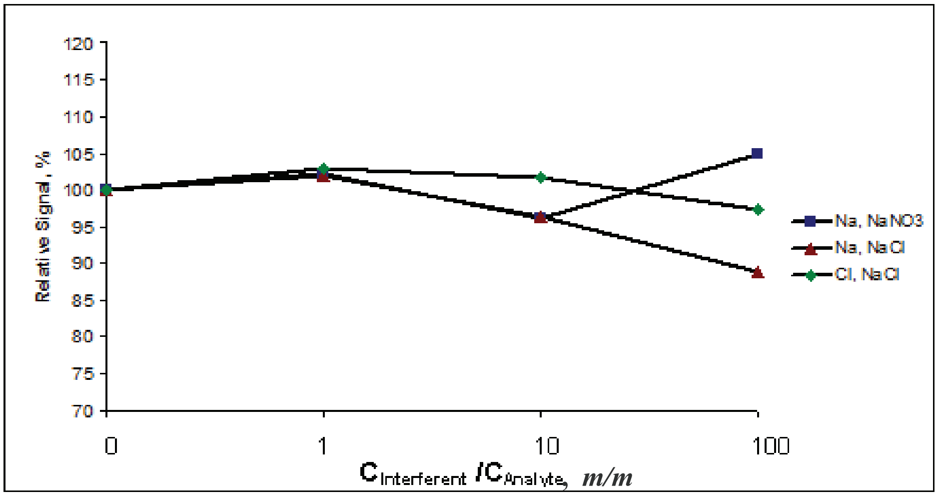


Figure 3.39 Interference effects of Cl^- and NO_3^- as counter ions on 200 ng/mL Tl signal in use of SQT-AT-FAAS method

As it seen in the Figure 3.39, one and ten folds of each interferent anion and cation did not have any significant interfering effects on Tl signal. When the concentration of interferents was increased to 100 folds of the analyte concentration; 10 % suppression was observed in the presence of Na^+ originated from NaCl medium whereas the Na^+ originated from $NaNO_3$ did not result in any interference. Therefore, the source of interference should be chloride ion rather than sodium ions. NaCl was used both for Na and Cl^- ions; when Na is taken as an interferent, the molar concentration of Cl^- is higher as compared to the case where Cl- was taken as an intereferent; the ratio is 4.35/2.82, or 1.54. The result is a higher interference effect in case where Na was taken as the interferent, although the real cause is chloride ion.

The interference effect of NaCl may be due to the devitrification effect of NaCl on quartz surface. Since all the solutions were prepared in 1.0 M HNO_3, the medium is buffered with respect to nitrate ions and no interference would be detected even if there is any.

3.11 Accuracy Check for SQT-AT-FAAS Method

The CRM, SCP SCIENCE, EnviroMAT-Waste Water, Low (EU-L-2), was used for accuracy check of SQT-AT-FAAS method. The direct calibration was employed and three replicate measurements were done under optimum conditions. The results were in good agreement with the certified value as shown in the Table 3.10.

Table 3.10 The Result of the Accuracy Test for SQT-AT-FAAS Method

SCP SCIENCE, EnviroMAT **Waste Water EU-L-2**	**Certified Value,** *mg/L*	**Experimental Result,** *mg/L*
	8.0 ± 0.4	7.9 ±0.3

3.12 Optimization of Coated Slotted Quartz Tube Atom Trap Flame AAS, Coated-SQT-AT-FAAS, Conditions for Determination of Thallium

After the evaluation of SQT-AT-FAAS technique, the next step was to modify the inner surface of the SQT so that better detection limits could be obtained. The aim of this approach was to create a better surface than the quartz surface so that analyte could be trapped more efficiently in the inner surface of the tube and then released successfully. The working principle of the method was same with SQT-AT-FAAS technique. In addition to optimization of coating material, since the chemical properties of the trapped surface of the SQT was different from the SQT-AT-FAAS technique, all the parameters optimized for SQT-AT-FAAS were optimized again for this technique. Optimizations were done by 100 ng/mL and 250 ng/mL Tl standard solutions as indicated.

3.12.1 Investigation of Coating Material on SQT-AT-FAAS Method

Coating materials were chosen according to their boiling and melting point of them and their availability in the laboratory. Effect of tungsten, palladium, molybdenum, gold, tantalum, zirconium, titanium and osmium were investigated. Coatings of these materials on the inner surface of SQT were done using the same procedure described in the experimental part.

As seen in the Table 3.11, use of Pd coated and W coated SQT devices were not suitable for the purpose. Gold, molybdenum, tantalum, zirconium and titanium provided some enhancement for determination of thallium by use of coated SQT-AT-FAAS technique. However, since Os-Coated-SQT-AT-FAAS provided 5.71 fold enhancement comparing to the SQT-AT-FAAS, osmium was chosen as the optimum coating material for this technique.

Table 3.11 Effect of Coating Material on Tl Signal for SQT-AT-FAAS*

Coating Material	**Absorbance**	**Enhancement Factor****
Tungsten	No Signal	-
Palladium	No Signal	-
None	0.018	1.00
Molybdenum, Mo	0.020	1.14
Gold, Au	0.025	1.43
Tantalum, Ta	0.033	1.86
Zirconium, Zr	0.058	3.29
Titanium, Ti	0.058	3.29
Osmium, Os	0.10	5.71

*Conditions are: Suction Rate of Sample Solution: 7.5 mL/min, 100 µL MIBK as organic solvent, Flow rate of acetylene: 1.8 L/min, Flow rate of air: 25 L/min,
Height of SQT: 2.0 mm, Trapping period: 5.0 min, 100 ng/mL Tl.

**$\mathbf{A}_{\text{coated-SQT-AT-FAAS}}/\mathbf{A}_{\text{SQT-AT-FAAS}}$

Since Tl signals decreased by 30% every after 50-60 shots of Os-coated-SQT, it was recoated by aspirating 25 mL of 1000 mg/L Os.

3.12.2 Optimization of Suction Rate of Sample Solution

Sample suction rate was investigated between 3.0 mL/min and 12.0 mL/min. While the optimum sample suction rate was 3.5 mL/min for SQT-AT-FAAS, it was found as 5.0 mL/min for Os-coated-SQT-AT-FAAS technique (Figure 3.40). This means more amount of analyte were trapped by Os-coated-SQT in unit time. Although this seems as a disadvantage of the technique since such a sensitivity could possibly be also achieved by SQT-AT-FAAS technique by increasing trapping time so that more analyte could be trapped, it was proved that this technique is still more sensitive than the former one when normalized values of the both of the techniques were used according to E_v and E_t values given in the Table 3.15.

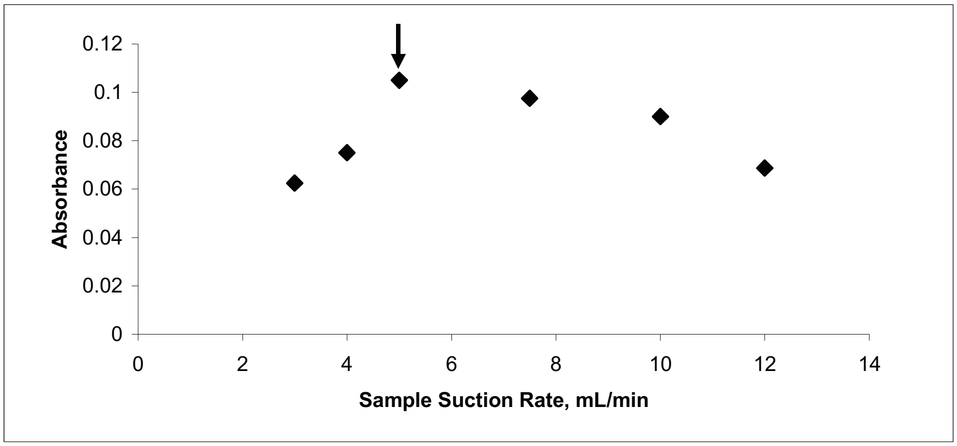


Figure 3.40 Optimization of sample suction rate using 250 ng/mL Tl in Os Coated-SQT-AT-FAAS

100 µL MIBK as organic solvent, Flow rate of acetylene: 1.8 L/min,
Flow rate of air: 25 L/min, Height of SQT from burner head: 1.4 mm,
Trapping period: 2.0 min.

3.12.3 Optimization of Type of Organic Solvent

For revolatilization of trapped analytes from the inner surface of SQT, MIBK was again the best organic solvent for this technique in terms of completeness of the revolatilization step (Table 3.12).

Table 3.12 Effect of Organic Solvent Type for Os-Coated-SQT-AT-FAAS*

Type of Organic Solvent	**Absorbance**	**Enhancement Factor****
SQT-AT-FAAS	0.045	1.00
→ MIBK	0.093	2.07
MEK	0.080	1.78
EtOH	0.051	1.13
Isopropanol	0.060	1.33
Acetonitrile	0.064	1.42

*Conditions are: Sample suction rate: 5.0 mL/min, 100 μL MIBK as organic solvent, Flow rate of acetylene: 1.8 L/min, Height of SQT from burner head: 1.4 mm, Trapping time: 5.0 min, 100 ng/mL Tl.

** $A_{\text{Coated-SQT-AT-FAAS}}$ /$A_{\text{SQT-AT-FAAS}}$

3.12.4 Optimization of Flame Condition

As seen in the Figure 3.41, possible leanest flame gives the best result for collection step. Therefore, 1.6 mL/min was chosen as the optimum acetylene flow rate for the technique. For acetylene flow rate lower than 1.6 L/min, the flame was extinguished.

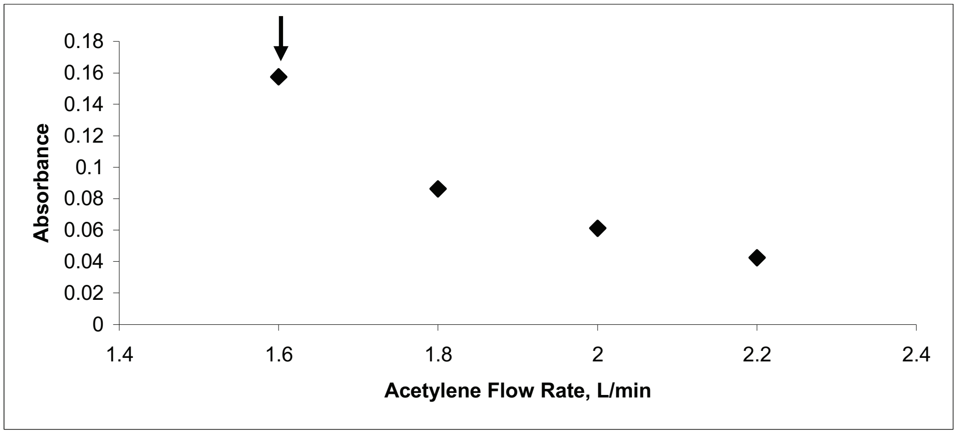


Figure 3.41 Optimization of acetylene flow rate using 250 ng/mL Tl in Os Coated-SQT-AT-FAAS

Sample suction Rate: 5.0 mL/min, Flow rate of air: 25 L/min, 100 μL MIBK as organic solvent, Height of SQT: 1.4 mm, Trapping period: 2.0 min

3.12.5 Optimization of Amount of Organic Solvent

As seen in the Figure 3.42, 60 µL of MIBK was sufficient for the complete revolatilization step. However, in order to study in plateau, aspiration of 80 µL of MIBK was chosen for this step.

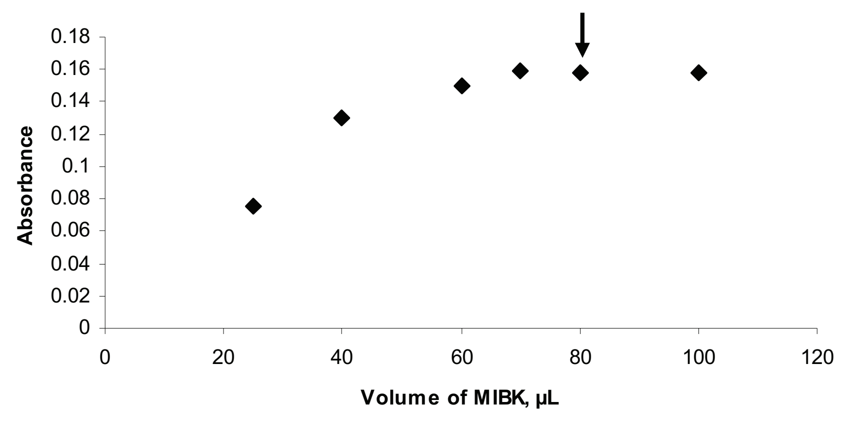


Figure 3.42 Optimization of amount of organic solvent using 250 ng/mL Tl in Os Coated-SQT-AT-FAAS

Sample suction rate: 5.0 mL/min, MIBK as organic solvent,

Flow rate of acetylene: 1.6 L/min, Flow rate of air: 25 L/min,

Height of SQT from burner head: 1.4 mm, Trapping period: 2.0 min.

3.12.6 Investigation of Trapping Period

As the trapping period was increased, signals also increased proportionally. However, due to the same reasons for SQT-AT-FAAS, 300 s was chosen as the optimum trapping period (Figure 3.43**)**.

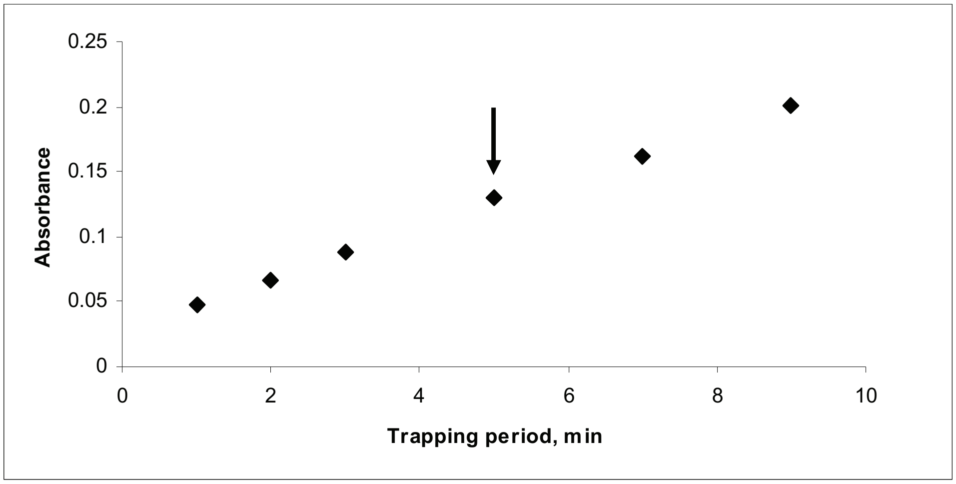


Figure 3.43 Effect of trapping period on Tl signal using 100 ng/mL Tl in Os Coated-SQT-AT-FAAS

Sample suction rate: 5.0 mL/min, 80 μL of MIBK as organic solvent: MIBK,
Flow rate of acetylene: 1.6 L/min, Flow rate of air: 25 L/min
Height of SQT from burner head: 1.4 mm.

3.12.7 Optimization of Height of the SQT from the Burner Head

As seen in Figure 3.44, the optimum height of the SQT from the burner head of FAAS was defined as 1.8 mm. Although the absorbance signals did not show significant increase between 0.9 mm and 3.0 mm, it decreased in the higher heights sharply.

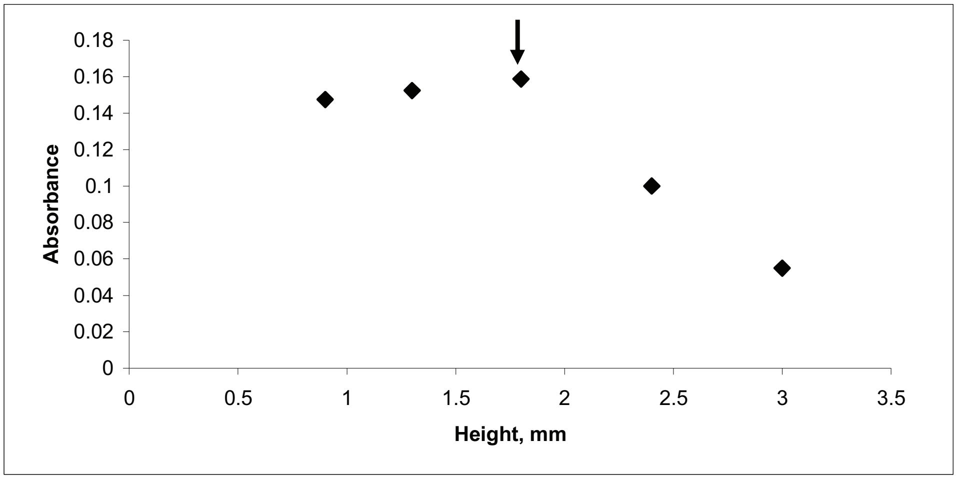


Figure 3.44 Optimization of height of SQT from burner head using 100 ng/mL Tl in Os Coated-SQT-AT-FAAS

Sample flow rate: 5.0 mL/min, 80 µL of MIBK as organic solvent: MIBK,
Flow rate of acetylene: 1.6 L/min, Flow rate of air: 25 L/min Trapping Period: 5.0 min.

The optimized conditions for Os-Coated-SQT-AT-FAAS method are given below (Table 3.13). The signal for 100 ng/mL Tl using optimum conditions was given in Figure 3.45 and the half bandwidth of signal was found as 0.8 s.

Table 3.13 Optimized Conditions for Os-Coated-SQT-AT-FAAS method

Parameters	Optimized Conditions
Coating Material	Osmium
Type of Organic Solvent	MIBK
Sample Suction Rate	5.0 mL/min
Volume of Organic Solvent	80 µL
Trapping Period	5.0 min
Height of The SQT from the head of the burner	1.8 mm
Flow Rate of Acetylene	1.6 L/min

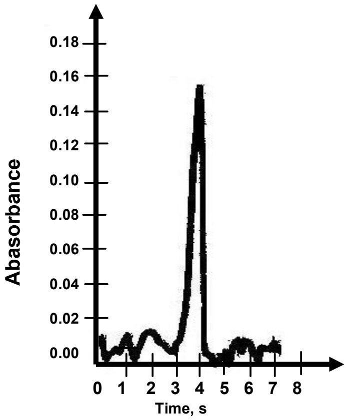


Figure 3.45 The signal of Os- Coated-SQT-AT-FAAS for 100 ng/mL Tl solution.

3.13 Analytical Figures of Merit

For the SQT-AT-FAAS technique calibration plot was obtained under the optimum conditions. Limit of detection as 3s/m, limit of quantitation as 10s/m and characteristic concentration were calculated. Enhancement in sensitivity was calculated by the ratio of characteristic concentration values.

3.13.1 Calibration Plots for Os–Coated-SQT-AT-FAAS Method

As it is seen in the Figures 3.46 and 3.47, the calibration plot was linear between 10.0-200 ng/mL. The best line equation and correlation coefficient of $y = 0.0014x + 0.0091$ and 0.9998, respectively. While the limit of detection was found as 3.5 ng/mL, limit of quantitation was calculated as 12 ng/mL, characteristic concentration was 2.8 ng/mL.

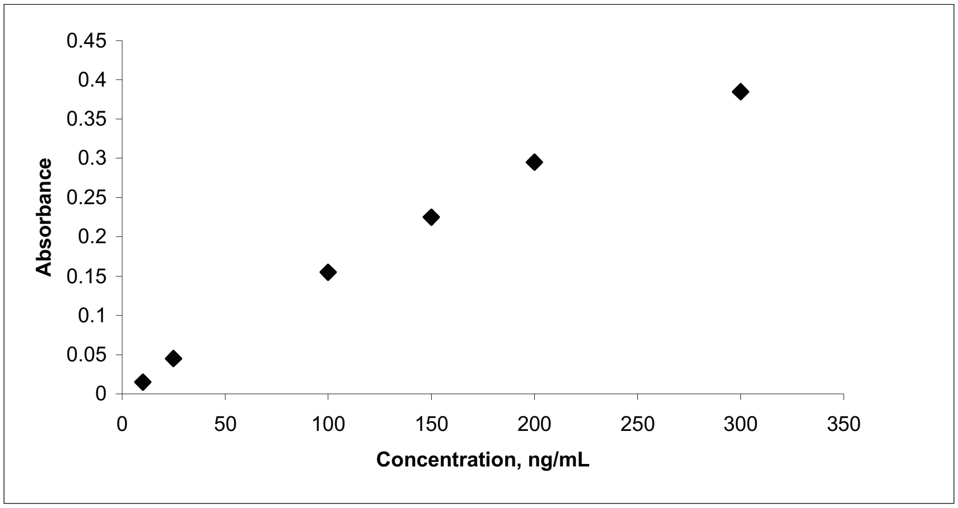


Figure 3.46 Calibration plot for Os-Coated-SQT-AT-FAAS method

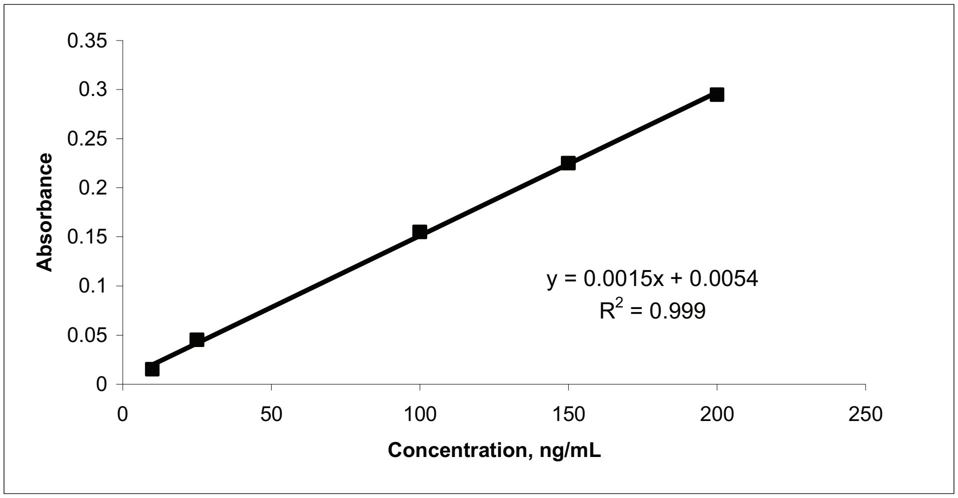


Figure 3.47 Linear calibration plot for Os-Coated-SQT-AT-FAAS method

In this method, considerable enhancement in sensitivity in terms of characteristic concentration was obtained as compared to conventional flame AAS. As seen in the Table 3.14, compared to FAAS method approximately 319 times more sensitive method has been developed. The detection limit and characteristic concentration of the method were 3.5 and 2.8 ng/mL, respectively.

Table 3.14 Analytical Figures of Merit

	Detection Limit, LOD, 3s/m *(N=6)* ng/mL,	**Limit of Quantitation,** LOQ, 10s/m *(N=6)* ng/mL	**Characteristic Concentration,** C_0 ng/mL	**Enhancement Factor***	**Dynamic Ranges,** ng/mL
FAAS	$1.3x10^3$	$4.2x10^3$	894	1.00	$2x10^3$-$25x10^3$
SQT-FAAS	$3.4x10^2$	$1.1x10^3$	230	3.89	$1x10^3$-$10x10^3$
SQT-AT-FAAS	38	$1.3x10^2$	9.7	92	50-300
Os-Coated-SQT-AT-FAAS	3.5	12	2.8	319	10.0-200

C_0(FAAS) / C_0(selected method)

3.14 Evaluation of System Performance

As seen in the Table 3.15, besides determining the C_0 and LOD values, normalization is also done according to the total time and the total volume for atom trapping as mentioned in a recent study [13].

Table 3.15 Comparison of Methods in Terms of E, E_t and E_v Values

Technique, Period, Volume	**C_0,** *ng/mL*	**LOD,** *ng/mL*	**E**	**E_t,** min^{-1}	**E_v,** mL^{-1}
FAAS	894	1.3×10^3	1.00	-	-
Propanol-FAAS	634	9.5×10^2	1.41	-	-
SQT-FAAS	230	3.4×10^2	3.89	-	-
Propanol-SQT-FAAS	199	1.4×10^2	4.49	-	-
SQT-AT-FAAS 5.0 min, *17.5 mL*	9.7	38	92	18.4	5.3
Os-Coated-SQT-AT-FAAS 5.0 min, *25 mL*	2.8	3.5	319	63.8	12. 8

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

As seen in the Table 3.15, although the amount of introduced sample for Os-Coated–SQT-FAAS is more than the amount for SQT-AT-FAAS technique; it is still approximately 2.4 fold more sensitive than the latter in terms of unit volume. Furthermore, in terms of time need for trap, it is already the most sensitive technique among the ones above.

3.15 Interference Studies for Os-Coated-SQT-AT-FAAS Method

During the interference studies, standards at concentrations of 50.0 ng/mL Tl in 1.0 mol/L HNO_3 was used together with interferents. This analyte concentration was decided by using the enhancement factor between Os-Coated-SQT-AT-FAAS and SQT-AT-FAAS method which is approximately 4 fold. The interferent concentrations were 1, 10, 100 and 1000 folds of the analyte concentration.

Figures between 3.48 and 3.51 are graphical representation of the interferences of Na, Ca, Mg, Co, Cu, Ni, Cr, Mn, Fe, Pb, Al and Zn on the absorbance signals of Tl. In addition to these elemental interference effects, Cl^- and NO_3^- ions as counter ion were also investigated under the optimum conditions. (Figure 3.52).

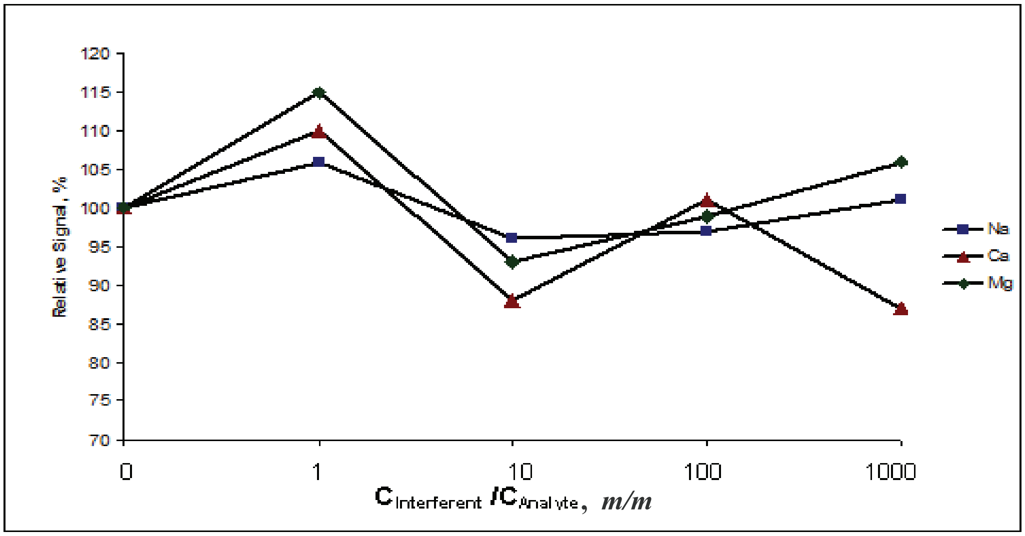


Figure 3.48 Interference effects of Ca, Mg and Na on 50 ng/mL Tl signal in Os-Coated-SQT-AT-FAAS

As it is seen in the Figure 3.48, one fold of Mg, Ca and Na resulted in enhancement on Tl signal by percent of 15%, 10% and 6 %, respectively. When the interferent concentrations become ten folds of analyte, while Na did not result in so significant interference; Mg and Ca decreased the relative signal to 93% and 88%, respectively

While the elevated concentration of Na did not show any interfering effect on the signal, the presence of 50 mg/L Mg and Ca caused enhancement and suppressing on the Tl signal by 6 % and 13%, respectively.

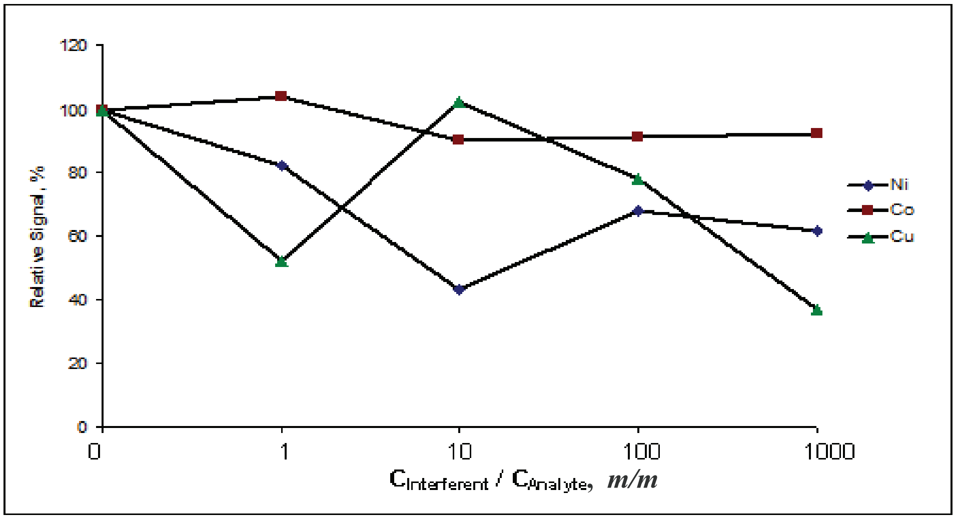


Figure 3.49 Interference effects of Ni, Co and Cu on 50 ng/mL Tl signal in Os-Coated-SQT-AT-FAAS

As it is seen in Figure 3.49, among those elements; the least interfering element was cobalt. While the presence of one fold of cobalt did not interfere with thallium, in the other concentrations of cobalt resulted approximately 10 % decrease. On the other hand, one fold of Ni and Cu had showed suppressing effect by 17 % and 48 %, respectively. While the Cu did not affected the Tl signal in the concentration of 500 ng/mL, the same concentration of Ni depressed it down to 43%. Moreover, when the concentration of Cu became 1000 folds of the analyte, the most serious interference effect was observed which was a 63 % decrease of Tl signal and the surface of slotted tube needed to be cleaned up by keeping in 20% HF solution for three minutes and recoating by the described procedure before the next analysis.

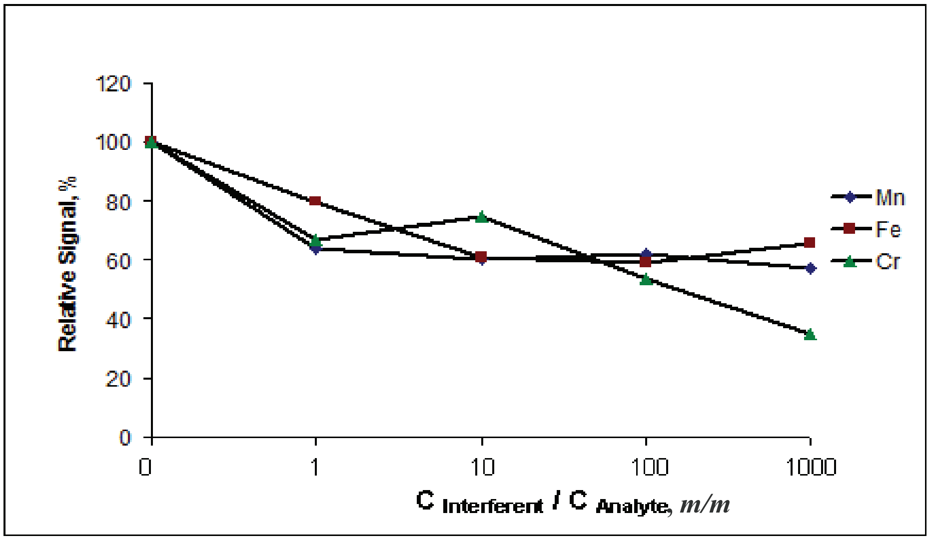


Figure 3.50 Interference effects of Ca, Mg and Na on 50 ng/mL Tl signal in Os-Coated-SQT-AT-FAAS.

As it is seen in the Figure 3.50; Mn, Fe and Cr had generally depressing effects on Tl determination by Os-Coated-SQT-AT-FAAS method. Each concentration of Mn had depressed the Tl signal by approximately 40%. While one fold of Fe concentration affected the signal by 20% in a negative way, the more concentrated Fe medium gave rise to the more depression on Tl signal as seen in the Figure 3.46. On the other hand, as one and 100 folds of Cr showed similar suppressing effect on Tl signal with Mn, 10 and 1000 folds of it caused 26 % and 65 % decreases.

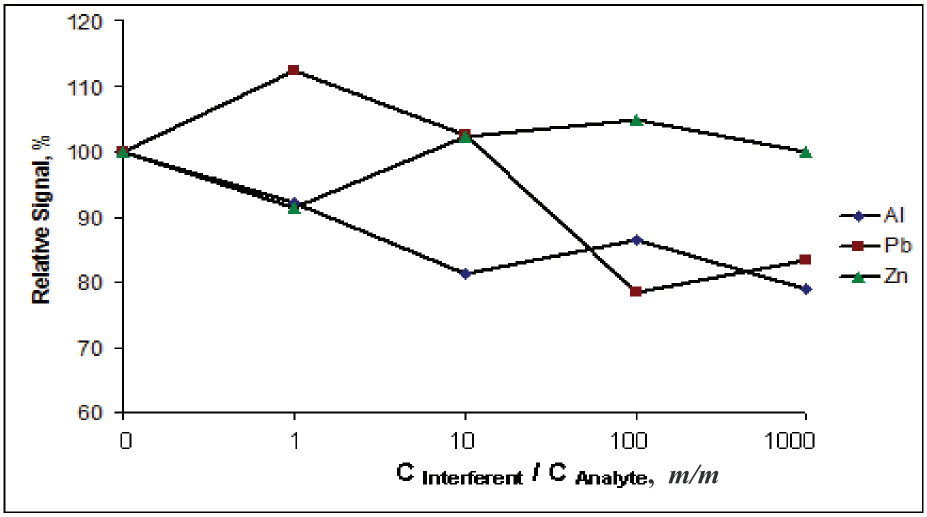


Figure 3.51 Interference effects of Al, Pb and Zn on 50 ng/mL Tl signal in Os-Coated-SQT-AT-FAAS.

In the presence of one fold of interferent concentration; while aluminum and zinc showed the similar suppressing effect by 10 %, lead resulted in 18 % increase on Tl signal (Figure 3.51). When the interferent concentrations were increased to 500 ng/mL; while Zn and Pb did not interfere with Tl, Al caused a 19 % decrease. For higher concentration of interferents, although Zn did not interfere with thallium so seriously, Pb and Al caused approximately 20 % suppression.

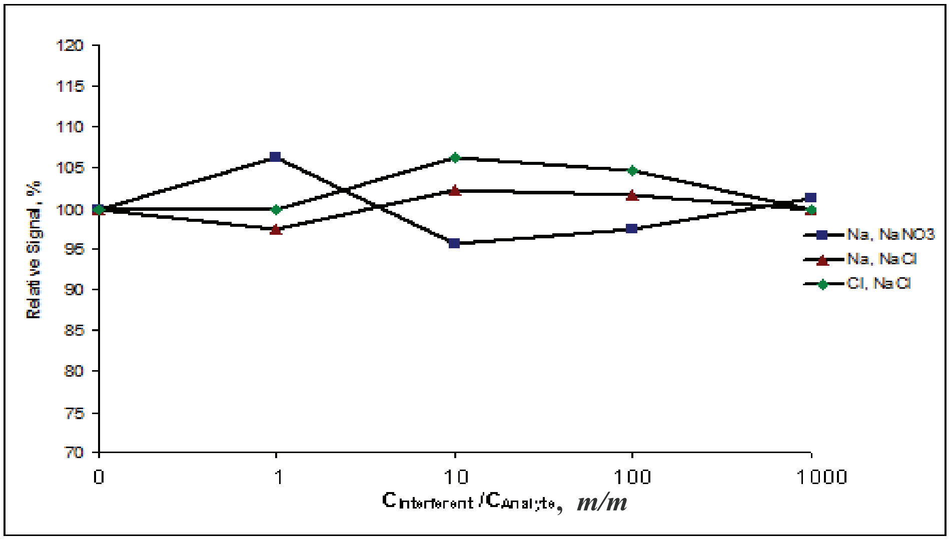


Figure 3.52 Interference effects of Cl^- and NO_3^- as counter ions on 50 ng/mL Tl signal in Os-Coated-SQT-AT-FAAS.

As it is seen in the Figure 3.52, there is no significant interference effect of Cl^- anions on Tl signal. Moreover, it could be concluded that the presence of nitrate anions was not important, since all the solutions were prepared in 1.0 M HNO_3. This corresponds to 62000 mg/L NO_3^- and thus all the solutions are nitrate buffered.

The general summary of interference studies of both atom trap techniques is given in Table 3.16. Interference effects of some kind of elements such as Ni, Mn, Fe and Cr appeared to be more serious in the case of using Os-Coated-SQT-AT-FAAS method.

Table 3.16 Summary for Interference Studies of SQT-AT-FAAS and Os-Coated-SQT-AT-FAAS Methods

Method / **Elements**	**Folds of Interferent**	**SQT-AT-FAAS**	**Os-Coated-SQT-AT-FAAS**
		Relative Signal	**Relative Signal**
Na ($NaNO_3$)	1	102	106
	10	96	96
	100	105	97
	1000		101
Mg	1	86	115
	10	96	93
	100	100	99
	1000		106
Ca	1	91	110
	10	89	88
	100	86	101
	1000		87
Ni	1	102	83
	10	108	43
	100	102	68
	1000		61
Co	1	99	104
	10	108	90
	100	90	91
	1000		92
Cu	1	94	52
	10	62	102
	100	32	78
	1000		37
Mn	1	98	64
	10	98	60
	100	94	62
	1000		58
Fe	1	105	80
	10	101	61
	100	95	59
	1000		65
Cr	1	93	67

	10	98	74
	100	84	54
	1000		35
Al	1	106	92
	10	100	81
	100	81	86
	1000		79
Pb	1	100	113
	10	99	103
	100	61	78
	1000		83
Zn	1	102	91
	10	97	102
	100	99	105
	1000		100
Na (NaCl)	1	102	98
	10	96	102
	100	89	102
	1000		100
Cl (NaCl)	1	103	100
	10	102	106
	100	97	105
	1000		100

3.17 Accuracy Check for Os-Coated-SQT-AT-FAAS Method

The CRM, SCP SCIENCE, EnviroMAT-Waste Water, Low (EU-L-2), was used for accuracy testing of Os-Coated-SQT-AT-FAAS method. The direct calibration was employed and three replicate measurements were done under optimum conditions. The results were in good agreement with certified value as shown in the Table 3.17.

Table 3.17 The Result of the Accuracy Test for Os-Coated-SQT-AT-FAAS Method

SCP SCIENCE, EnviroMAT **Waste Water** **EU-L-2**	**Certified Value,** *mg/L*	**Experimental Result,** *mg/L*
	8.0 ± 0.4	8.78 ± 0.46

CHAPTER IV

CONCLUSIONS

In this study, investigations were done to improve sensitivity for thallium determination by FAAS.

In the first part of the study; while the better nebulization efficiency was achieved by mixing 100 µL of propanol with 500 µL of Tl standard solution just before aspiration into the flame, more stable chemical environment was also achieved by use of SQT as first described by Wattling [9]. This method was called as Propanol-SQT-FAAS. The detection limit, 3s/m, and characteristic concentration of this method are 140 ng/mL and 199 ng/mL, respectively Therefore, 4.49 fold in sensitivity enhancement was achieved with respect to conventional FAAS method.

In the second part of the study, slotted quartz tube has been used for atom trapping apparatus as uncoated and Os-coated. All the conditions for both techniques were separately optimized. In addition to optimization parameters of SQT-AT-FAAS method, eight different elements, tungsten, palladium, molybdenum, gold, tantalum, zirconium, titanium and osmium were investigated for Coated-SQT-AT-FAAS method. Although the detection limit, 3s/m, and characteristic concentration of SQT-AT-FAAS were calculated as 38 ng/mL and 9.7 ng/mL, Os-Coated-SQT-FAAS provided 3.46 fold enhancement in sensitivity and those values for latter were calculated as 3.5 ng/mL and 2.8 ng/mL, respectively.

The interference studies of some major elements, some transition elements and also some anions as counter ion effect for SQT-FAAS, Propanol-SQT-FAAS, SQT-AT-FAAS and Os-Coated-AT-FAAS methods were investigated. In general as the sensitivity was improved from one method to another, interference effects became more serious. This is a general trend for analytical techniques. As the sensitivity is improved, it is usually at a cost of higher interferences. In the case of SQT-AT-FAAS better collection efficiency of analyte takes place together with more efficient collection of interferents. The result is higher interference effects. This effect is also observed for Os-Coated-SQT-AT-FAAS since it is the most sensitive method among all.

For accuracy check, the analyses of standard reference material were performed by use of SCP SCIENCE EnviroMAT Low (EU-L 2) and results for Tl was to be in good agreement with the certified value for each of the four methods.

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