DETERMINATION OF CADMIUM USING SLOTTED QUARTZ TUBE ATOM TRAP ATOMIC ABSORPTION SPECTROMETRY AND METAL COATINGS

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ABSTRACT

DETERMINATION OF CADMIUM USING SLOTTED QUARTZ TUBE ATOM TRAP ATOMIC ABSORPTION SPECTROMETRY AND METAL COATINGS

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Flame atomic absorption spectroscopy (FAAS) is a common technique for detecting metals and metalloids in environmental, biological and metallurgical samples. Although it is a rather old technique, it is still very reliable, simple to use and inexpensive. The technique can be used to determine the concentration of over 70 different metals in a solution. However, it has detection limits at mg/L levels. Some atom trapping methods have been developed to reach the detection limits of ng/mL levels. Slotted quartz tube (SQT) is one of these atom trapping methods. It is an important technique, since it is easy to use, applicable in all laboratories, commercially available and economical. This thesis consists of development of a sensitive method for cadmium with the help of SQT atom trap. In this study, it was used for two different purposes. One was for keeping the analyte atoms more in the light path; in other words, for increasing the residence times of analyte atoms in the measurement zone. This first application was provided a 2.9 times enhancement with respect to conventional FAAS. Second application was for trapping the analyte on the surface of the SQT, in other words, for performing on-line preconcentration of cadmium in SQT. In the presence of a lean flame, analyte samples were trapped and collected for a few minutes at a low suction rate. After finishing the collection period, analyte atoms were revolatilized with the help of a small volume of (10-50 µL) methyl isobutyl ketone (MIBK) and a rapid atomization occurred. This introduction also altered the flame composition momentarily and analyte atoms were released from the surface of the SQT. Application of this method enhanced the sensitivity 2065 times with respect to conventional FAAS. Another approach to this type of atom trapping has been investigated also in this study, which was coating of SQT with some metals having low volatility. Therefore, some transition metals were coated to the surface of SQT and among them zirconium was selected as the best coating material as having the most sensitivity enhancement factor. That is why, rest of the study was performed with the Zr coated SQT. The enhancement was 3368 as compared with FAAS. Cd determination with this method provides LOD value of 8 pg/mL and Co value of 19 pg/mL. In order to see the effect of some other type of elements or ions on determination of cadmium, interference study was done.

Keywords: slotted quartz tube, flame atomic absorption spectrometry, cadmium, preconcentration, sensitivity enhancement factor, atom trapping.

ÖZ

YARIKLI KUVARS TÜP ATOM TUZAĞI VE METAL KAPLAMALAR KULLANARAK ALEVLİ ATOMİK ABSORPSİYON SPEKTROMETRİ İLE KADMİYUM TAYİNİ

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Alevli atomik absorpsiyon spektroskopisi (FAAS) çevresel, biyolojik ve metalurjik örneklerde metaller ve metaloidlerin tespiti için kullanılan yaygın bir tekniktir. Eski bir teknik olmasına rağmen, hala çok güvenilir, kullanımı kolay ve ucuzdur; bu teknik bir çözeltide 70'in üzerinde metalin derişimini tayin etmek için kullanılabilir. Ancak, gözlenebilme sınırları çoğunlukla mg/L düzeyindedir. Bazı atom tuzak yöntemleri geliştirilmiştir ve gözlenebilme sınırları böylece ng/mL seviyesine düşürebilmiştir. Yarıklı kuvars tüp (YKT) bu atom tuzak yöntemlerden birisidir. Tüm laboratuvarlarda kullanılabilir, ticari ve ekonomik olarak uygulanabilir olmasından ve kullanım kolaylığından dolayı önemli bir tekniktir. Bu tez, YKT atom tuzağı kullanarak kadmiyum elementinin tayininde kullanılan bir metod geliştirmeyi içermektedir. Bu çalışmada YKT, iki farklı amaç için kullanılmıştır. İlk olarak, analit atomlarını ışın yolu üzerinde daha fazla tutmak, bir başka deyişle; analit atomlarının ölçüm bölgesindeki kalma sürelerini artırmak için kullanılmıştır. Bu uygulamada, geleneksel FAAS yöntemine gore 2.9 kat iyileştirme sağlanmıştır. YKT ikinci olarak, kadmiyum elementinin önzenginleştirme işlemi gerçekleştirmek amacıyla kullanılmıştır. Düşük asetilen akış hızındaki aleve gönderilen analit YKT'nin iç yüzeyinde birkaç dakika içinde toplanır. Daha sonra aleve düşük hacimde (10-50 μL) metil izobutil keton (MIBK) püskürtülmesi ile tuzaklanmış analit atomları buharlaşır ve hızla atomlaşır. Bu püskürtme aynı zamanda alevin kompozisyonunu anlık olarak değiştirir ve analit atomları yarıklı kuvars tüp yüzeyinden kolayca ayrılırlar. Bu yöntem ile, geleneksel FAAS'ye gore 2065 kat duyarlılık artışı gözlenmiştir. Bu tür atom yakalama tekniklerine başka bir bakış açısı getirmek için, son olarak YKT bazı kolay uçmayan geçiş metalleriyle kaplanmıştır. En iyi sonucu zirkonyum elementi vermiştir ve geri kalan tüm çalışmalarda Zr kaplı Yarıklı Kuvars Tüp kullanılmıştır. Bu yöntem ile de FAAS'ye gore 3368 kat duyarlılık kazanılmıştır. Cd için gözlenebilme sınırı ve C_0 değerleri sırası ile 8 pg/mL ve 19 pg/mL olarak bulunmuştur. Ayrıca, çeşitli iyonların ve elementlerin Cd tayinindeki etkisini araştırmak üzere girişim çalışmaları yapılmıştır.

Anahtar Kelimeler: yarıklı kuvars tüp, alevli atomik absorbsiyon spektrometri, kadmiyum, önderiştirme, duyarlılık artırma faktörü, atom tuzağı

To my family

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LIST OF ABBREVIATIONS

ABBREVIATIONS	
AAS	Atomic Absorption Spectrometry
CRM	Certified Reference Material
D-FAAS	Derivative Flame Atomic Absorption Spectrometry
ETAAS	Electrothermal Atomic Absorption Spectrometry
FAAS	Flame Atomic Absorption Spectrometry
GF	Graphite Furnace
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HGAAS	Hydride Generation Atomic Absorption Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IAT	Integrated Atom Trap
LOD	Limit of Detection
LOQ	Limit of Quantitation
MEK	Methyl Ethyl Ketone
MIBK	Methyl Isobutyl Ketone
SQT	Slotted Quartz Tube
SQT-AT	Slotted Quartz Tube Atom Trap
SQT-AT-FAAS	Slotted Quartz Tube Atom Trap Flame Atomic Absorption Spectrometry
SQT-FAAS	Slotted Quartz Tube Flame Atomic Absorption Spectrometry
W-Coil	Tungsten Coil
Zr-Coated-SQT-AT-FAAS	Zirconium-Coated-Slotted Quartz Tube Atom Trap Flame Atomic Absorption Spectrometry

CHAPTER 1

INTRODUCTION

Human body needs some elements such as iron, cobalt, copper, manganese, iodide, selenium, molybdenum, and zinc. High amount of these can be harmful. On the other hand, some elements such as Hg, Cd, As, Cu, Ni and Pb have toxic effects on human health even at very low concentrations [1]. Therefore, determination of these elements is very important. Since they are at very low concentrations, powerful methods are required to detect these low amounts of such elements in environmental, biological and metallurgical samples. Consequently, the methods should be highly sensitive and precise with low detection limits.

Recently, the inductively coupled plasma optical emission (ICP-OES) and inductively coupled mass spectrometry (ICP-MS) have been used widely to detect trace levels. These techniques combine easy sample introduction and rapid analysis capabilities with accuracy and sensitivity. Nevertheless, both the purchase and running costs of these instruments are usually high. On the other hand, atomic absorption spectrometry (AAS), a traditional technology, provides a wide range of advantages to analysts especially in the developing countries for its low cost, simplicity and availability.

In this study, a sensitive technique was developed by using flame atomic absorption spectrometry (FAAS) with a device, named slotted quartz tube-atom trap (SQT-AT).

1.1 Cadmium Occurance and Uses

Cadmium is a rarely found metal and it occurs generally in nature as a minor component of other non-ferrous metal ores [2].

It is a soft, malleable, ductile and silvery-white metal with an atomic number of 42 and atomic mass of 112.40 amu [3]. Its density varies from 8.63 to 8.69 g/cm^3 depending on the thermal and mechanical treatment [4]. It is chemically similar to the two other metals; zinc and mercury. It prefers +2 oxidation state in its compounds similar to zinc [1]. It was first discovered by Friedrich Stromeyer as a by-product of the zinc refining process in Germany, in 1817. The word *cadmium* is derived from the Latin *cadmia* and the Greek *kadmeia* [5].

Cadmium is rarely found as a pure element in nature; it generally occurs in association with the sulfide ores of zinc, lead and copper [3]. Cadmium is usually found as cadmium oxide, cadmium chloride or cadmium sulphate [5]. Among these compounds some cadmium compounds are quite soluble in water e.g. acetate, chloride and sulfate; on the other hand, cadmium oxide, carbonate and sulfide are almost insoluble [6].

Cadmium and inorganic cadmium compounds are used in various industry areas such as electroplating of metals, pigments or stabilizers for plastics, storage batteries and constituents of alloys [4].

It is important to identify and quantify the sources of cadmium metal in the environment to understand the biogeochemical cycle of it. [2]. Its concentration increases in the environment when forest fires and volcanoes occur. However, the largest increase occurs by burning of fossil fuels, use of phosphate fertilizers and industrial processes [6]. Cadmium can also be present in air because of human activities. For example, iron and steel industries, coal combustion, refuse incineration and cigarettes are sources of cadmium in air [3].

Cadmium can also be present in soil and water besides air. However, cadmium is much less mobile in soil than in air and water [5]. It can also be present in cultivated and non-cultivated soils due to atmospheric deposition, fertilizers, pesticides, and irrigation water [2].

Cadmium is also a minor constituent of surface and groundwater. According to OECD (Organization for Economic Cooperation and Development) report published in 1984, Cd may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids [5]. WHO (World Health Organization) reported also in 1992 that the average cadmium content in the world's give values as <5 ng/L [6].

1.2 Cadmium and Health Effects

Cadmium is a highly toxic metal [7]. It can enter the human body via air, drinking water and food. Especially, food and cigarette smoke are the biggest sources of cadmium intake [8]. In addition, air and drinking water also contain cadmium. According to water supply (water quality) the Cd level in tap water should not exceed 5 μg/L [9]. Moreover, the average amount of cadmium daily inhaled by humans in rural, urban and industrialized areas should not exceed 0.01, 0.2 and 0.4 μg, respectively [10]. If the limits are exceeded, cadmium can be very toxic to human body. Especially, people smoking cigarettes are in trouble because of inhaling toxic materials including cadmium element. Agha and Gökmen have shown in their article that blood Cd concentration was found to be about two times higher in smokers as compared to non-smokers [11.] High levels of Cd in blood and tissues can cause renal damage, kidney failure and carcinogen. It also causes renal injuries and affects the renal regulation of calcium and phosphate balance [12].

As mentioned above, cadmium is taken into human body via drinking water, food and air. It has a very long half-life in human body. The average amount of cadmium absorbed via food can be predicted as about 1.0 μg/day [10]. The risk of cadmium damage is common in smokers. Studies have shown that cadmium accumulates in kidney cortex, kidney medulla, lung, prostate, and muscle more in smokers than in non-smokers. In fat tissue, the mean Cd level shows a superior amount in smokers than in non-smokers. Moreover, the harmful effect of cadmium inhaled through smoking is mostly seen in pregnancy. Pregnant smokers have higher placental cadmium level than non-smokers [13]. According to World Health Organization (WHO), for an adult the weekly intake of cadmium should not exceed 400 μg [6]. However, high industrialization causes more exposure and accumulation of cadmium in the body [14].

1.3 Determination of Cadmium

Since cadmium shows a variety of toxic properties to human body, it is significant to have effective, fast, precise and accurate approaches for the determination of this element in biological and environmental materials using various analytical methods [12].

The mostly used methods for determination of cadmium are atomic absorption spectrometric techniques such as electrothermal atomic absorption spectrometry (ETAAS), hydride generation atomic absorption spectrometry (HGAAS) and flame atomic absorption spectrometry (FAAS), and plasma techniques such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma emission spectrometry (ICP-OES).

1.3.1 Plasma Techniques Used in Cadmium Determination

In ICP-OES, determination of elements is possible with emission of light of atoms at their characteristic wavelengths via excitation due to high temperature of plasma source. Cadmium can be determined by using ICP-OES [15, 16]. However, Cd detection limit with ICP-OES is not suitable for some samples such as drinking water [15].

In ICP-MS, inductively coupled plasma source is used to produce ions. These ions are then determined by mass spectrometry. It is a powerful technique in ultra trace elemental analysis [17]; multi-element analysis is possible. It is highly sensitive, selective and high throughput method. Nevertheless, its cost is a disadvantage for many laboratories [16, 17].

ICP-MS has several advantages compared to AAS. For instance, due to high temperature of plasma and large dynamic range obtained, rapid and multi-element analysis is possible even in very low concentrations [18].

1.3.2 Determination of Cadmium by Atomic Absorption Spectrometry

AAS is generally used to determine the concentration of an analyte in a sample solution. It was introduced by Walsh [19]. Simply, conversion of molecules or ions into free atoms and the measurement of absorption of radiation by these free atoms are known as the analytical process [20]. The sample solution containing analyte of interest is aspirated into the flame. The hallow-cathode lamp emits radiation characteristic of the cathode material. This beam is electronically pulsed. At this time, analyte atoms are produced thermally in the atom reservoir. Ground-state atoms, absorb resonance radiation from the lamp and the intensity of incident beam is reduced [19, 20]. The intensity change is converted into a computer data system as an absorbance.

Atomizer, monochromator, detector, and electronics for data acquisition are the four part of an atomic absorption spectrometer [21]. Atomizer for FAAS is flame where a graphite furnace is used in ETAAS and a heated quartz tube is employed in HGAAS.

In general three atomic absorption techniques are used for determination of cadmium: electrothermal atomic absorption spectrometry (ETAAS), hydride generation atomic absorption spectrometry (HGAAS) and flame atomic absorption spectrometry (FAAS).

1.3.2.1 Electrothermal Atomic Absorption Spectrometry

An electrically heated electrothermal or graphite furnace is the atomizer of this technique. After introduction of sample (10-50 μL) in to the atomizer, temperature is increased gradually to remove solvent and then matrix before atomization. Then, the temperature is raised to the atomization temperature, and a rapid atomization occurs. A time dependent peak is obtained and area under the peak is proportional to the concentration of analyte [21].

ETAAS is one of the most frequently used methods for determination of Cd because of its high sensitivity; however, the sensitivity advantage is eliminated by the relatively high cost and susceptibility to chemical interferences [12].

1.3.2.2 Hydride Generation Atomic Absorption Spectrometry

In HGAAS, the acid sample solution and the sodium tetraborohydride solution are mixed to form volatile analyte species. Atomization takes place with an externally heated quartz tube by flame or electrical means. To decompose hydrides and form analyte atoms, the temperature of atomizer is kept at 800-900 °C [20, 22]. HGAAS has some important advantages; such as high transport efficiency, good sampling frequencies, preconcentration potentiality, enhanced sensitivity, simplicity and automation [23]. However, multielement determinations are rather limited due to specific conditions for each element [23].

1.3.2.3. Flame Atomic Absorption Spectrometry

Flame is used as an atomizer in FAAS. By means of a nebulizer the sample is sprayed into the flame in the form of an aerosol. Flame atomization provides a laminar flow burner employing a concentric tube nebulizer. The conversion of the sample solution into an aerosol is provided by nebulization. Aerosol, oxidant, and fuel are then burned in a slotted burner and it supplies a flame usually 5 or 10 cm in length [20, 22].

In FAAS; flame is formed using air, oxygen, or nitrous oxide as the oxidant and hydrogen, acetylene, coal gas, or the butane as the fuel. Air-acetylene and nitrous oxide-acetylene are the generally used flames. In fuel-oxidant mixtures, temperature of the flame varies from 2000 K to 3000 K [20, 22].

FAAS is a simple, fast and widely accessible technique. However, there are some limitations of this technique. Firstly, nebulization efficiency of the system is a disadvantage, because only 1-10% of solution reaches the flame. A large portion of the sample flows down the drain as waste. Therefore, most of the sample is not transported to the atomizer. Secondly, high velocity of flame gases result in dilution of analyte species. Thirdly, residence time of individual analyte atoms in the optical path in the flame is short, about 10^{-4} seconds. Because of all these reasons, sensitivity of FAAS is limited. However, sensitivity can be improved in atomic absorption spectrometry by developing new techniques. Pre-concentration or trapping techniques have been developed to improve the sensitivity of atomic absorption spectrometry.

1.4. Atom Trapping Techniques in Atomic Absorption Spectrometry

As mentioned before, traditional FAAS has limited sensitivity, basically because of short residence time of analyte atoms in the light path. Therefore, to increase the residence time of analyte atoms in the optical path, some on-line preconcentration techniques have been developed. Several atom traps have been introduced for different techniques.

1.4.1 Atom Traps for Hydride Generation Atomic Absorption Spectrometry

Metal and quartz traps and graphite furnace may be used for preconcentration in HGAAS. Hydride generation technique has become very popular due to enhanced concentration detection limits. However, number of hydride-forming elements are limited. Only 11 elements are forming hydrides, which are As, Bi, Ge, Hg, In, Pb, Sb, Se, Sn, Te, Tl. Fortunately, recent researches have shown that this technique can also be applied for other elements. Cadmium is one of these elements. Matusiewicz [24] developed a method in which Cd atoms are generated as cadmium hydrides and trapped with graphite furnace.

Graphite furnace is generally named as electrothermal atomizer. It was firstly marketed in 1970's and shown that it provides enhanced sensitivity because the entire sample is atomized in a very short period of time, and the residence time of analyte atoms in the optical path is very short [22]. However, it can also be used as a trapping system for HGAAS providing an excellent ultra trace determination of metal hydrides. This process starts with transportation of metal hydrides to preheated graphite furnace (GF). GF provides decomposition of metal hydrides and subsequently analyte species are trapped on the graphite tube surface; this provides a rapid and clean separation from matrix. When trapping period is finished, analytes are atomized by cycling the temperature programming and the analyte signal is obtained [25]. Coating the inner surface of graphite tube is also possible to improve sensitivity [26].

In addition to graphite tubes, quartz traps have also been used in HGAAS technique. Quartz atom trap has been first introduced for determination of Pb [27]. This study involves the use of quartz particles obtained by crushing and placing in the inlet arm of quartz T-tube atomizer, near its connection point to the horizontal arm which was heated externally using a resistively heated wire.

Ataman [28] has described this technique in four stages.

i. By the reaction of analyte in an HCl solution with $NaBH_4$ in a continuous flow system Lead hydride (PbH_4) is formed in the presence of $K_3Fe(CN)_4$.
ii. After separation of the analyte vapor from the liquid stream by using a gas-liquid separator, it is transported to the quartz T-tube and passed through the trap held at an optimized collection temperature; some of the analyte hydride molecules are trapped here.
iii. When the collection stage ends, analyte introduction is stopped.
iv. The trap is rapidly heated to its revolatilization temperature. Analyte species are released by means of hydrogen gas formed by reactivation of pumps so the resultant analyte species are transported to the quartz T-tube atomizer and a transient signal is formed.

This technique was applied also to the Sb [29], As and Se [30].

Another alternative atom traps are the metal atom traps. These are mainly used by heating the metal with electricity. W-coil metal trap is the most popular one among the metal traps, and it is known as the alternative of the graphite furnace atom trap. W-coil metal trap is heated by passing electricity directly; where in quartz atom trap external heating is used. Therefore, metal device can be heated more efficiently than quartz traps. W-coil is also very accessible because, it can be extracted from any commercial tungsten lamp. Hence, whenever a W-coil is needed it can be obtained easily and economically. Recent studies have been performed in Ataman Research Group for Bi [31], Se [32], and Sb determination [33]. This method includes 4 stages.

i. Analyte hydride is generated in an acidic medium by reaction with $NaBH_4$.
ii. Volatile analyte species are preconcentrated on W-coil, previously, that was heated to an optimized *collection temperature*.

iii. After collection period, collected analyte species are revolatilized by heating the trap to a higher temperature under optimized flow of argon and hydrogen gases.

iv. The species are transported to an externally heated quartz atomizer, and finally, a transient signal is obtained in less than 0.5 seconds. [32]

The efficiency of W-coil is increased by coating its surface with some transition metals. Coated W-coil trap gives more sensitive results. For example, the first coated tungsten atom trap was prepared in 2002 by Barbosa et al. [34]. They coated tungsten trap with 300 µg rhodium and determined selenium with hydride generation technique. The detection limit was 50 ng/L with only 60 s trapping of selenium hydride species for 2.5 mL total sample volume. Similarly, Kula [32] et al. coated tungsten coil with gold and lowered the detection limit of Se to ng/L level. W-coil trap used in this experiment can be seen in Figure 1.1. [32]

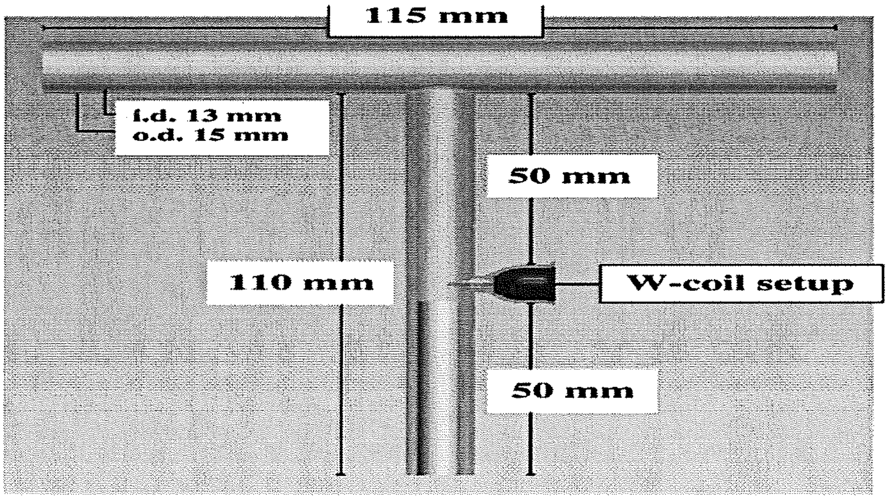


Figure 1.1 Schematic representation of Quartz T-tube and W-coil trap [32].

1.4.2 Atom Traps for Flame Atomic Absorption Spectrometry

As mentioned before, FAAS is not sensitive enough to determine most heavy metals at trace and ultra-trace levels, because of the limited atom number density in the light path associated with poor nebulization [35]. In order to enhance sensitivity in FAAS, sample solution should be introduced to the system with an effective nebulization. Briefly, the main idea of trapping system is to perform on-line preconcentration in the flame so that much higher population would be available for AAS measurements [36]

There are several atom trapping methods for flame atomization technique. Long-path tube method, Delve's micro-sampling cup method, slotted quartz tube method, water-cooled silica atom trap method, integrated atom trap method are the widely used methods [37].

There is also another method called ***slotted quartz tube FAAS,*** which is quite popular nowadays. Watling [38] has first described this technique in 1978 in order to increase analytical sensitivity in atomic absorption analysis. Volatile elements, including Cd, Pb Zn, Co, Ag, Bi, Mn, Hg, As, Se, Sb and Te have shown a 2-5 times sensitivity improvement with this method. In this procedure, a slotted quartz tube is required which is held in a metal bracket and be positioned above the burner slot in the air-acetylene flame, so the light beam from the hollow cathode lamp passed through the quartz tube [38].

The tube had two slots. The larger one is the entrance slot and it allows the flame to enter. The shorter one is the exit slot and it allows the flame leave the tube. [39]. The angle between the slots can be either 120^o or 180^o [39].

The schematic representation of SQT is given in Figure 1.2.

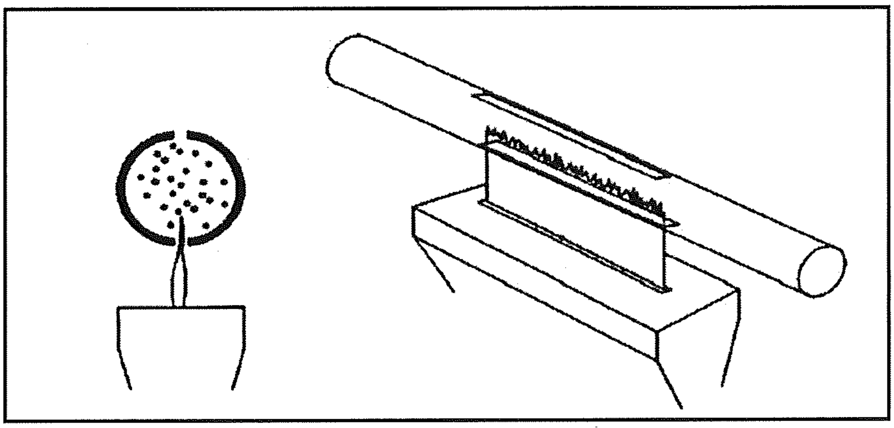


Figure 1.2 Schematic representation of 180° angled slotted quartz tube, SQT [27].

In this method, sensitivity improvement occurs as a result of increasing density of analyte atoms in the light path due to the increase in residence time of analyte atoms in the measurement zone. Moreover, this tube partially isolates flame from air; so chemical environment inside the tube can be more stable. As a result, sensitivity is enhanced.

SQT also provides a reduction in the potential interferences due to lowered detection limits. Obviously, it is due to the ability of dilution of samples. Consequently, SQT is advantageous compared to the conventional flame method. It is inexpensive and easily manufactured. It is also an important method in terms of being a simple and rapid method. However, it is only applicable for volatile elements [38].

After introduction of SQT, another atom trapping method was introduced by Lau *et al* [40] which is called ***water-cooled U-tube atom trap method.*** As understood from its name, the tube used in this method is a U-shaped, and for this study the tube is 4 mm od and 3 mm id silica tube. It is fixed on an air-acetylene flame and positioned just below the light path of the beam of hallow cathode lamp. The procedure is as follows:

i. A continuous flow of water through the U-tube provides a cooler surface than that of flame.

ii. As the cooling water passes through the tube, aspiration of sample via nebulizer occurs. This stage is called collection stage, because atoms are condensed and collected on the relatively cooler surface of the tube.

iii. Lastly, the cooling water was replaced manually with pressurized air. This provides rapid heating and release of the analyte species back into the flame and measurement zone and a transient signal is obtained. This step is called revolatilization [27].

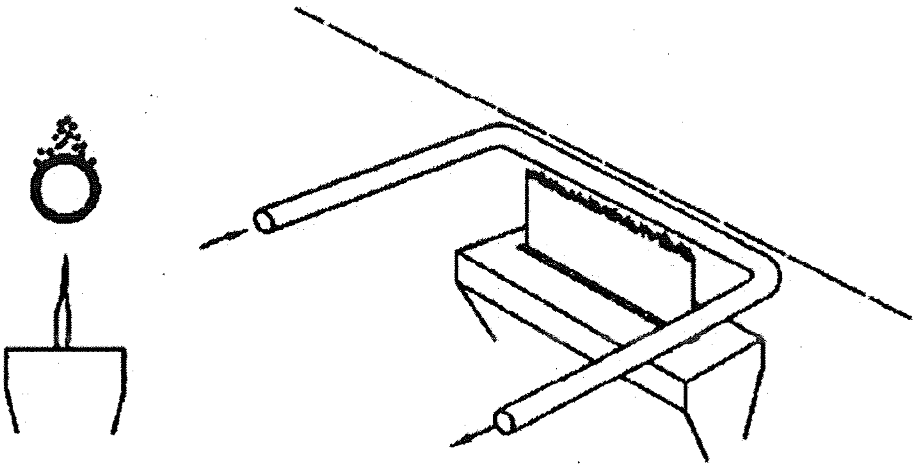


Figure 1.3 Schematic Representation of Water Cooled U-Tube Atom Trap [27].

This method is advantageous in terms of increasing sensitivity and reducing interferences. It is also comparatively inexpensive and simple to use. The most important advantage is probably the permission of analysis of various materials such as volatile and some non-volatile metals. However, it is slower than the conventional FAAS because of time needed in atom trapping step. Moreover, significant volume of sample consumption is required during trapping and this could be a disadvantage when small volume of sample is present [38].

A combination of U-tube and a SQT around the tube formed a new method, which is called ***integrated atom trap (IAT)***. This device offers combined advantages of SQT and U-tube method. Schematic representation of IAT method is shown Figure 1.4. It is generally used for determination of some elements like Ag, Cd, Cu, Fe, In, Mn, Pb, Zn and Tl. Matusiewicz and Kopras have shown that sensitivity of this system is similar to ETAAS [41].

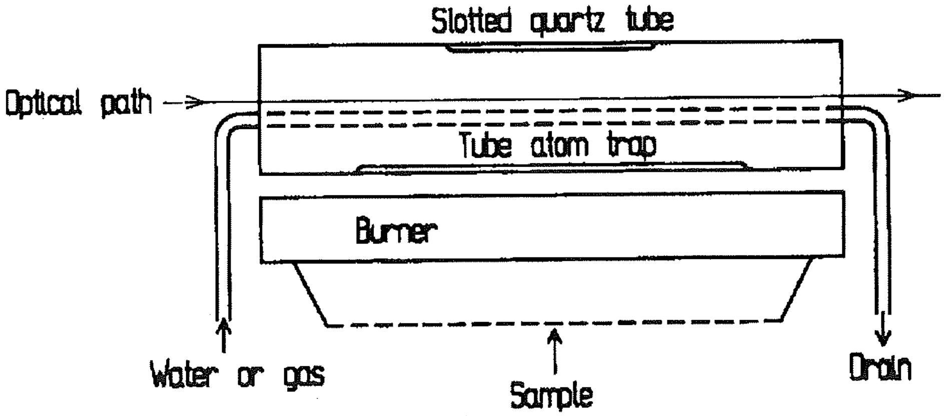


Figure 1.4 Schematic Representation of Integrated Atom Trap [38].

Another atom trapping method is called ***slotted quartz tube atom trap (SQT-AT).*** In this method *in situ* preconcentration of analyte atoms is realized on the inner surface of slotted quartz tube. It is a very important method in many aspects; low cost, simple and very sensitive applications are possible. Especially, in developing countries this atom trap method can be an alternative to expensive plasma techniques in terms of performing trace and ultra trace elemental analysis [42].

The procedure consists of 3 main steps, which are as follows:

i. ***Collection step***; SQT is positioned above the flame and with the optimized flame sample solution is aspirated. This step takes a few minutes. Analyte atoms are trapped in the inner surface of the SQT.
ii. ***Revolatilization step;*** this step includes an introduction of a rather low volume (10-50 μL) of an organic solvent, usually MIBK (methyl isobutyl ketone). This changes the flame composition for a very short period of time. Thanks to this introduction analyte atoms are released from the inner surface of SQT.

iii. ***Atomization step;*** revolatilization is followed by rapid atomization in flame and a transient signal is obtained [42].

As Ataman mentioned in his article [42], some experimental parameters are critical in SQT-AT technique. Flame composition, the distance between burner head and tube, suction rate are three of these. After optimizing these parameters, SQT-AT will be a very sensitive method as plasma techniques. Besides these advantages, low sample consumption and less interference due to much dilution of samples. However, only volatile species can be determined in this system; since only volatile elements can easily be revolatilized and atomized from the trap surface.

SQT-AT technique can be applied either by using uncoated SQT or coated SQT. Kumser [43] has shown that by using water cooled SQT-AAS, there is a decrease in detection limits as compared with conventional FAAS for the elements Au, Bi and Mn. Karadeniz [44] has also shown that by using SQT the sensitivities of the elements Pb, Cd and In have improved 90, 137, 181 times with respect to conventional FAAS, respectively. Moreover, with coated SQT-AT Arı [45] has shown that with Os coated SQT Tl determination is 3.5 fold more sensitive than uncoated SQT-AT, total sensitivity enhancement is 319 fold with respect to conventional FAAS. In addition, Demirtaş [46] has investigated Pb determination by Ta coated SQT-AT and she obtained 2.9 fold enhancement in sensitivity as compared to uncoated SQT-AT, and total sensitivity enhancement with respect to conventional FAAS was 1650 fold.

In Figure 1.5 there is a schematic representation of SQT which Watling has used in his experiments [47].

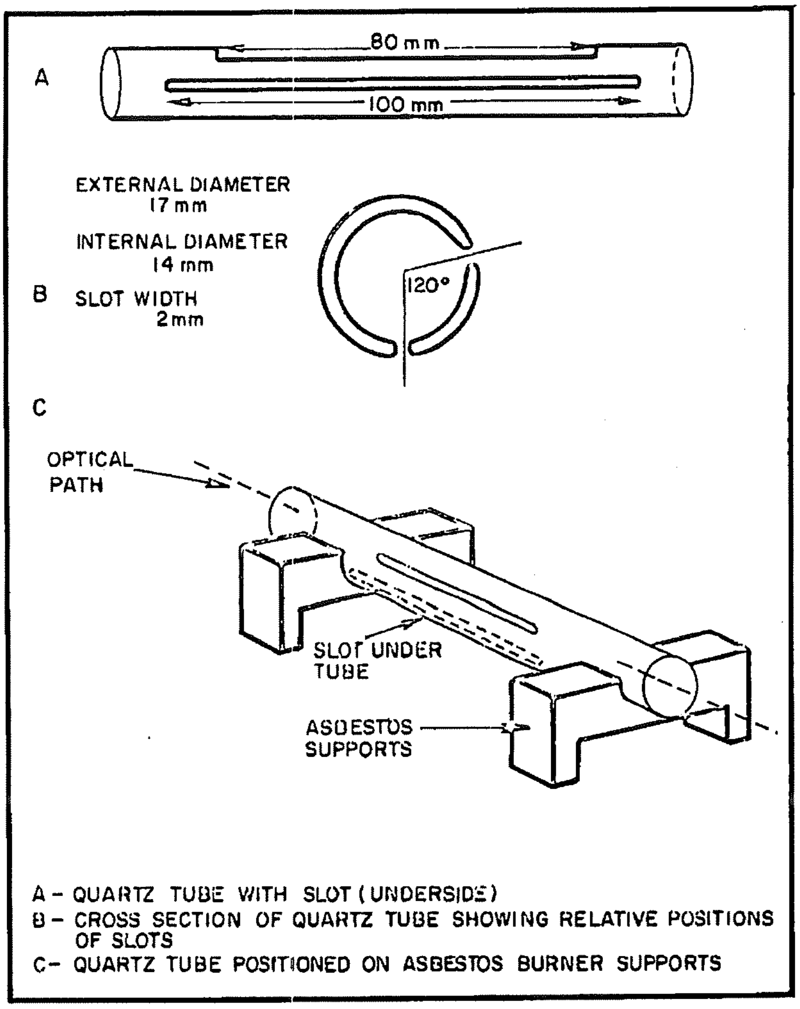


Figure 1.5 Schematic representation of an SQT [47].

1.5. Atomization Techniques in FAAS-SQT-AT

Flame alteration and organic solvent aspiration are two main techniques in FAAS-SQT-AT.

In ***flame alteration*** technique, composition of flame is changed by introducing excess fuel (acetylene) into the flame gas stream to effect revolatilization following analyte collection. By the change of flame composition, revolatilization and rapid atomization occurs [42].

In ***organic solvent aspiration technique,*** flame composition changes for a very short period of time by aspirating an organic solvent to the flame immediately after analyte collection. This action is equivalent to introduction of excess fuel. Therefore, various kinds of organic solvents can be used such as, methyl isobutyl ketone, acetonitrile, methyl ethyl ketone, n-hexane and acetone. Among these solvents MIBK is the most preferable. Because it is the most effective one in terms of giving a complete atomization, in other words there is no memory effect [48].

This is a more effective atomization technique than flame alteration; because, by using organic solvent a rather low volume of organic solvent (10-50 μl) is consumed and this is sufficient to release analyte samples from the surface of SQT. On the other hand, by flame alteration there is an unnecessary consumption of acetylene gas [42].

1.6. Aim of the Study

The main purpose of this study is to establish a sensitive, simple and reproducible method for the determination of cadmium by using FAAS-SQT-AT with metal coatings that provides low detection limit with low analytical costs. For this purpose, firstly conventional FAAS technique will be applied for determination of Cd. Then, uncoated SQT having an entrance and an exit slot with angle of 180^o was used for the sensitivity enhancement of Cd solutions. In the following step, some coating materials were applied to the inner surface of SQT and the effect of coatings on the results were investigated. Consequently, a sensitivity comparison among conventional FAAS, SQT-FAAS, SQT-AT-FAAS and coated SQT-AT-FAAS techniques were done. Before performing these techniques all the optimizations were done for uncoated and coated FAAS-SQT-AT. Finally, interference studies were performed to see whether any element interfere with Cd species.

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus and Materials

The slotted quartz tube used in experiments was 15 cm long and it has an inner diameter of 13 mm, and an outer diameter of 17 mm. It has also two slots; namely the entrance and exit slots. Entrance slot was 10 cm and exit slot was 8 cm long. These slots were positioned at 180° with respect to each other. Entrance slot was made 10 cm, because burner slot of the instrument is also 10 cm so that flame could enter through the slot and reach the tube. These slotted quartz tubes were made by Çalışkan Cam in OSTİM (Ortadoğu Sanayi ve Ticaret Merkezi), Ankara and made by Ataman research group.

To prepare standard solutions adjustable Eppendorf micropipettes (100-1000 µL and 500-5000 µL) and 100 mL of glass volumetric flasks were used. For storage of these standards 100 mL of polyethylene containers were used. Moreover, for aspiration of organic solvent, 1.0 mL plastic cup and a 10-100 µL of micropipette were used.

2.2 Chemicals and Reagents

Working standard solutions were prepared by 1000 mg/L cadmium stock solution (High Purity Standards). Necessary volumes for different concentrations were taken from this stock solution and diluted with deionized water, which was obtained from a Millipore (Molsheim, France) Milli-Q water purification system. Deionized water was 18 MΩ·cm and fed using the water produced by Millipore Elix 5 electrode ionization system. All Cd solutions were prepared in 1.0 M HNO_3 solution. An analytical grade HNO_3 (65% (w/w), Merck) was used.

All materials (plastic containers, glass volumetric flasks, beakers, etc.) were kept in a 10% (v/v) of HNO_3 solution, namely cleaning tank to eliminate contaminations. 10% (v/v) of HNO_3 refers to the solution containing 10.0 mL of concentrated HNO_3 in 100 mL solution. All containers were kept in this solution at least 24 hours. After cleaning, deionized water was used for rinsing.

Interference studies were conducted by using several elements which were stored in the refrigerator. These solutions were prepared by dilution from 1000 mg/L stock solution of Na (High Purity Standards), Mg (Merck), K (Merck), Fe (Merck), Co (High Purity Standards), Ni (High Purity Standards), Cu (Merck), Cd (High Purity Standards), Se (High Purity Standards), Sb (Ultra Scientific), Zn (High Purity), Sn (Merck), Al (Merck).

As the CRM (Certified Reference Material), SCP SCIENCE EnviroMAT Waste Water Low (EU-L-2) was used. Certificate of analysis is given in Table 2.1.

Table 2.1 Certified values for SCP SCIENCE EnviroMAT Waste Water, Low (EU-L2).

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 Varian AA140 single beam atomic absorption spectrometer was used throughout the experiments. It is equipped with a Deuterium (D_2) background corrector. This instrument was used with a software program, which is called SpectrAA. Via this program data could also be saved. As a radiation source Unicam Cd hallow cathode lamp was used, it was operated at 6.0 mA and measurements were done at a wavelength of 228.8 nm and at a spectral band pass of 1.0 nm. Moreover, air-acetylene flame with a burner head of 10 cm was used. The operating conditions for FAAS are given in Table 2.2.

Table 2.2 Operating Conditions for FAAS, Varian AA140

Flame Type	Air-Acetylene
Wavelength of Cd, nm	228.8
Hollow Cathode Lamp Current, mA	6.0
Spectral Band Pass, nm	1.0
Air Flow Rate, L/min	3.5
Acetylene Flow Rate, L/min	0.5 – 1.5

2.4 Coating Procedure of Slotted Quartz Tube

Some of the slotted quartz tubes were coated to perform FAAS-coated SQT-AT technique. These are coated with 100 mL of 100 mg/L solutions of Pd, Ta, Zr, W, and Mo. Pd, Ta, W, and Mo coated tubes were already available in the laboratory. Only Zr coated tube was prepared by aspirating 100 mg/L of Zr solution, which is diluted from a 1000 mg/L Zr stock solution (Fischer Scientifics).Pd and Ta solutions were prepared from their solid reagents: $K_2[PdCl_6]$, Ta_2O_5. W and Mo solutions were prepared from their 1000 mg/L standard solution (Ultra Scientific Standards). All coatings were made by aspirating solutions at a suction rate of 4.2 mL/min and in the presence of a lean flame. During interference studies, coated quartz tubes sometimes were damaged due to introduction of some elements causing deformation on quartz surface, so tubes were stored in 20% solution of HF for three minutes and recoated again.

CHAPTER 3

RESULTS AND DISCUSSION

This study includes development of a sensitive analytical method for determination of cadmium. Development of these analytical methods consist of four stages.

To make a comparison between the developed methods and conventional FAAS method, first of all, determination of Cd should be performed with simple FAAS.

Second step includes the usage of SQT. This provides an increase in the residence time of analyte atoms in the light path. In other words, it supplies a measurement zone and due to the elimination of air diffusion of flame; therefore a more stable chemical environment for flame is provided. 180^0 angled-slotted tubes were used in this step and no trapping was performed. Second step was named SQT-FAAS.

Third step includes trapping of analyte atoms in the uncoated SQT. This step is also known as *in-situ* preconcentration by trapping the atoms on the surface of SQT. Therefore, this step was named as SQT-AT-FAAS (Slotted **Q**uartz **T**ube-Atom **T**rap-**F**lame Atomic **A**bsorption **S**pectrometry).

The last step involves a coated SQT in order to investigate the improvement of the method development. The 180^0 slotted quartz tube was coated with different materials having high melting points and a trapping time was applied. Hence, this last step was named coated SQT-AT-FAAS.

This study mainly involves the improvement of trapping methods. In these methods analyte atoms are trapped in the measurement zone within a measured period prior to revolatilization so sensitivity is improved. As the tapping period increases, number of measured atoms increase, so sensitivity of the system also increases. This sensitivity improvement can be evaluated with the term "enhancement", E. This is calculated by taking the ratio of characteristic concentration, C_o, values with and without trap methods. These terms were introduced by Ataman [28]. Moreover, he claimed in his paper [28] that sensitivity improvement should be evaluated also in terms of time and mass because trapping techniques depend on total time and total analyte mass consumed. As the trapping period increases, sensitivity increases; however, mass of the analyte spent also increases. Therefore, comparison terms E_v and E_t, which are enhancement factors with respect to unit volume and unit time, respectively, should be used. These "E" values are found firstly by calculating respective C_0 value, which is the concentration corresponding 0.00436 absorbance (1.0% absorption).

$C_0 = 0.00436 \, x \, (analyte\ concentration/absorbance)$.

By comparing C_0 values of methods, sensitivity enhancement factor is found. In other words, E value is the ratio of calibration sensitivities (slopes). Then, E_v and E_t values are found by dividing E value by total volume spent in terms of milliliters and by total time spent in terms of minutes, respectively. These calculations enable a proper comparison between the methods using the terms of the trapping period and the total amount trapped. There is also another term used in defining trapping efficiency, which is characteristic mass, m_0, it is calculated as follows:

$m_0 = (Volume\ of\ trapped\ analyte\ solution) \, x \, (C_0)$. Besides these enhancement factors, limit of detection (LOD) and limit of quantification (LOQ) are calculated as follows:

$LOD: 3s/m$

$LOQ: 10s/m$

In the above equations, "m" is the slope of the linear calibration plots of developed methods and "s" is the standard deviation of the smallest concentration of the linear range Cd solutions.

3.1 Flame Atomic Absorption Spectrometry Study

This study investigates an applicable, easy, robust and inexpensive method for determination of Cd. To compare the sensitivities between the new applied methods and the conventional FAAS, analysis should be performed with simple FAAS, firstly. In order to get the best signal to noise ratio (S/N), some of the parameters of the instrument were optimized. These parameters were acetylene flow rate and sample flow rate. 1.0 mg/L solution of Cd was used during all the optimizations.

3.1.1 Optimization of Fuel Flow Rate

Throughout the study, airflow rate was kept constant at 3.5 L/min, where acetylene flow rate was changed to get best S/N ratio. While varying the acetylene flow rate, sample nebulization flow rate was also kept constant at 7.6 mL/min. As can be clearly seen from Figure 3.1, acetylene flow rate was chosen as 1.50 L/min because maximum absorbance value was obtained at that flow rate.

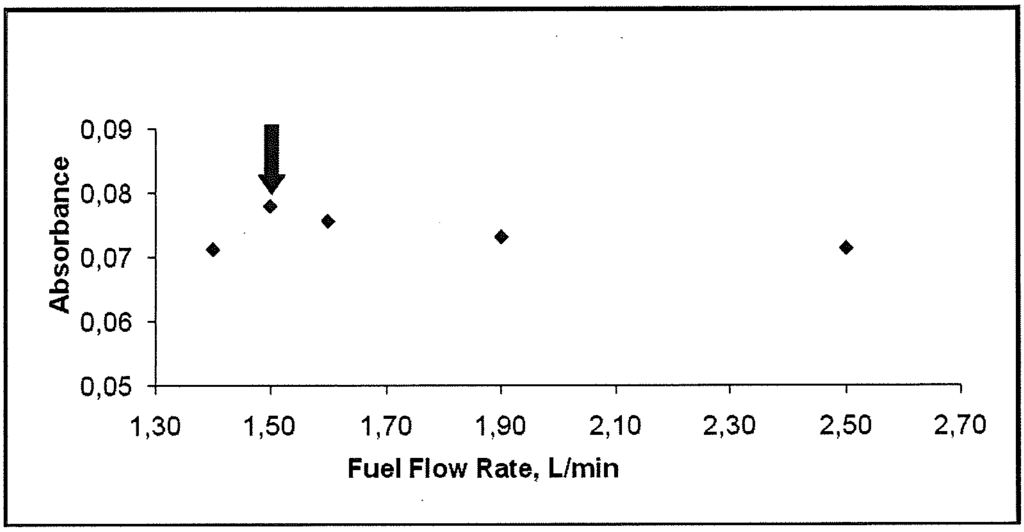


Figure 3.1 Optimization of acetylene flow rate with use of 1.0 mg/L of Cd solution in FAAS.

Air flow rate: 3.5 L/min, sample suction rate: 7.6 mL/min.

3.1.2 Optimization of Suction Rate of Sample Solution

After optimization of fuel flow rate, sample suction rate is optimized at 3.5 L/min airflow rate, 1.5 L/min acetylene flow rate. Suction rate is an important parameter because nebulization efficiency is affected by suction rate. As it increases, nebulization efficiency decreases. On the other hand, when nebulization efficiency decreases, analyte atoms decrease in flame so absorbance signals of Cd atoms decrease. Therefore, suction rate should be optimized. As can be seen in Figure 3.2., suction rate was chosen as 5.6 mL/min at 1.5 L/min fuel rate and 3.5 L/min airflow rate by using 1.0 mg/L of Cd solution. Although at 7.6 mL/min maximum absorbance value was obtained, 5.6 mL/min was chosen as sample suction rate, since it was an optimum value. Moreover, at 7.6 mL/min absorbance values were not reproducible.

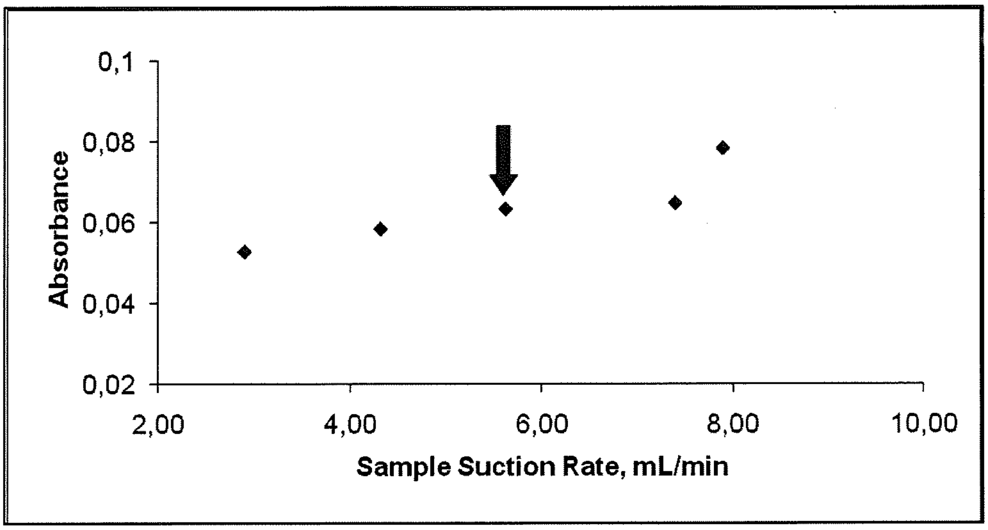


Figure 3.2 Optimization of sample suction rate with use of 1.0 mg/L of Cd solution in FAAS.

Acetylene flow rate: 1.5 L/min, Air flow rate: 3.5 L/min.

By using these optimized parameters a transient signal for 0.5 mg/L Cd standard solution was obtained, as can be seen in Figure 3.3.

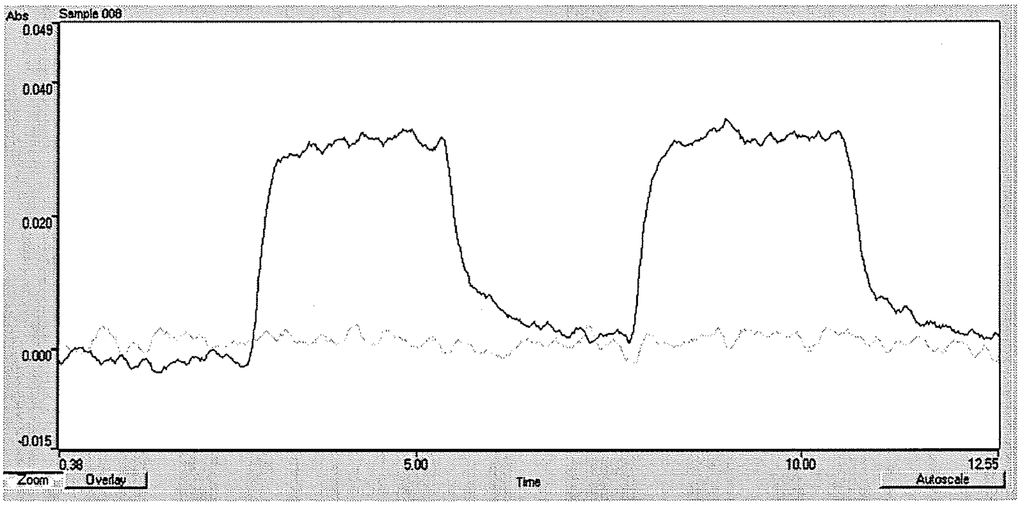


Figure 3.3 The signal of the 0.5 mg/L Cd solution with FAAS at optimum conditions.

3.1.3 Calibration Plot for FAAS Method

Using the optimized parameters, the absorbance values of samples containing Cd between 0.25-20.0 mg/L were measured and a linear calibration curve was obtained by taking the absorbance results of samples between 0.25-2.00 mg/L. The best line equation and the correlation coefficient were, $y = 0.0643x + 0.0004$ and 0.997, respectively. LOD was calculated by measuring 10 replicates of 0.25 mg/L Cd solution. LOD and LOQ were calculated as 15 ng/mL and 51 ng/mL, respectively and these are given in Table 3.1.

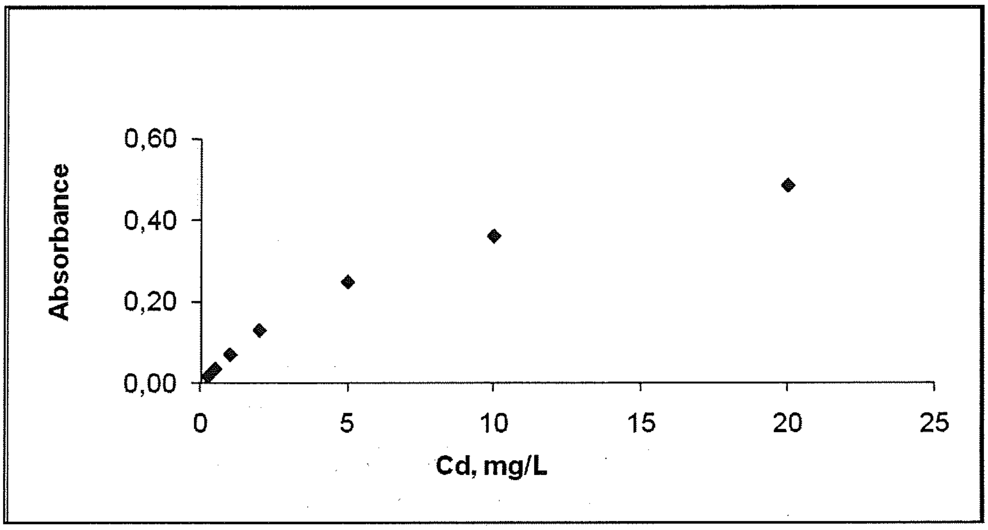


Figure 3.4 Calibration plot for FAAS method.

Acetylene flow rate: 1.5 L/min, Air flow rate: 3.5 L/min, Sample suction rate: 5.6 mL/min.

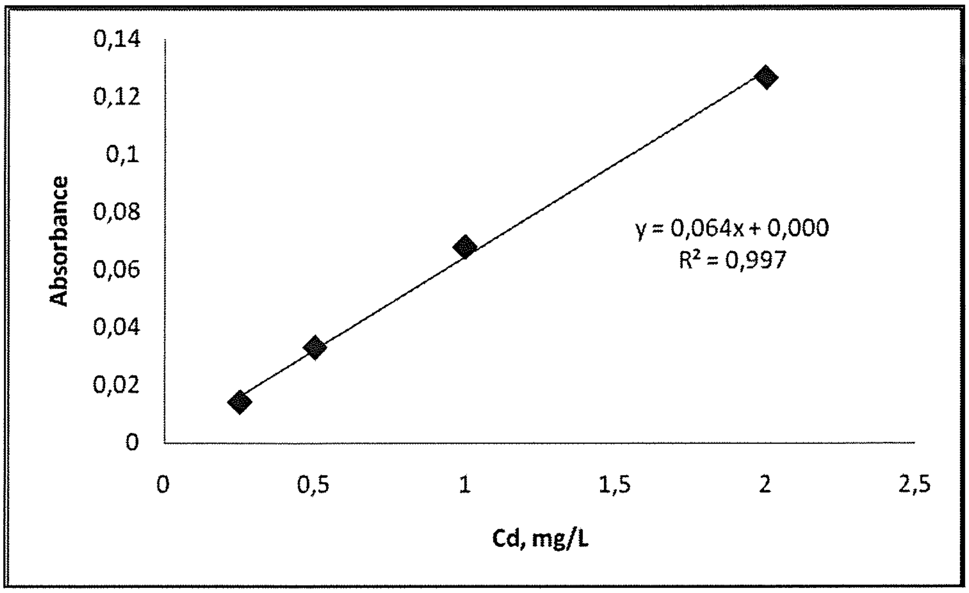


Figure 3.5 Linear calibration plot for FAAS method

Acetylene flow rate: 1.5 L/min, Air flow rate: 3.5 L/min

Sample suction rate: 5.6 mL/min

Table 3.1 summarizes the LOD, LOQ and C_0 values of this method.

Table 3.1 Analytical Performance of FAAS for Cd determination

Linear Range, *mg/L*	0.25-2.00
Limit of Detection (LOD), *ng/mL*	15
Limit of Quantitation (LOQ), *ng/mL*	51
Characteristic Concentration (C_0), *ng/mL*	64

3.2 Optimizations of Slotted Quartz Tube Flame AAS Method (SQT-FAAS)

SQT-FAAS method is developed in order to enhance sensitivity, as mentioned in the introduction chapter. It provides mainly, an increase of atoms in the light path by increasing the residence time of atoms in the measurement zone. SQT is positioned above the burner head of FAAS, and flame enters through the longer entrance slot and leaves from the shorter exit slot. Therefore, this technique requires an additional optimization parameter, which is height of the SQT with respect to burner head, so it is needed besides fuel flow rate and sample suction rate to get a better S/N ratio. All optimizations were done with 1.0 mg/L Cd solution with an SQT of 180^o angled between the entrance and exit slot.

3.2.1 Optimization of Fuel Flow Rate

Firstly, fuel flow rate was optimized in this method by keeping air flow rate constant at 3.5 L/min. In addition, the optimization of this parameter was done when sample suction rate was 3.4 mL/min and the height of SQT with respect to burner head was 1.0 mm. As can be seen in Figure 3.6, different acetylene flow rates have not changed the absorbance values dramatically. Therefore, 0.9 L/min was chosen as the fuel rate due to its highest absorbance value.

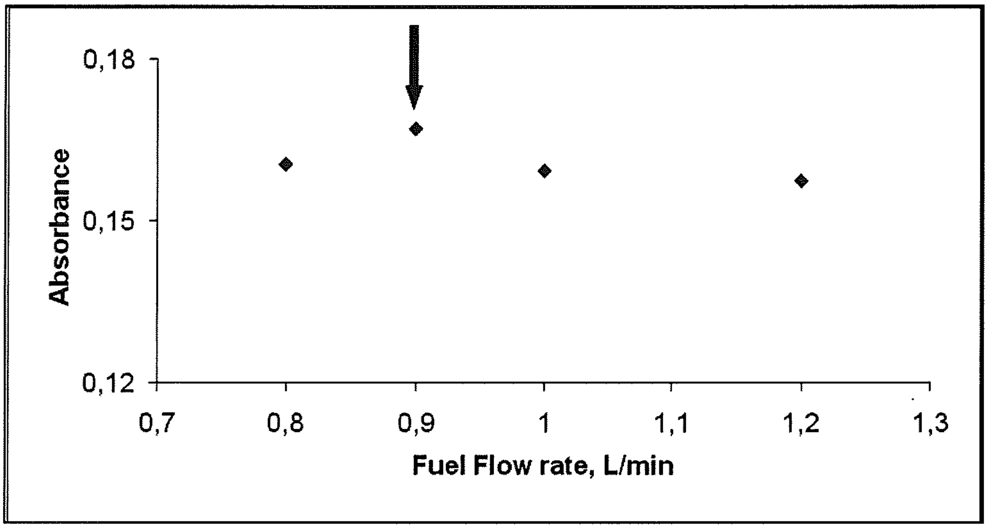


Figure 3.6 Optimization of fuel flow rate using 1.0 mg/L of Cd solution in SQT-FAAS.

Sample suction rate: 3.4 mL/min, Air flow rate: 3.5 L/min,
Height of SQT from the burner head: 1.0 mm

3.2.2 Optimization of Sample Suction Rate

Sample suction rate should also be optimized to get best S/N ratio. At 3.5 L/min airflow rate, 0.9 L/min acetylene fuel rate and 1.0 mm SQT height above the burner slot FAAS-SQT method gave a maximum absorbance value at a suction rate of 8.4 mL/min, as can be seen in Figure 3.7.

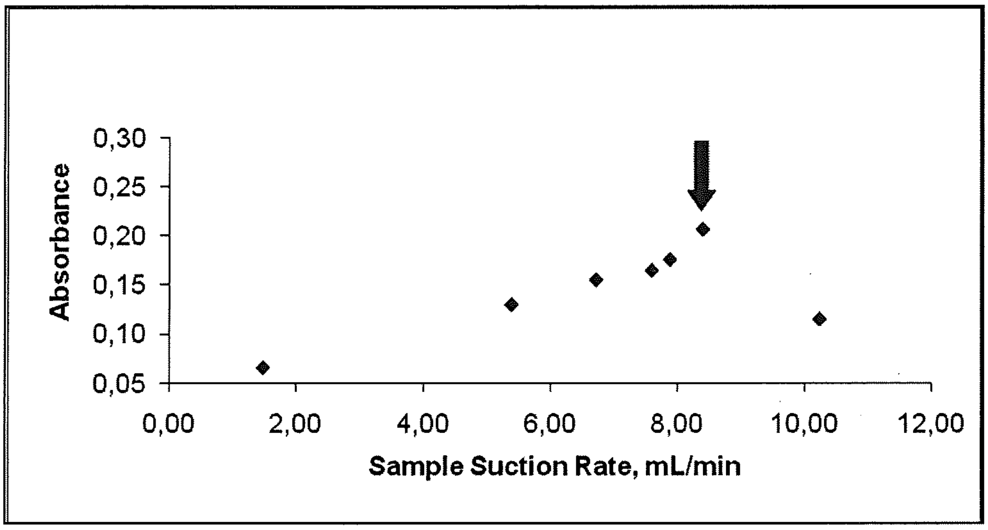


Figure 3.7 Optimization of sample suction rate using 1.0 mg/L of Cd solution in SQT-FAAS.

Fuel flow rate: 0.9 L/min, Air flow rate: 3.5 L/min,
Height of SQT from the burner head: 1.0 mm

3.2.3 Optimization of Height of the SQT from the Burner Head

Height of the SQT from the burner head is another important parameter that should be optimized. Four different heights were experienced to find the best absorbance value. As it is seen in Figure 3.8, at 8.4 mL/min sample suction rate, 0.9 L/min acetylene fuel rate, the maximum absorbance value was obtained at 1.0 mm height of the bottom surface of the SQT with respect to the burner head. It should be also noted that analyte atoms could enter the tube easily when the height between the burner head and surface of the SQT bottom is short. The reason why heights lower than 1.0 mm were not used is that, it was impossible to adjust the heights since at lower heights tube touches the head of burner.

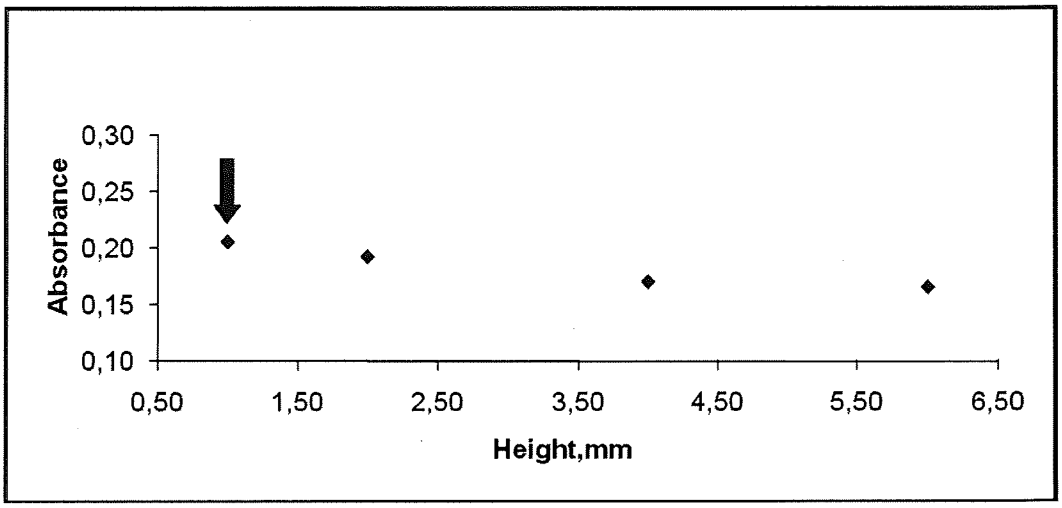


Figure 3.8 Optimization of height of SQT from the burner using 1 mg/L of Cd solution in SQT-FAAS.
Fuel flow rate: 0.9 L/min, Air flow rate: 3.5 L/min,
Sample suction rate: 8.42 mL/min.

In Figure 3.9 a transient Cd signals for 0.5 mg/L Cd standard were shown under the optimized parameters for SQT-FAAS method.

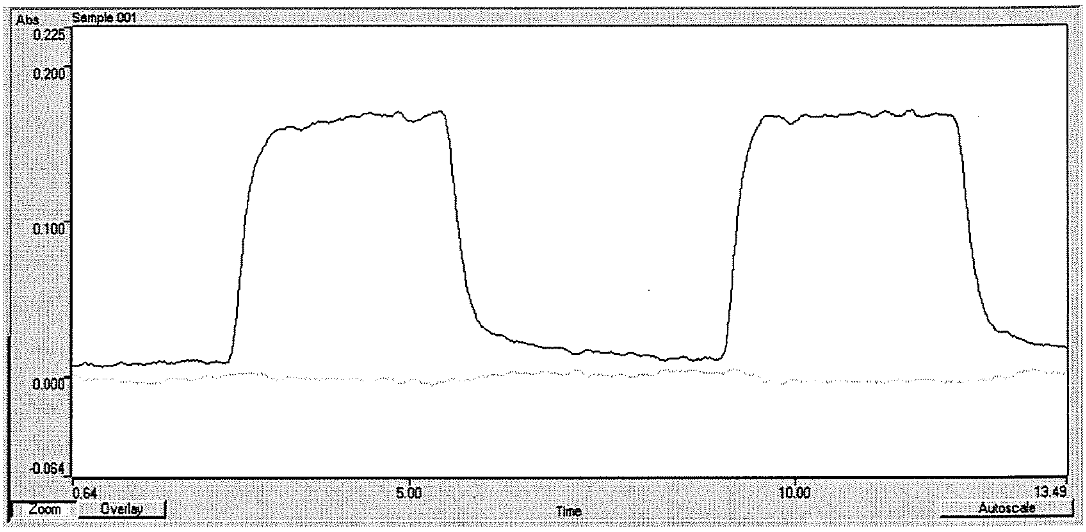


Figure 3.9 The signal of the 0.5 mg/L Cd solution with SQT-FAAS at optimized conditions.

3.2.4 Calibration Plots for SQT-FAAS Method

Calibration curve is drawn by using Cd standard samples having a concentration range between 0.050-20 mg/L. Linear calibration plot was obtained using Cd concentration range of 0.050-0.50 mg/L. y=0.1946x + 0.0017 is the best line equation and the best correlation factor is found as 0.9993. LOD, LOQ and C_0 values were found as *3.9 ng/mL*, 13 *ng/mL* and 22 *ng/mL*, respectively. These results are shown in Table 3.2.

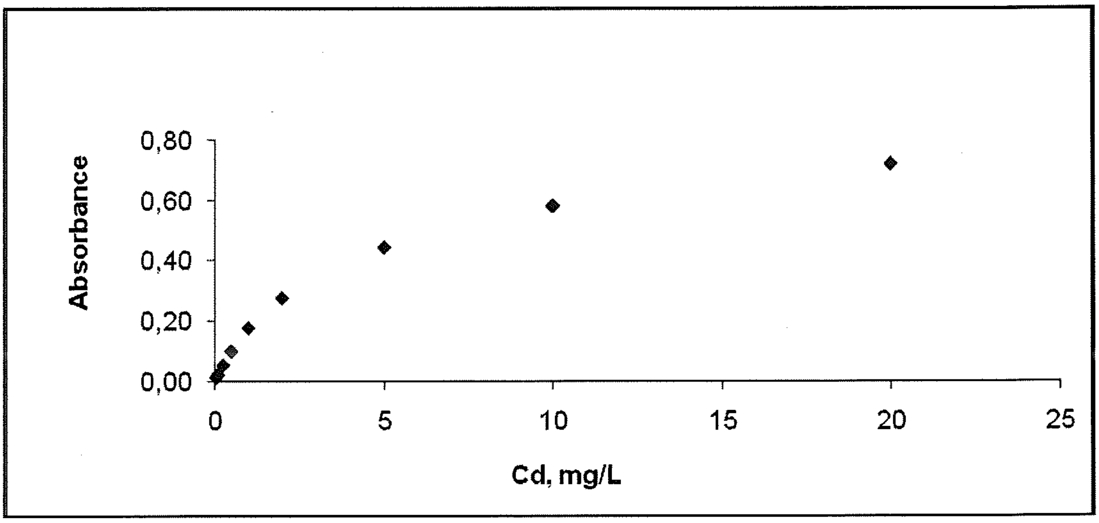


Figure 3.10 Calibration plot for SQT-FAAS method.

Acetylene flow rate: 0.9 L/min, Air flow rate: 3.5 L/min

Sample suction rate: 8.4 mL/min.

Height of SQT from the burner head: 1.0 mm.

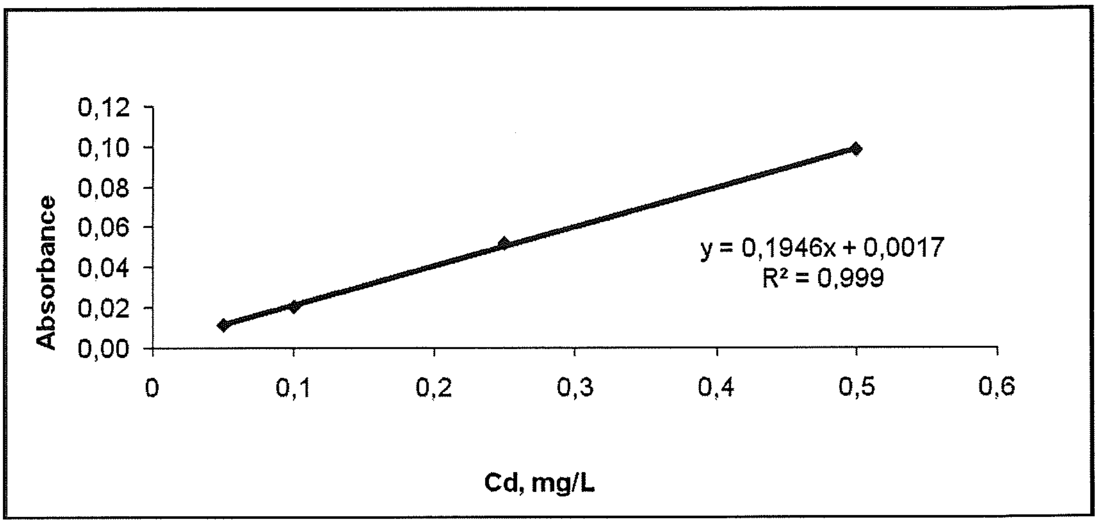


Figure 3.11 Linear Calibration plot for SQT-FAAS method.

Acetylene flow rate: 0.9 L/min, Air flow rate: 3.5 L/min

Sample suction rate: 8.4 mL/min

Height of SQT from the burner head: 1.0 mm

Table 3.2 Analytical Performance of SQT-FAAS Method

Linear Range, *mg/L*	0.050-0.50
Limit of Detection (LOD), *ng/mL*	3.9
Limit of Quantification (LOQ), *ng/mL*	13
Characteristic Concentration (C_0), *ng/mL*	22
Enhancement (E) *(with respect to FAAS)*	2.9

As can be clearly seen from Table 3.2, SQT-FAAS method is about 3 times more sensitive than FAAS. As mentioned before, enhancement factor was calculated by dividing C_0 *(characteristic concentration)* values of FAAS and SQT-FAAS method. Moreover, LOD value was calculated by considering standard deviation of 10 replicates of 0.05 mg/L Cd solution and the slope of linear calibration curve.

3.3 Optimizations of Slotted Quartz Tube Atom Trap FAAS Method (SQT-AT-FAAS)

In this step, slotted quartz tube was used as a trapping material. It was placed again on the burner slot of FAAS. Cadmium atoms were aspirated by using a lean flame and trapped in the inner surface of tube for an optimized period of time, so they were collected in the SQT. Afterwards, an optimized amount of an organic solvent was aspirated to the flame and Cd atoms were released from the surface and a transient signal was obtained.

In order to obtain high S/N ratios, some of the parameters should be optimized such as fuel flow rate, suction rate, organic solvent, volume of organic solvent and trapping period of analyte atoms. During the optimizations, 5.0 ng/mL of Cd solution was used.

3.3.1 Optimization of Organic Solvent FAAS-SQT-AT Method

In order to release analyte samples from the surface of the SQT, organic solvent aspiration technique was used. Therefore, a careful optimization should be performed when deciding on an organic solvent and its volume.

3.3.1.1. Effect of Type of Organic Solvent

For revolatilization of analyte atoms an optimum organic solvent was searched. Therefore, several organic solvents were used such as MIBK, methyl ethyl ketone (MEK), isopropyl alcohol, methyl alcohol, ethyl alcohol, cyclopentanol and n-butanol. As can be seen in Table 3.3 that the best Cd signals were obtained from the aspiration of MIBK. MEK was also successfully used for revolatilization; however, after several evaluations MIBK was chosen due to high absorbance values compared to other solvents and it was also seen that MIBK had no memory effects. On the other hand, isopropyl alcohol, methyl alcohol, ethyl alcohol, cyclopentanol and n-butanol did not show any visible change in the flame composition, so no important results were obtained after introduction of these solvents.

The optimizations were done with the 5.0 ng/mL of Cd solution with 3 minutes collection period. 40 µL of organic solvent was aspirated. A lean flame having a fuel flow rate of 0.6 L/min, and a sample flow rate of 3.7 mL/min were used. These parameters were kept constant and different organic solvents were applied to the trapped species on the surface of the SQT to find out the best solvent giving the maximum absorbance.

Table 3.3 Effect of Organic Solvents on Cd Signals for SQT-AT-FAAS Method

Type of organic solvent	**Absorbance**
⟶**MIBK**	0.167
MEK	0.163
Isopropyl alcohol	0.116
Cyclopentanol	0.020
Ethanol	0.039
Methanol	0.040
n-butanol	0.042

Concentration of Cd: 5.0 ng/mL, Fuel flow rate: 0.6 L/min, Air flow rate: 3.5 L/min,
Sample suction rate: 3.7 mL/min, Height of SQT from burner head: 1.0 mm,
Sample trapping period: 3.0 min, Volume of organic solvent: 40 µL,

3.3.1.2. Effect of Organic Solvent Amount

After deciding on the type of organic solvent, its amount should be optimized because the amount of it must be enough to revolatilize all the trapped species so that the highest signal is obtained. Generally, a portion of solvent between 10-50 µL is sufficient to revolatilize the trapped species. In this step, 40 µL of MIBK showed a complete revolatilization as can be seen in Table 3.4. Actually, the absorbance values of Cd samples have not shown a significant change by increasing or decreasing organic solvent amount, as Cd is easily released. Hence, the amount giving the highest absorbance value was chosen, which was 40 µL. Moreover, higher amounts can damage to the quartz windows of the instrument. Obviously, it was not advantageous to use higher amounts of organic solvent. MIBK was also chosen as the best organic solvent because it has no memory effects.

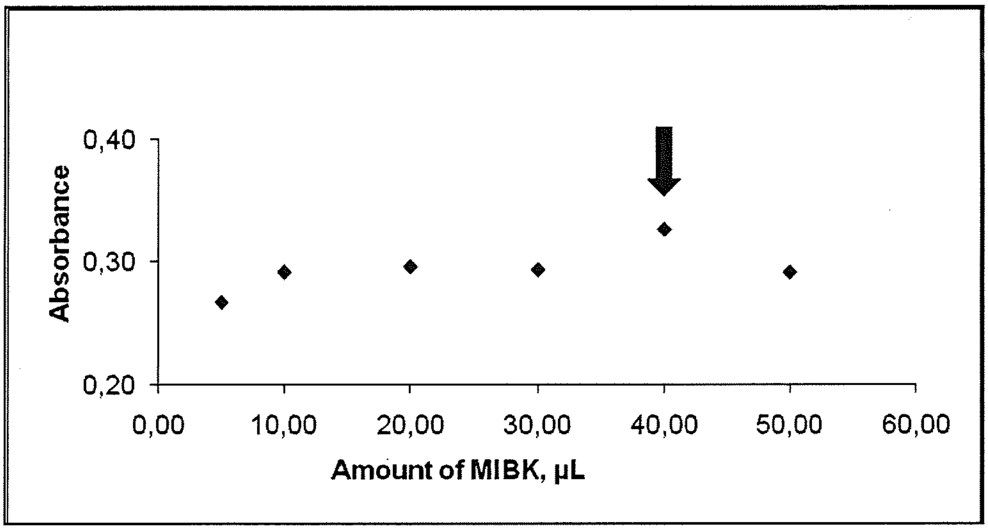


Figure 3.12 Optimization of volume of organic solvent by using 5.0 ng/mL of Cd in SQT-AT-FAAS.

Fuel flow rate: 0.6 L/min, Air flow rate: 3.5 L/min,

Sample suction rate: 3.7 mL/min, Height of SQT from burner head: 1.0 mm,

Organic solvent: MIBK, Trapping period: 3.0 min

3.3.2. Optimization of Sample Suction Rate

Suction rate is one of the most important parameter that should be optimized in trapping techniques since it affects nebulization efficiency. When suction rate increases nebulization efficiency decreases but amount of sample transferred to the flame increases, so at the optimum point combination of nebulization efficiency and sample amount in the flame reaches maximum.

Suction rate also affects flame conditions during atomization procedure. Therefore, optimization of sample suction rate was optimized during these trapping methods. In order to send the same amount of analytes in different flow rates, 20 mL of 5.0 ng/mL Cd solutions were used for optimizing suction rate. As can be clearly seen from the Figure 3.13, lower suction rates give higher absorbance values due to higher nebulization efficiency. Therefore, 4.7 mL/min was chosen as optimum suction rate.

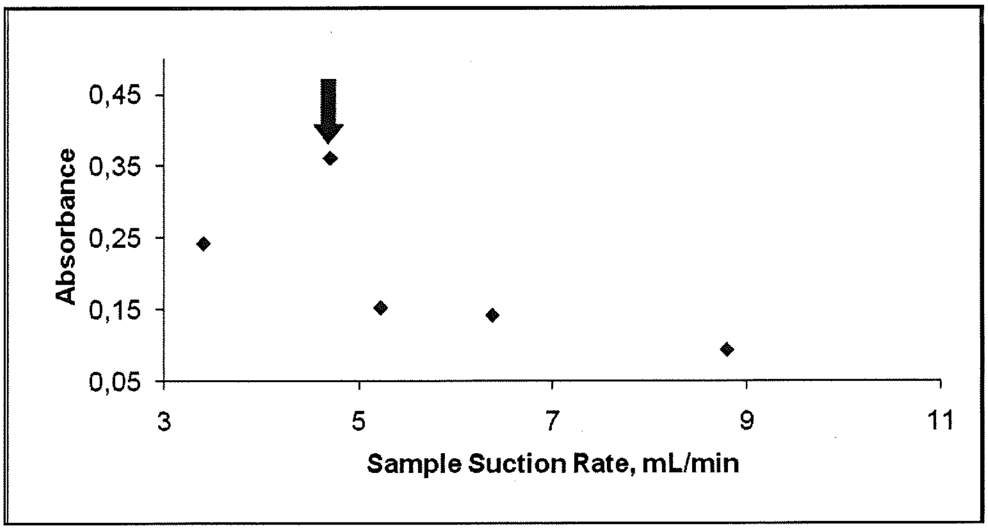


Figure 3.13 Optimization of suction rate of 5.0 ng/mL 20.0 mL Cd solution in SQT-AT-FAAS.

Fuel flow rate: 0.6 L/min, Air flow rate: 3.5 L/min,

Height of SQT from burner head: 1.0 mm,

Volume of organic solvent: 40 µL, Organic solvent: MIBK

3.3.3 Optimization of Trapping Period

Sensitivity improvement is linearly proportional to the period of analyte species collected. As the collection period increases, sensitivity increases. However, longer time periods are not advantageous, so 5.0 minutes of collection period was chosen from the time range between the trapping periods of 1-10 minutes. The results of trapping period can be seen from the Figure 3.14.

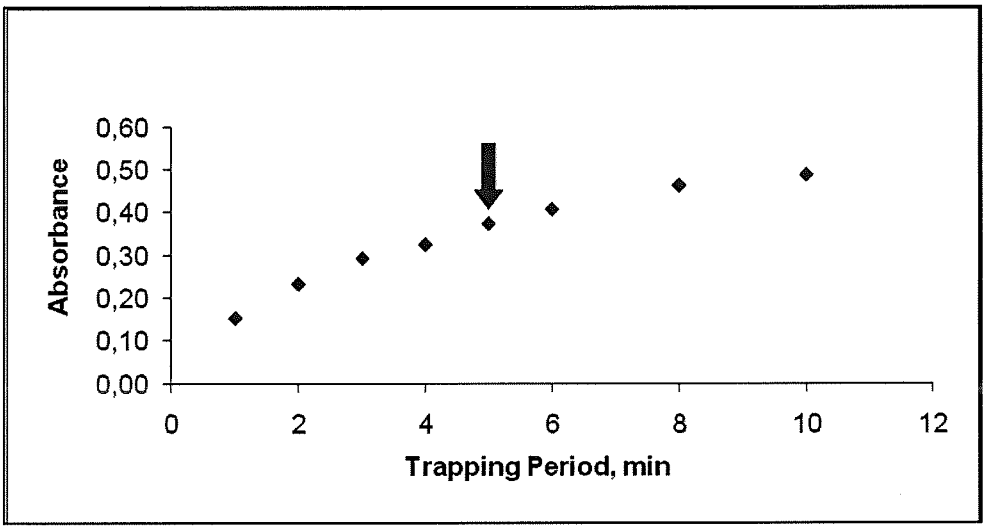


Figure 3.14 Effect of trapping period using 5.0 ng/mL of Cd solution in SQT-AT-FAAS.

Acetylene flow rate: 0.6 L/min, Air flow rate: 3.5 L/min,

Sample suction rate: 4.7 mL/min, Height of SQT from burner head: 1.0 mm,

Volume of organic solvent: 40 µL, Organic solvent: MIBK

3.3.4 Optimization of Fuel Flow Rate

Throughout these trapping studies, optimization of fuel rate is also very important, because at rich or stochiometric flame, analyte species can not be trapped; on the contrary, they are removed from the measurement zone. Therefore, a lean flame should be used to trap the analyte in the inner surface of SQT. In addition, in this step a 0.6 L/min fuel flow rate was used as can be seen in Figure 3.15.

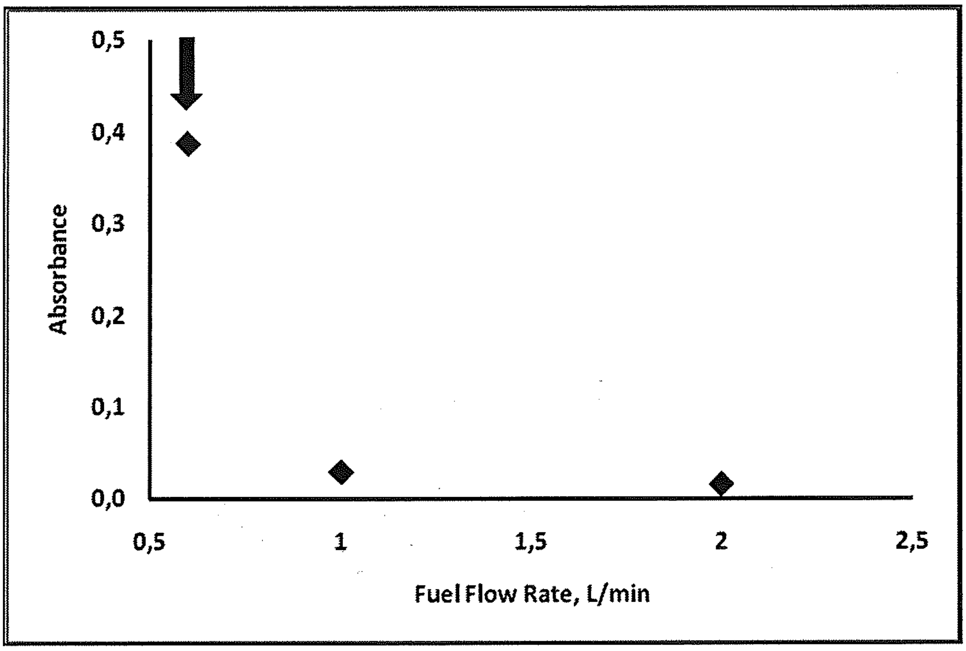


Figure 3.15 Effect of fuel flow rate using 5.0 ng/mL of Cd in SQT-AT-FAAS.
Air flow rate: 3.5 L/min,
Sample suction rate: 4.7 mL/min, Height of SQT from burner head: 1.0 mm,
Volume of organic solvent: 40 µL, Organic solvent: MIBK
Trapping Period: 5.0 min

3.3.5 Optimization of Height of the SQT from the Burner Slot

The effect of height should also be optimized due to the change in the value of absorbance at different heights. As SQT was put higher above the burner slot, absorbance decreases due to escaping of analyte atoms from the reaction zone of flame. Therefore, SQT should be placed 1.0 mm above the burner slot. As can be seen from the Figure 3.16, maximum absorbance value was obtained when SQT was at 1.0 mm above.

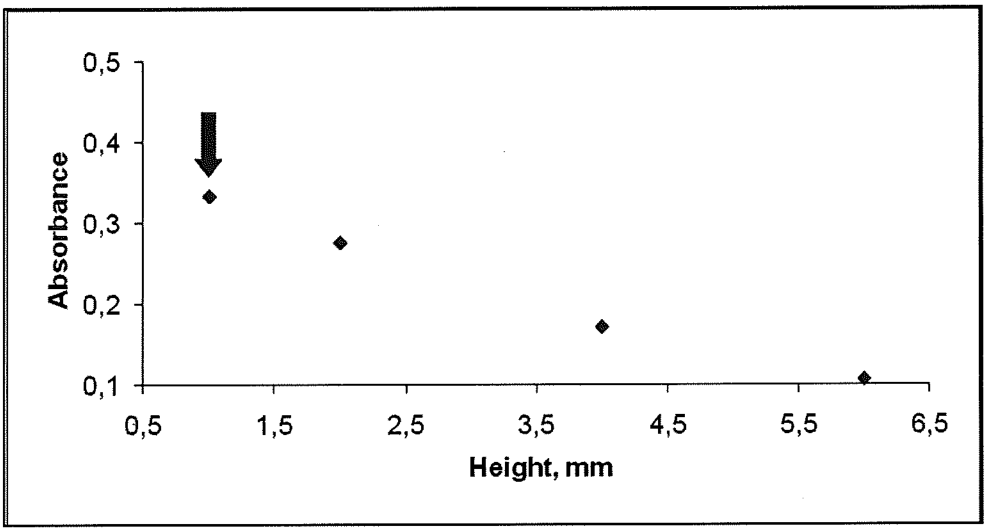


Figure 3.16 Effect of SQT height from the burner head for 5.0 ng/mL of Cd in SQT-AT-FAAS.

Air flow rate: 3.5 L/min,

Sample flow rate: 4.7 mL/min, Fuel Flow rate: 0.6 mL/min

Volume of organic solvent: 40 µL, Organic solvent: MIBK

Trapping Period: 5.0 min

Table 3.4 Conditions for SQT-AT-FAAS Method

Parameter	Condition
Type of Organic Solvent	MIBK
Sample Suction Rate	4.7 mL/min
Volume of Organic Solvent	40 µL
Trapping Period	5.0 min
Height of The SQT from the Head of the Burner	1.0 mm
Acetylene Flow Rate	0.6 L/min
Air Flow Rate	3.5 L/min

By using the parameters given in Table 3.4, 5.0 ng/mL Cd solution was sent to the system and a transient signal was obtained, as can be seen in Figure 3.17.

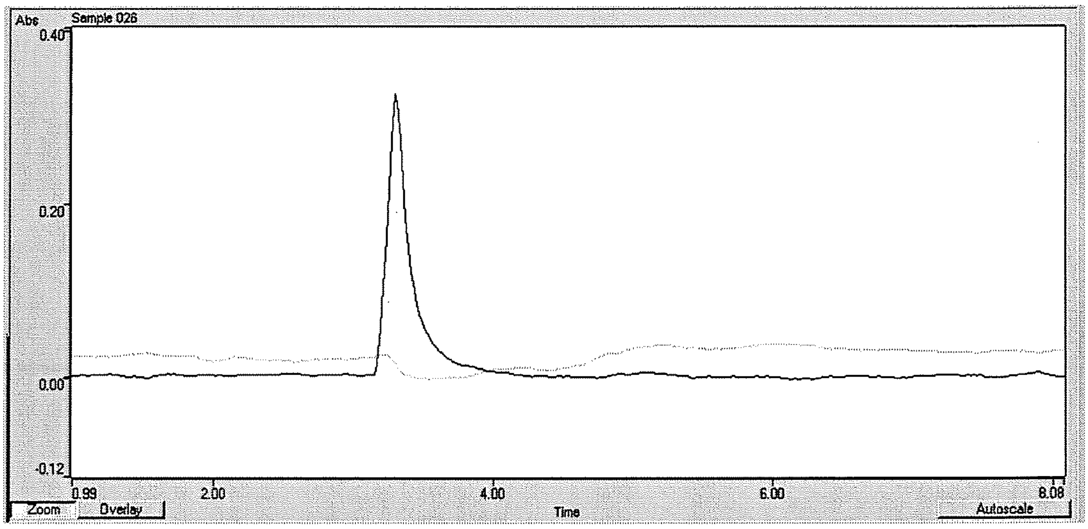


Figure 3.17 The Cd signal of SQT-AT-FAAS for 5.0 ng/mL Cd solution.

3.3.6 Calibration Plots for SQT-AT-FAAS Method

After optimizing all the parameters given in Table 3.4, a calibration plot was obtained by using a standard range of 0.25-10 ng/mL Cd (Figure 3.18). A linear calibration plot was obtained between the 0.25-1.00 ng/mL of Cd solution. As can be seen from Figure 3.19, linear line equation was found as y= 0.1097x + 0.0241 and the correlation coefficient was 0.9949.

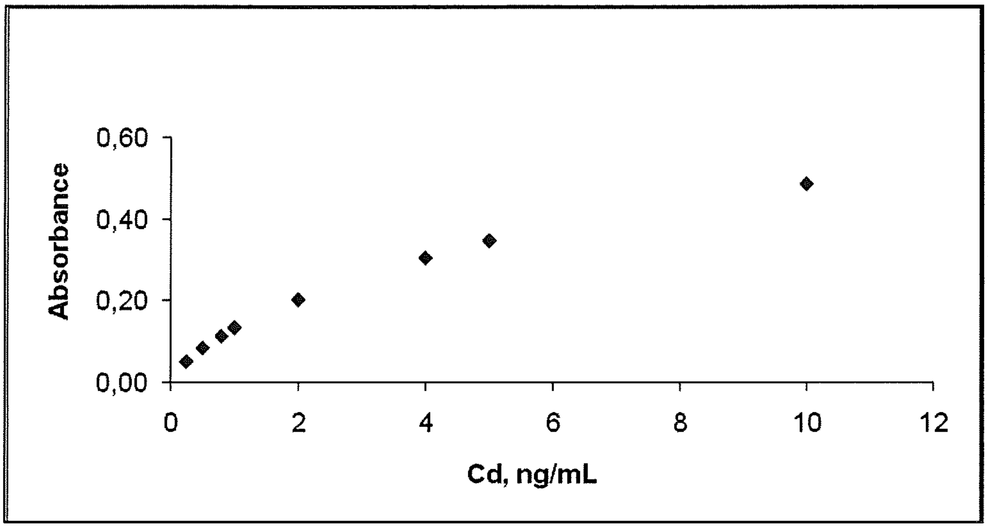


Figure 3.18 Calibration plot for SQT-AT-FAAS method using the conditions in Table 3.4.

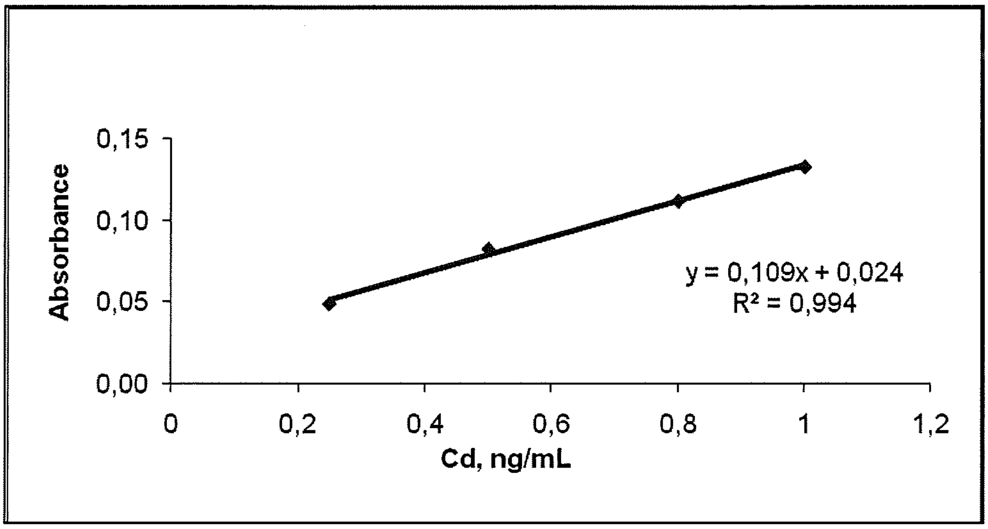


Figure 3.19 Linear calibration plot for SQT-AT-FAAS method using the conditions in Table 3.4.

3.3.7 Analytical Performance of Cd Using SQT-AT-FAAS

Trapping of analyte atoms at the inner surface of SQT has highly affected the sensitivity. To understand the enhancement factors, LOD and LOQ calculation becomes important, so they were calculated with using the equation 3s/m and 10s/m, respectively. LOD and LOQ were found by reading the minimum standard Cd concentration (0.25 ng/mL) value 6 times consecutively and calculating the standard deviation of these values and by considering the slope of the linear calibration curve. By performing these calculations, LOD was found as 0.071 ng/mL and LOQ was found as 0.24 ng/mL. These values were rather low as compared with the previous two methods; namely SQT-FAAS and FAAS. As a matter of fact, C_o values of each method were calculated to find out enhancement factors of this method. Enhencements factor is 710 with respect to SQT-FAAS method and 2065 with respect to conventional FAAS method.

Table 3.5 Analytical Performance of SQT-AT-FAAS

Method Conditions	SQT-AT-FAAS
Linear Range, ng/mL	0.25-1.00
Limit of Detection (LOD), *ng/mL*	0.071
Limit of Quantification (LOQ), *ng/mL*	0.24
Characteristic Concentration (C_0), *ng/mL*	0.031
Characteristic mass (m_0), *ng*	0.74
Enhancement (E) *(with respect to FAAS)*	2065
Enhancement (E) *(with respect to SQT-FAAS)*	710

Table 3.6 Comparison of Analytical Figures of Merit.

	Limit of Detection, LOD, 3s/m *(N=6)* ng/mL,	**Limit of Quantification,** LOQ, 10s/m *(N=6)* ng/mL,	**Characteristic Concentration,** C_0 ng/mL	**Enhancement Factor***	**Dynamic Ranges,** ng/mL
FAAS	15	51	64	1	250-2000
SQT-FAAS	3.9	13	22	2.9	50-500
SQT-AT-FAAS	0.071	0.24	0.031	2065	0.25-1.0

* C_0 (FAAS) / C_0 (selected method)

3.4 Optimizations and Conditions of Coated Slotted Quartz Tube Atom Trap Flame AAS (Coated-SQT-AT-FAAS) for Determination of Cadmium

This step aims to reach higher sensitivity than SQT-AT-FAAS by coating the surface of quartz. Modifying the surface may provide a better surface to trap the analyte species and also better releasing properties upon aspiration of organic solvent. The working principles were the same with those of SQT-AT-FAAS method. Therefore, optimizations to be done, were the same with the previous method. All optimizations were performed with a standard solution having 5.0 ng/mL Cd.

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

FAAS-SQT-AT has provided a sensitive approach to atomic spectroscopy analysis for the determination of Cd. In this step, different coating materials on the surface of quartz were used to obtain more sensitive results than SQT-AT-FAAS method. Some metals such as, Palladium (Pd), Tantalum (Ta), Iridium (Ir), Molybdenum (Mo), Zirconium (Zr) were coated on the surface of quartz and the effect of these metals on trapping and releasing the analyte atoms were investigated. The common properties of these metals are that they have high melting points. It is expected that as the analyte is revolatilized, coating material will stay on the surface. The physical properties of these coating materials are shown in Table 3.7.

Table 3.7 Some physical properties of Coating Materials [49]

	Atomic Number	Atomic Weight (g/mol)	Boiling Point (^{0}C)	***Melting Point*** ***(^{0}C)***
Pd	46	106.42	2963.0	***1554.9***
Ta	73	180.95	5458.0	***3017.0***
Ir	77	192.22	4428.0	***2466.0***
Mo	42	95.94	4639.0	***2623.0***
Zr	40	91.22	4409.0	***1855.0***

All coatings were performed separately and it was observed that Ir and Mo coated quartz tubes gave the lowest absorbance values with respect to the others. On the contrary, Pd and Zr gave maximum values of absorbance; however, the best signals were obtained with the Zr coated tube. Pd was not preferred due its high cost. Actually, there was no significant difference in the results of SQT-AT-FAAS and Zr-coated-SQT-AT-FAAS at this step. However, after optimizations the results could be evaluated more accurately. The absorbance values of coating materials are shown in Table 3.8.

Table 3.8 Effect of Coating Material on 5.0 ng/mL Cd Signal for SQT-AT-FAAS Method.

	Absorbance	**%RSD (n=3)**
None	0.167	1.16
Pd	0.172	1.21
Ta	0.142	1.47
Ir	0.053	2.87
Mo	0.039	2.94
→ Zr	0.189	1.16

Acetylene flow rate: 0.5 L/min
Air flow rate: 3.5 L/min
Concentration of Cd solution: 5.0 ng/mL
Sample suction rate: 4.4 mL/min
Height of SQT from burner head: 1.0 mm,
Volume of organic solvent: 40 μL
Organic solvent: MIBK
Trapping period: 2.0 min

3.4.2 Optimization of Organic Solvent Type

In this step effects of various kinds of organic solvents, which were already available in our laboratory, were investigated and again MIBK was chosen as the best solvent due to having the ability to revolatilize the all analyte species. The results are shown in Table 3.9.

Table 3.9 Effect of Organic Solvents on 5.0 ng/mL Cd Signal for Zr-coated-SQT-AT-FAAS Method.

Type of Organic Solvent	**Absorbance**
→ **MIBK**	0.27
MEK	0.26
Acetonitrile	0.25
Methanol	No signal
Ethanol	No signal
N-butanol	No signal
Cyclopentanol	No signal
Isopropyl Alcohol	No signal

Acetylene flow rate: 0.5 L/min, Air flow rate: 3.5 L/min,
Sample suction rate: 4.4 mL/min, Height of SQT from burner head: 1.0 mm,
Volume of organic solvent: 40 μL, Trapping period: 3.0 min

3.4.3 Optimization of Amount of Organic Solvent

As can be seen in Figure 3.20, the change in volume of organic solvent did not affect the absorbance value of Cd solution very much after the introduction of 20 μL. Therefore, the maximum absorbance value among the attempted volumes was chosen as 40 μL of MIBK. MIBK was also chosen as it can revolitilize all the species from the surface of SQT and it has no memory effect.

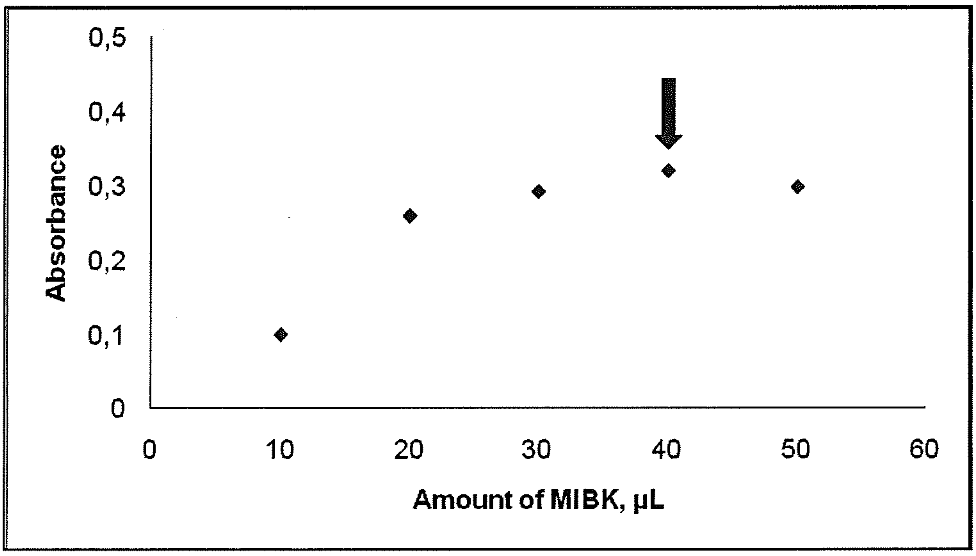


Figure 3.20 Optimization of volume of organic solvent using 5.0 ng/mL Cd in Zr-coated-SQT-AT-FAAS.

Other Conditions:
Acetylene flow rate: 0.5 L/min
Air flow rate: 3.5 L/min,
Sample suction rate: 4.41 mL/min
Height of SQT from burner head: 1.0 mm
Organic solvent: MIBK, Trapping period: 3.0 min

3.4.4 Optimization of Sample Suction Rate

Sample suction rate was also optimized for this method by using a 5.0 ng/mL Cd. As can be seen from the Figure 3.21, the change was observed by varying the sample suction rates between 4.2 and 9.5 and it was also found that at lower suction rates absorbance values of Cd was higher due to higher nebulization efficiency. To send equal amounts of analyte in different suction rates, optimization of sample suction rate was performed by using 20 mL of 5.0 ng/mL Cd standard .4.7 mL/min was selected as optimum sample suction rate

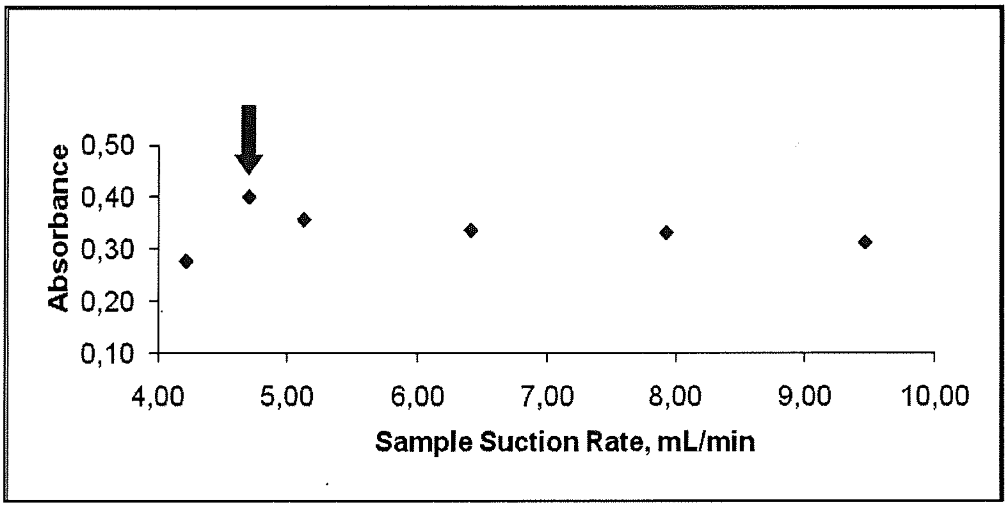


Figure 3.21 Optimization of sample suction rate using 20 mL of 5.0 ng/mL of Cd in Zr-coated-SQT-AT-FAAS.

Other Conditions:
Acetylene flow rate: 0.5 L/min
Air flow rate: 3.5 L/min,
Height of SQT from burner head: 1.0 mm
Organic solvent: MIBK
Volume of organic solvent: 40 μL
Trapping period: 3.0 min

3.4.5 Optimization of Fuel Flow Rate

Optimization of fuel flow rate was also performed and it was seen that again as leaner the flame, higher the absorbance value. It is seen in Figure 3.22 that at 0.5 L/min acetylene flow rate the absorbance value was found as maximum. However, as the acetylene flow rate increases, it was seen that analyte species were not trapped anymore on the surface of the tube. Moreover, at lower fuel flow rates, flame was shut off.

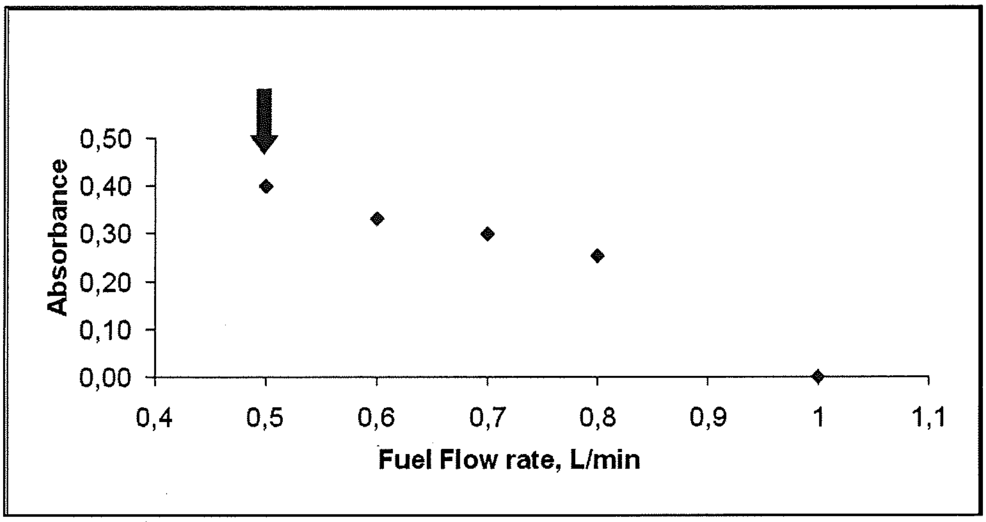


Figure 3.22 Optimization of acetylene flow rate using 5.0 ng/mL of Cd in Zr-coated-SQT-AT-FAAS.

Other conditions:

Air flow rate: 3.5 L/min
Sample suction rate: 4.7 mL/min,
Height of SQT from burner head: 1.0 mm
Organic solvent: MIBK,
Volume of organic solvent: 40 µL
Trapping period: 5.0 min

3.4.6 Optimization of Height of the SQT from the Burner Head

The optimum height of the SQT from the burner slot was found as 1.0 mm. As the tube height increases, signals became lower and less reproducible. Figure 3.23 shows the effect of height of SQT from the burner slot. Moreover, placing the SQT at lower distances was impossible because the SQT was touching the burner head.

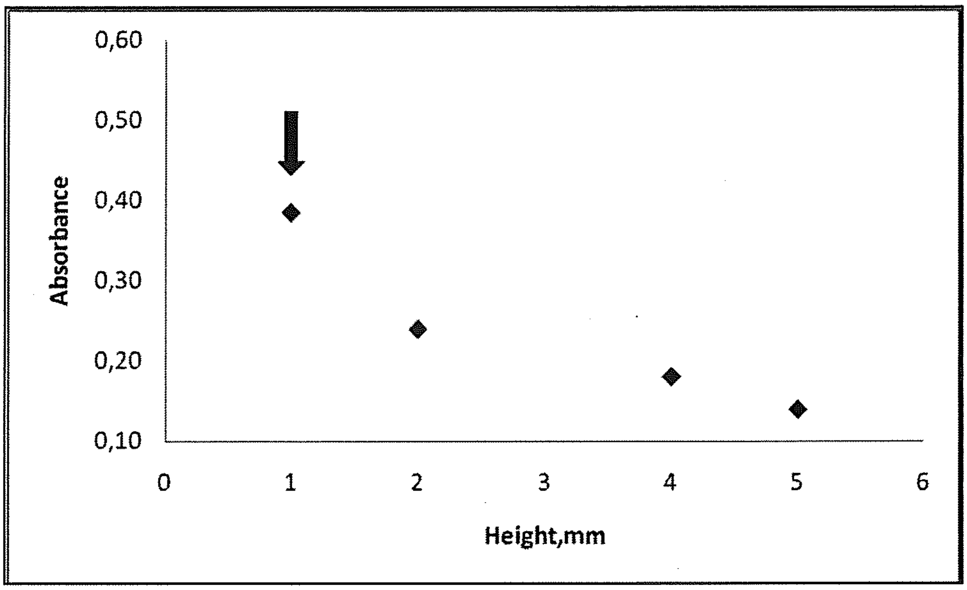


Figure 3.23 Optimization of height of SQT from burner head using 5.0 ng/mL of Cd in Zr-coated-SQT-AT-FAAS

Other conditions:
Acetylene flow rate: 0.5 L/min
Air flow rate: 3.5 L/min
Sample suction rate: 4.7 mL/min
Organic solvent: MIBK
Volume of organic solvent: 40 µL
Trapping period: 3.0 min

3.4.7 Investigation of Trapping Period

Trapping period was also optimized in this method and it was seen that again as the period increases, absorbance values increase due to much trapping of analyte atoms on the surface of the tube. However, as mentioned in the previous method, higher collection periods are not advantageous in terms of being waste of time. Moreover, it is also clear in the Figure 3.24 that this parameter has an ascending and then a stabilizing behavior. That means, absorbance value increases as trapping period does, but after a specific period is stable. Therefore, again 5.0 minutes were chosen as the trapping period, as can be seen in Figure 3.24.

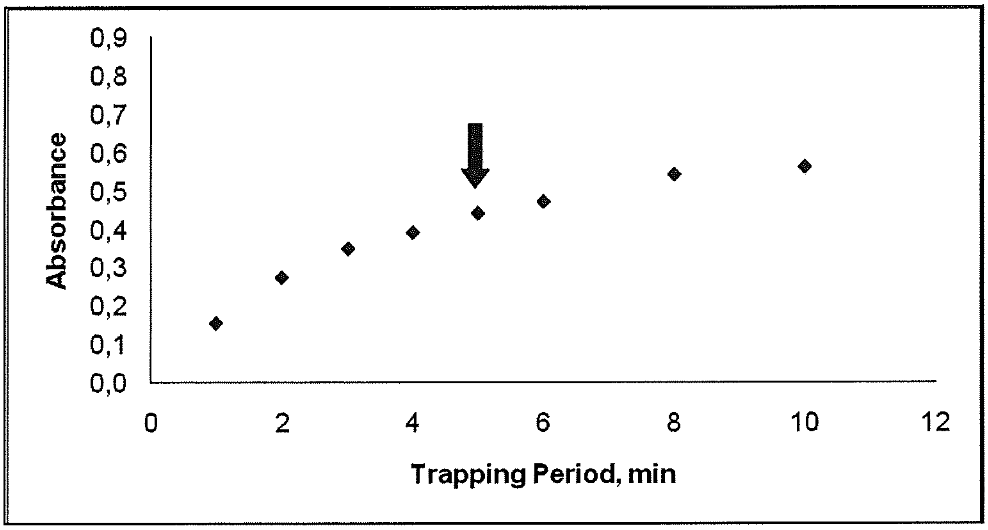


Figure 3.24 Effect of trapping period on signal using 5.0 ng/mL of Cd in Zr-coated-SQT-AT-FAAS.

Other Conditions:
Acetylene flow rate: 0.5 L/min
Air flow rate: 3.5 L/min,
Sample suction rate: 4.7 mL/min
Height of SQT from burner head: 1.0 mm,
Organic solvent: MIBK
Volume of organic solvent: 40 µL

Table 3.10 summarizes the optimized conditions for Zr-coated-SQT-AT-FAAS Method. Moreover, Figure 3.25 shows a signal in the linear range of this method.

Table 3.10 Optimum Conditions for Zr-coated-SQT-AT-FAAS Method

Experimental Parameters	**Optimum Conditions**
Coating Material	Zirconium
Type of Organic Solvent	MIBK
Volume of Organic Solvent	40 µL
Sample Suction Rate	4.7 mL/min
Trapping Period	5.0 min
Height of The SQT from the head of the burner	1.0 mm
Acetylene Flow Rate	0.5 L/min
Air Flow Rate	3.5 L/min

After optimizing the parameters, a transient signal was obtained for 0.5 ng/mL Cd standard as can be seen from the Figure 3.25.

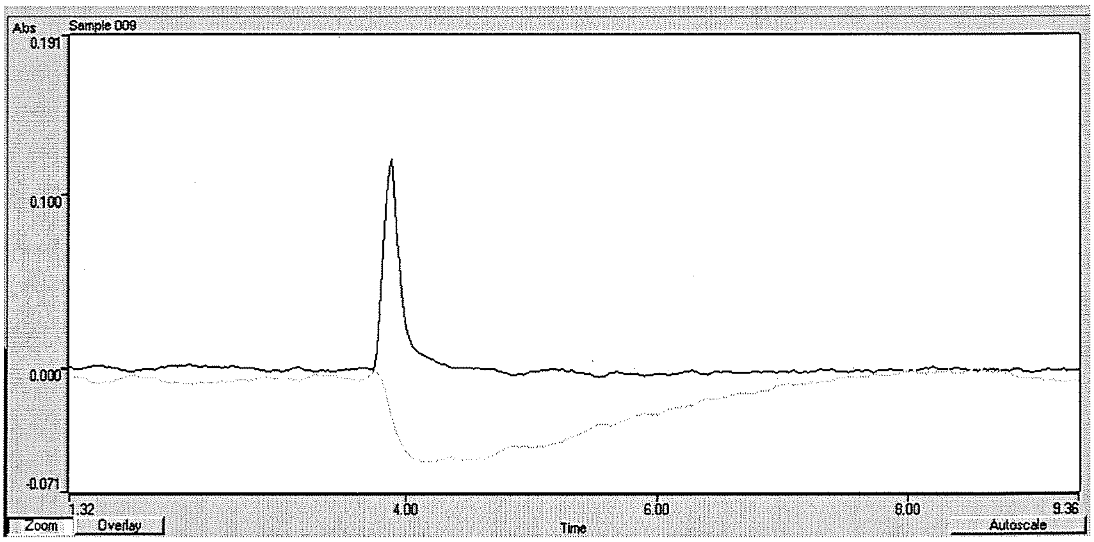


Figure 3.25 The signal of Zr- Coated-SQT-AT-FAAS for 0.5 ng/mL Cd solution using the conditions in Table 3.10 (Upper trace)

Lower trace denotes the D_2 signal of the instrument.

3.4.8 Calibration Plots for Zr-coated-SQT-FAAS Method

After optimizing the all parameters, calibration plot was obtained by considering the concentrations between 0.1-20.0 ng/mL of Cd (Figure 3.26). Experimental conditions given in Table 3.10 were used. Linearity was obtained between the Cd concentration of 0.1-0.8 ng/mL (Figure 3.27).

The best line equation and determination coefficient were y=0.2103x + 0.0085 and 0.9987, respectively.

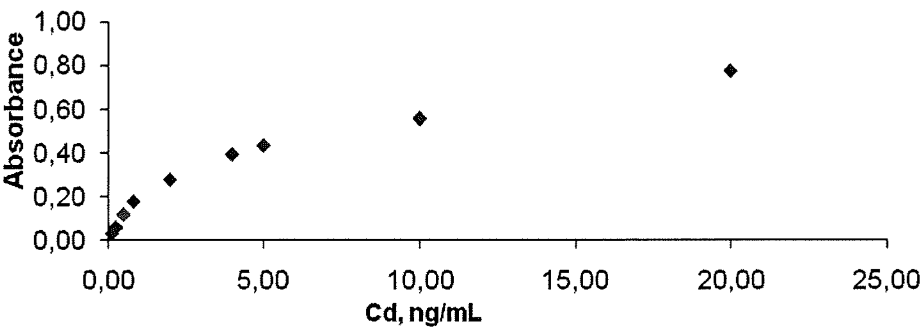


Figure 3.26. Calibration plot for Zr-coated-SQT-AT-FAAS method, conditions in Table 3.10 were used.

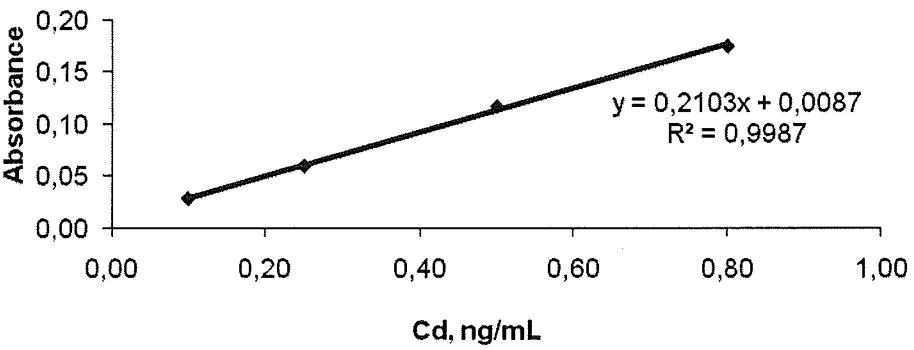


Figure 3.27 Linear calibration plot for Zr-coated-SQT-AT-FAAS method, conditions in Table 3.10 were used.

3.4.9 Analytical Figures of Merit for Zr-coated-SQT-AT-FAAS

For this method, LOD and LOQ values were also calculated with the equations 3s/m and 10s/m, respectively. Moreover, characteristic concentration (c_0) and characteristic mass (m_0) were calculated. As can be seen from Table 3.11, LOD and LOQ was found 0.008 ng/mL and 0.027 ng/mL, respectively. Characteristic concentration was also determined as 0.019 ng/mL and characteristic mass was determined as 0.46 ng and 3368 fold sensitivity enhancement was obtained with respect to conventional FAAS.

Table 3.11 Analytical Performance of Zr-coated-SQT-AT-FAAS.

	Zr-Coated SQT-AT-FAAS
Linear Range, *ng/mL*	0.1-0.8
Limit of Detection (LOD), *ng/mL*	0.008
Limit of Quantification (LOQ), *ng/mL*	0.027
Characteristic Concentration (C_0), *ng/mL*	0.019
Characteristic mass (m_0), *ng*	0.46
Enhancement (E) *(with respect to FAAS)*	3368

3.4.10 Accuracy Check for Zr-coated-SQT-AT-FAAS Method

To check the accuracy of the method a CRM, SCP SCIENCE, EnviroMAT-Waste Water, Low (EU-L-2) was used. It was diluted two times. Firstly, 1.0 mL of stock CRM solution was diluted to 100 mL volumetric flask with 1.0 M HNO_3 and secondly, 1.0 mL from this solution was taken and diluted to 100 mL of volumetric flask with 1.0 M HNO_3. At certificate of analysis seen in Table 2.1, the certified results of CRM can be seen for a dilution factor of 100. The direct calibration was employed and measurements were done under optimum conditions. One sample was read three times and the results were compared with the results of the certified value. The results are shown in Table 3.12.

Table 3.12 Results of Accuracy Check for Zr-coated-SQT-AT-FAAS Method

SCP SCIENCE, EnviroMAT Waste Water EU-L-2	**Certified Cd Result,** *ng/mL*	**Found Result,** *ng/mL*
	0.22-0.24	0.23±0.06

3.6 Evaluation of System Performance

This study has aimed to develop a new method to determine Cd atoms at very low concentrations. As can be seen from the results, Zr-coated-SQT-AT-FAAS is the most sensitive method among the other applied methods. That is because of the higher trapping efficiency of the Zr-coated-SQT system. This is also understandable by looking at the enhancement factors between the applied methods. The different "enhancement, E, factors" are shown in Table 3.13. E_t (enhancement factor in terms of time) and E_v (enhancement factor in terms of volume) values were also calculated to evaluate the enhancement in terms of volume and time consumed. As it is seen from Table 3.13, a dramatic increase in sensitivity was found when conventional FAAS and Zr-coated-SQT-AT-FAAS methods were compared. There was a 3368 times enhancement. On the other hand, there is a slight enhancement were compared between the methods, SQT-AT-FAAS and Zr-coated-SQT-AT-FAAS. That is because of the ability of trapping of Zr-coated quartz surface. This can also be seen from the Figure 3.28.

Table 3.13 Comparison of Methods in Terms of E, E_t and E_v Values

Technique, Period, Volume	**LOD,** *ng/mL*	**LOQ,** *ng/mL*	**C_0,** *ng/mL*	**m_0,** *ng*	**E**	**E_t, min^{-1}**	**E_v, mL^{-1}**
FAAS	15	51	64	-	1	-	-
SQT-FAAS	3.9	13	22	-	2.9	-	-
SQT-AT-FAAS *5.0 min, 24 mL*	0.071	0.24	0.031	0.74	2065	413	86
Zr-coated-SQT-AT-FAAS *5.0 min, 24 mL*	0.008	0.027	0.019	0.46	3368	674	140

* $E = C_0$ (FAAS)/C_0 (Selected Method), $E_t = E/t_{total}$, $E_v = E/v_{total}$

Figure 3.28 shows the difference between the SQT-AT-FAAS and Zr-coated-SQT-AT-FAAS signals. By considering the areas under the curves, it can be seen that, Zr coated-SQT-AT method is more sensitive due to its higher trapping efficieny. By considering the areas under the curves, there was 1.60 times sensitivity difference between the two methods. The area under the peak of SQT-AT-FAAS was found as 0.0126 s and the area under the peak of Zr-coated-SQT-AT-FAAS was found as 0.0202 s. The enhancement factor between these two methods was also calculated as 1.63 by considering C_0 values obtained from the peak height absorbance values. In Figure 3.28, pink and green peaks refer to two replicates of Zr-coated-SQT-AT-FAAS, blue and red peaks refer to two replicates of SQT-AT-FAAS.

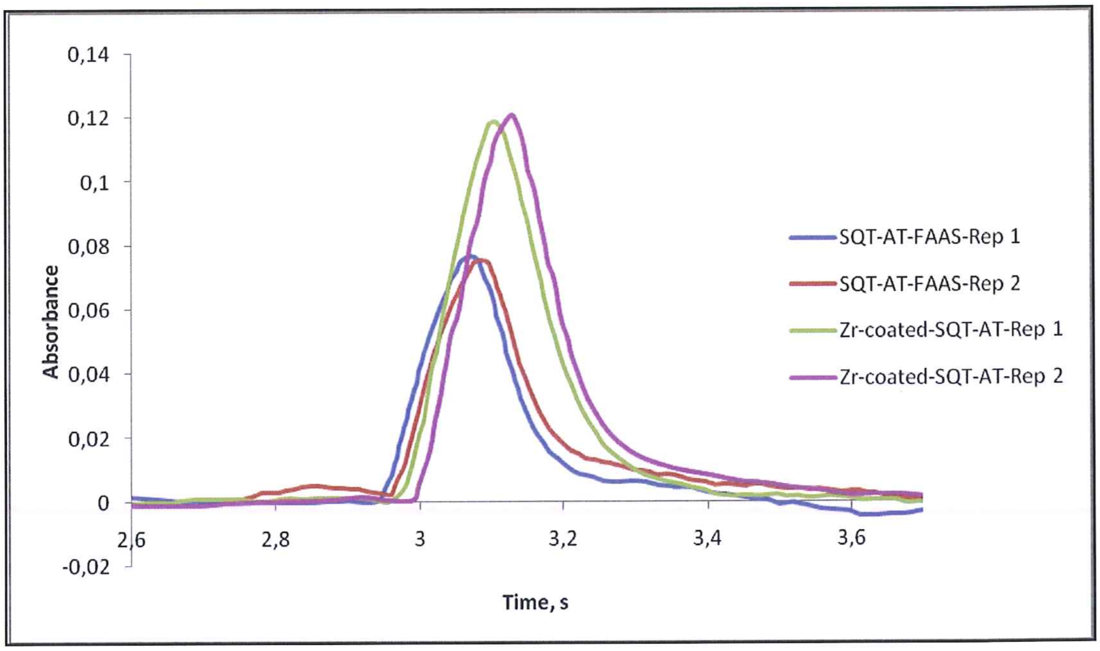


Figure 3.28 Comparison of the peaks between the SQT-AT-FAAS and Zr-coated-SQT-AT-FAAS Method.

For SQT-AT-FAAS method conditions in Table 3.4 were used.

For Zr-coated-SQT-AT-FAAS method conditions in Table 3.10 were used.

During the studies, uncoated SQT was found to be highly robust. In other words, sensitivity was constant when the SQT was used in the optimizations or calibrations. This corresponded to at least 350 readings. On the other hand, Zr Coated SQT was used approximately 75 times succesively without any loss of sensitivity.

In order to see the dramatic enhancement in Zr-coated-SQT-AT-FAAS method with respect to other techniques, a literature search was done to compare the LOD results of Cd in different sensitive methods. The results can be seen in Table 3.14. It is understood that levels of developed methods are at the levels of ICP-MS and HGAAS. Obviously, LOD results from obtained methods are much lower than LOD of ICP-OES and HGAAS.

Table 3.14 Comparison of Developed Methods with Other Techniques

	LOD Values (ng/mL)	Reference
GFAAS	0.007	50
CVAAS	0.004	51
ICP-MS	0.01	52
ICP-OES	5.8	53
SQT-AT-FAAS *5.0 min, 24 mL*	0.071	This study
Zr-coated-SQT-AT-FAAS *5.0 min, 24 mL*	0.008	This study

3.7 Interference Studies for Zr-coated-SQT-AT-FAAS Method

Interference studies were a significant step for the method. Two kinds of interference can be accounted with the analyte sample, which are spectral and non-spectral interference. Species other than free atoms of the analyte may absorb radiation and this causes spectral interferences. On the other hand, non-spectral interferences are caused by influence of sample constituents on the analyte signal. The mostly studied interference was caused by matrix in the sample. Because of all these reasons, interference studies were performed for Zr-coated-SQT-AT-FAAS method. Therefore, 4 different solutions were prepared in which concentration of Cd was kept constant, 0.50 ng/mL, and concentrations of interferent were 1.0, 10, 100 and 1000 folds of the analyte concentration using the mass ratios. From Table 3.10 conditions of the measurement of interference solutions can be seen.

To see the effects of elements and ions some groups of elements were chosen. For example, the effects of some 1A and 2A elements are shown in Figure 3.29. As it can be seen, 1.0, 10, 100 fold of Na, Mg, K and Ca showed similar effects on Cd determination. They suppressed the signal of Cd by 10%, approximately. However, 1000 fold of Ca has fixed the suppression.

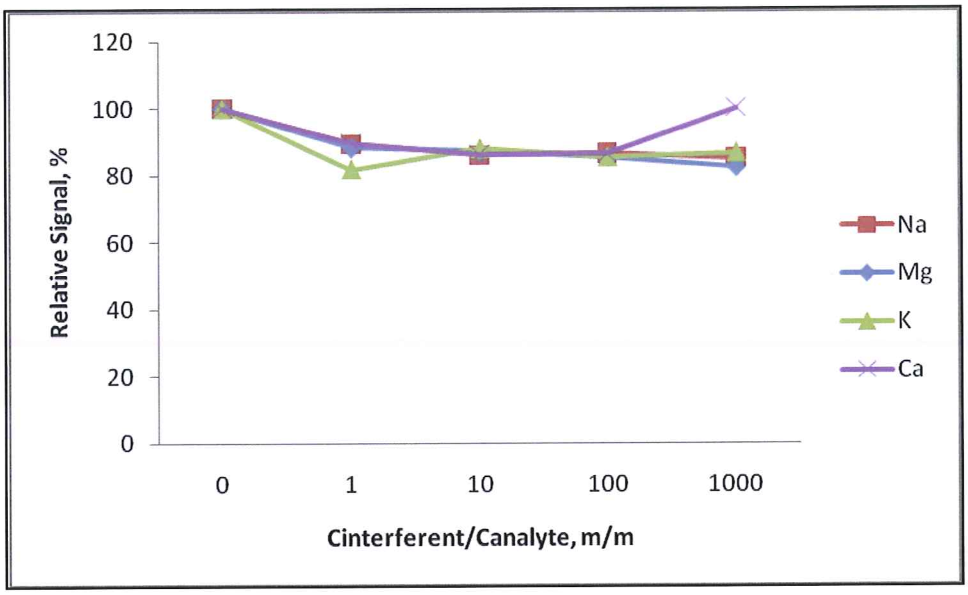


Figure 3.29 Interference effects of Na, K, Mg, Ca on 0.50 ng/mL Cd signal in Zr-coated-SQT-AT-FAAS.

Figure 3.30 shows the effects of some transition metals on Cd determination. As can be clearly seen from the figure, equal concentrations, 10 fold and 100 fold Mn concentrations supress the Cd signal. However, the most suppression occurs in the 10 fold of Fe, which was found as approximately 36 %. Surprisingly, 1000 fold Mn concentration causes no interference. Moreover, after Cr analysis, tube has lost its trapping capability since the results were not reproducible anymore, so SQT was coated again with 100 mg/L Zr solution, after keeping it in 20% HF solution for three minutes for cleaning.

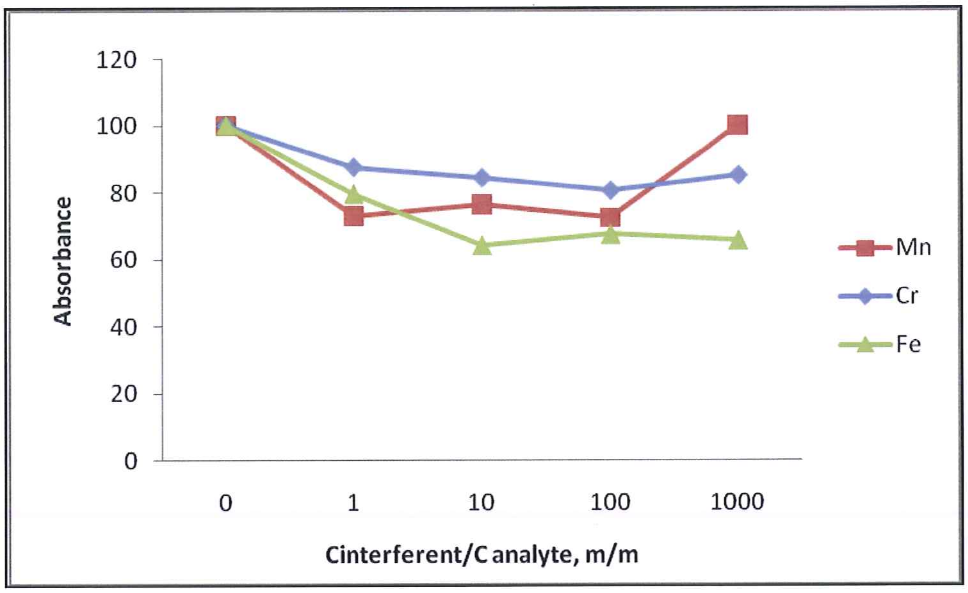


Figure 3.30 Interference effects of Mn, Cr, Fe on 0.50 ng/mL Cd signal in Zr-coated-SQT-AT-FAAS.

In Figure 3.31, the effects of two other transition metals (Ni and Co) on Cd signal are shown. As indicated in the figure clearly, Co showed an enhancement effect on Cd signals, especially at 10 fold Cd concentration. It increased Cd signal by 10%. On the other hand, Ni showed an enhancement effect on Cd signal, however at 100 fold, it decreases the signal by 19% and then when the concentration of interference is 1000 fold, it increases the signal by 14%. After trapping of 0.5 mg/L Ni, tube had to be recoated, as the normal analyte signal shape became broader and deformed; further analyte trapping was not possible.

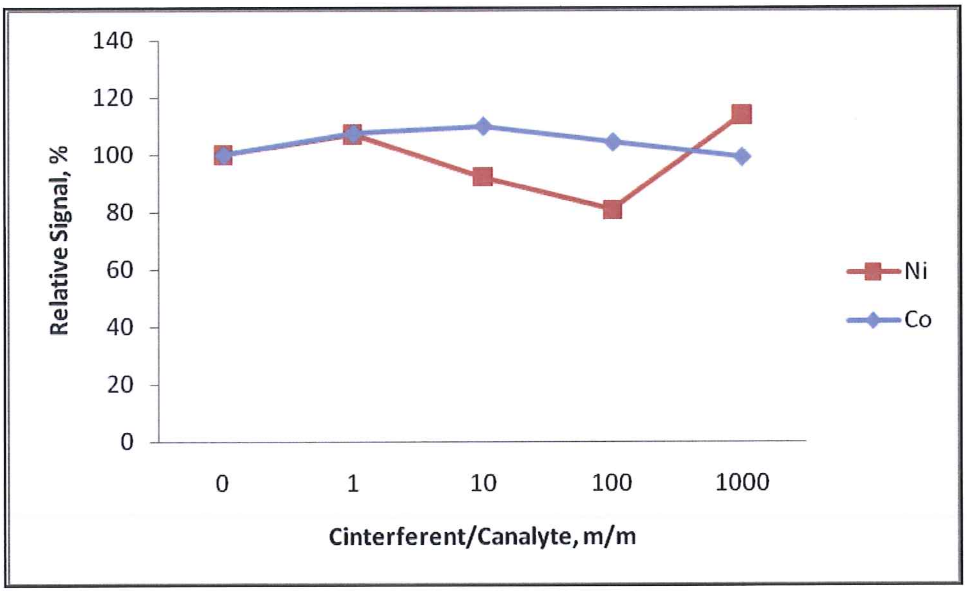


Figure 3.31 Interference effects of Ni, Co on 0.50 ng/mL Cd signal in Zr-coated-SQT-AT-FAAS.

Figure 3.32 shows some hydride forming elements such as Zn and Sn. As can be clearly seen, Zn and Sn have shown suppression effect on Cd signals. Especially, one fold and ten fold concentrations suppressed the signals by approximately 10%. However, as the concentration of interferent increases, signals of Cd also increase. While these two elements have shown similar properties, Al has shown a very different behaviour. It enhances Cd signals as the concentration of interferent increases. For example, at 1000 fold of Al concentration, signals of Cd has increased by 25%.

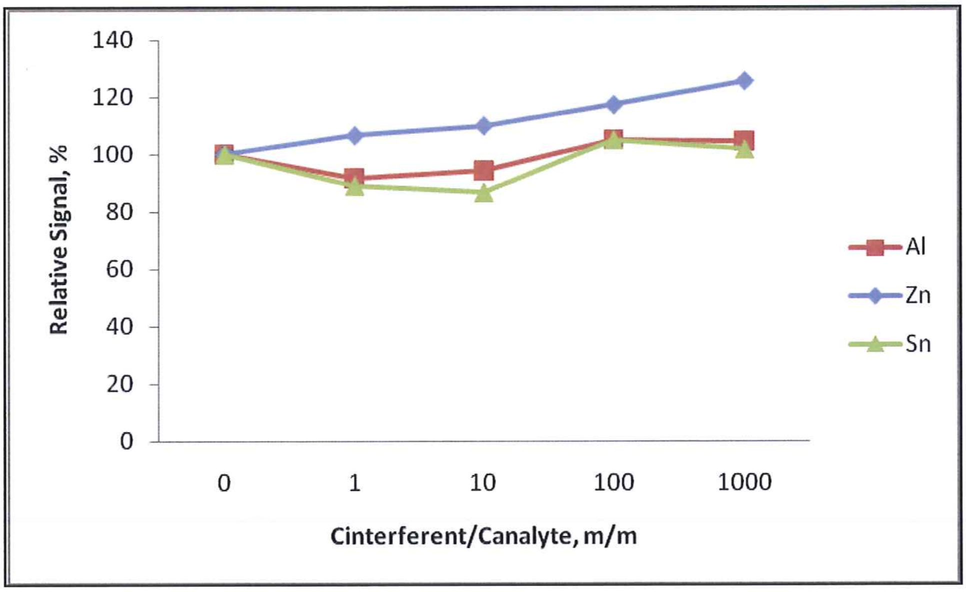
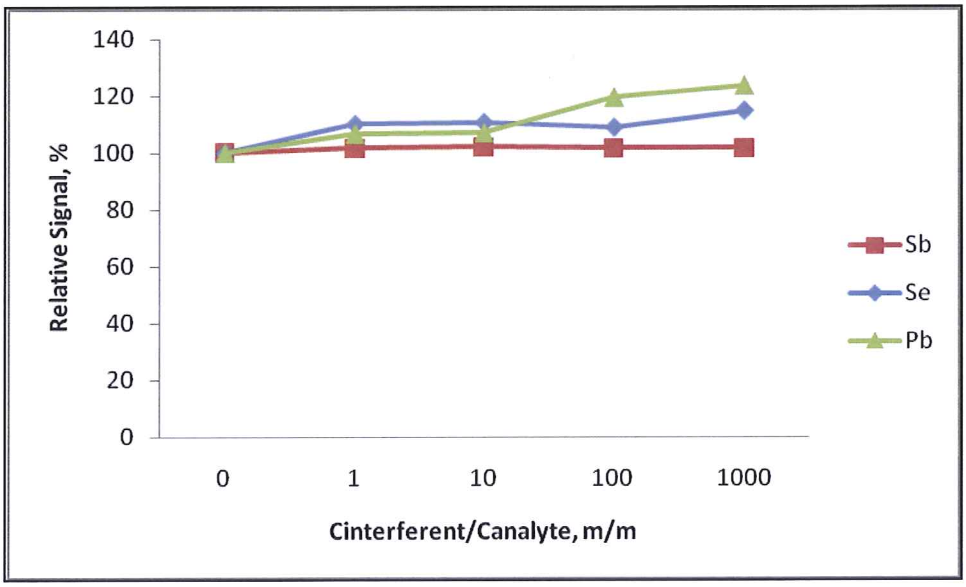


Figure 3.32 Interference effects of Al, Zn and Sn on 0.50 ng/mL Cd signal in Zr-coated-SQT-AT-FAAS.

The effects of hydride forming elements such as Sb, Se, Pb are shown in Figure 3.33. Sb does not affect Cd signals whereas Pb and Se interferents enhanced Cd signals. Especially, 100 and 1000 fold of Sb and Se concentrations increased absorbances of Cd approximately by 20%. The detailed results are given in Table 3.14.



Lastly, Figure 3.34 shows the behavior of Cd element in the presence of some ionic species, such as SO_4^{2-}, PO_4^{3-}, F^-. These anions have been prepared from their Na salts; which were Na_2SO_4, Na_3PO_4 and NaF, respectively. Although Na has 10% suppression effect on Cd signals, there was not a significant change in Cd signal in the presence of these anions, as shown in the Figure 3.34. However, as detailed, in the presence of SO_4^{2-} anions, Cd signal were decreased by approximately 7%. It can be concluded that there was no interference effect of SO_4^{2-} on Cd. However, the presence of PO_4^{3-} and F^- ions increase Cd signals. For example, in the presence of one fold of F^- ions, Cd increases by 6%. Then it shows similar values with increasing concentrations, as can be seen in Figure 3.34. This result can also interpreted as there was an enhancing property of these ions much more if they were not prepared with Na. The interference effect of NO_3^- on Cd signal was not investigated. The reason is that all standards were prepared in 1.0 M HNO_3 solution. As the blank solution was investigated throughout the study, there was no need to study its effect.

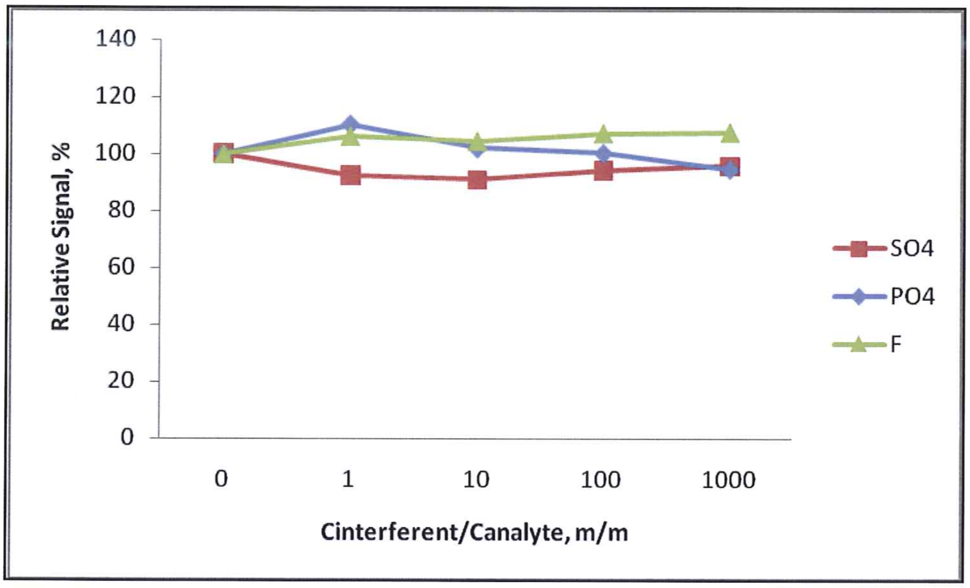


Figure 3.34 Interference effects of SO_4^{2-}, F^-, PO_4^{3-} on 0.5 ng/mL of Cd signal in Zr-coated-SQT-AT-FAAS.

The general summary of interference studies of Zr-coated-SQT-AT-FAAS are given in Table 3.14. According to these studies, the most interfering elements were Fe, Zn and Mn. When studying with real samples, one should be careful about the interferences.

Table 3.15 Summary for Interference Studies of Zr-coated-SQT-AT-FAAS.

Elements	**Folds of Interferent**	**Zr-coated-SQT-AT-FAAS**
		Signal Relative to 100
Na (Sodium)	1	89
	10	86
	100	87
	1000	85
Mg (Magnesium)	1	88
	10	87
	100	85
	1000	82
K (Potassium)	1	82
	10	88
	100	85
	1000	86
Ca (Calcium)	1	89
	10	86
	100	86
	1000	100
Mn (Manganese)	1	73
	10	76
	100	72
	1000	100
Cr (Chromium)	1	88
	10	85
	100	81
	1000	85
Fe (Iron)	1	80
	10	64
	100	68
	1000	66
Ni (Nickel)	1	107
	10	92
	100	81
	1000	114
Co (Cobalt)	1	108
	10	110
	100	104
	1000	99
Al (Aluminium)	1	92
	10	94
	100	105
	1000	104
Zn (Zinc)	1	107
	10	110
	100	117
	1000	125

Sn (Tin)	1	89
	10	86
	100	105
	1000	102
Sb (Antimony)	1	102
	10	102
	100	102
	1000	102
Se (Selenium)	1	110
	10	111
	100	109
	1000	115
Pb (Lead)	1	107
	10	107
	100	119
	1000	124
$SO4^{2-}$ (Sulphate)	1	92
	10	91
	100	94
	1000	96
$PO4^{3-}$ (Phosphate)	1	111
	10	102
	100	100
	1000	95
F^- (Fluoride)	1	106
	10	105
	100	107
	1000	107

CHAPTER 4

CONCLUSIONS

The purpose of this study was development of a sensitive analytical method for the determination of cadmium. By developing different methods in Flame Atomic Absorption Spectrometry (FAAS), the aim was achieved successfully.

This study was mainly based on the use of SQT. It was used mainly for two types of study. Firstly, SQT-FAAS was used only for increasing the residence time of analyte atoms in the light path and providing stable flame conditions, so a slight increase in sensitivity was achieved. LOD and C_0 values of this method was found as 3.9 and 22 ng/mL, respectively and this was a 2.9 times enhancement with respect to conventional FAAS. Secondly, in coated and uncoated SQT-AT-FAAS, SQT was used as a trapping device, which uses other improvement techniques such as flame alteration, atom trapping with optimum collection period, organic solvent aspiration to enhance sensitivity. Some different coating materials were investigated on quartz surface; and zirconium was the best material having the maximum absorbance values. On the other hand, Pd also gave similar results with zirconium but it was not preferred due to its high cost. After optimizing all the parameters, it was seen that Zr Coated SQT gave sensitive results, because LOD and C_0 were found 0.008 ng/mL and 0.019 ng/mL, respectively. Moreover, there was a sensitivity improvement of 3368 times with respect to conventional FAAS. This enhancement was performed with the use of 24 mL of analyte volume, so better analyte collection takes place for a constant sample volume. As compared to other analytical techniques, it was one of the most sensitive techniques among others.

In trap techniques it was also seen that the enhancement has occurred at lower sample aspiration rates. Because nebulization efficiency increases at lower sample aspiration rates.

Interference effects of some alkali, transition and hydride forming elements in addition to some anions were investigated for Zr-coated-SQT-AT-FAAS. It was understood in this interference study that hydride forming elements so not interfere to Cd very much. They interfere with the remaining 1A, 2A and 3A metals, especially when they are 1000 fold of Cd.

For the accuracy check, the analysis of standard reference material was performed by using SCP SCIENCE EnviroMAT Low (EU-L 2) and results for Cd was to be in good agreement with the certified value for Zr-coated-SQT-AT-FAAS.

To sum up, for trace and ultra-trace analyses of Cd, atom trapping techniques are advantageous. SQT-AT-FAAS and Zr-coated-SQT-AT-FAAS were very sensitive in terms of having LOD values at the levels of ng/L like ICP-MS. Moreover, these developed methods were simple, economical and applicable to all FAAS instruments.

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