OXIDATION STATE RELATED EVALUATION OF TELLURIUM DETERMINATION BY FLAME AAS AND USE OF SLOTTED SILICA TRAP

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ABSTRACT

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Tellurium is a toxic element and in bioligical, environmental and geological samples Te concentration is at trace and ultratrace level; therefore its determination is important. In this study a new determination technique is offered. A slotted silica tube trap on the flame is used. Analyte is preconcentrated on the silica surface by aspirating sample for a fixed time. Then, for reatomization a 50 μL volume of organic solvent (methylisobutylketone) that changes the condition of the flame is aspirated. By silica slotted tube trapping technique, a sensitivity improvement of 71 times as compared to conventional flame AAS is observed using a collection period of 60 s; determination at ng/mL concentration level can be possible. Low cost, simple instrumentation, ease of application, short analysis time and improved sensitivity that is close to sensitivity of ETAAS are advantages of slotted silica tube trapping technique.

When Te (VI) and Te (IV) solutions are prepared by deionized water, they give different absorbances both for flame AAS and slotted silica tube trapping techniques; Te (IV) has a higher signal for both techniques. However, if these solutions are prepared in 1.0 % (v/v) HNO_3, they have equal sensitivity for both flame AAS and silica trap AAS. This behavior allows one to determine total Te without any error.

An extensive interference study was done for Organic Solvent Atomization Technique. Solid phase and / or gas phase interferences of the ions Na^+, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, and NO_3^- on Te were investigated.

Keywords: Atom trap, Slotted Silica Tube, Tellurium, Organic Solvent Atomization, Solid phase Interference, Gas phase Interference

ÖZ

ALEVLİ AAS İLE TELLÜR TAYİNİNDE DEĞERLİKLE İLGİLİ DEĞERLENDİRME VE YARIKLI SİLİKA TUZAĞININ KULLANIMI

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Tellür zehirli bir eser elementtir ve biyolojik, çevre ve jeolojik örneklerde tellür erşimi eser ve ultra eser düzeyindedir; bu yüzden tayini için duyarlı yöntemlerin geliştirilmesi önemlidir. Bu çalışmada Te için yeni bir tayin tekniği önerilmektedir. Alev üzerine yerleştirilmiş çift yarıklı bir silika tübün iç yüzeyinde örneğin aleve püskürtülmesiyle toplanan analit; daha sonra 50 µL gibi çok az miktarda metilizobütilketon kullanımıyla alev yapısında oluşan değişiklik nedeniyle atomlaşmaktadır. Yarıklı silika tüplü tuzak yöntemiyle 60 s toplama ile alevli AAS yöntemine göre duyarlılıkta 71 kat iyileştirme gözlenmiştir; ng/mL düzeyinde tayin mümkün olmaktadır. Düşük gider, basit bir aygıt, kolay uygulama, kısa analiz süresi ve ETAAS'ye yaklaşan artırılmış duyarlılık bu önerilen tekniğin en önemli avantajlarıdır.

Ayrıca suda hazırlanan Te (IV) ve Te (VI) çözeltileri hem alevli AAS yönteminde hem de yarıklı silika tüp tuzak yönteminde farklı absorbanslar vermektedirler; Te (IV) için sinyal daha yüksektir. Te çözeltileri % 1.0 (v/v) HNO_3 içinde hazırlanırsa, her iki yöntemde de Te (IV) ve Te (VI)'nın verdiği absorbanslar birbirine eşit olmaktadır. Bu yöntemlerle toplam Te tayini hatasız olarak yapılabilmektedir.

Son olarak Organik Çözücü Atomlaştırması tekniği için kapsamlı bir girişim çalışması yapıldı. Na^+, K^+, Ca^{2+}, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, ve NO_3^- iyonlarının Te ile katı fazda ve / veya gaz fazında yaptıkları girişim incelendi.

Anahtar kelimeler: Atom Tuzağı, Yarıklı Silika Tüp, Teluryum, Organik Çözücüyle Atomlaştırma, Katı Faz Girişimi, Gaz Fazı Girişimi

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INTRODUCTION

Tellurium was discovered in 1782, by the Hungarian scientist Franz Müller von Reichenstein after several studies of a bluish gold ore, extracted in a mine in Transilvania. Müller accomplished a careful chemical analysis of this ore, and reported residues of a metal very similar to antimony. However, Müller was not able to identify this metal. The metal was isolated, in 1798, by Klaproth who was interested in the work of Müller, as he decided to check the existence of a new element. This scientist suggested its actual name, that derives of the Latin "tellus", that means earth. Tellurium ranks about 78th in natural abundance. The earth's crust contains 10^{-7} % or 0.001 ppm of tellurium. Tellurium has eight stable and approximately twenty man-made unstable isotopes. It is located in the group VI-A of the periodic table between selenium and polonium, which it resembles in some physical and chemical properties, though selenium is a metalloid and polonium is a metal. Te is found in period V of the periodic table between antimony and iodine. Antimony is a metal and iodine is a metalloid (1).

1.1 . Chemistry of Tellurium and Occurrence in Nature

Tellurium is a not very abundant element, however it is more often segregated in specific mineral deposits. It can be found associated to the gold, copper or sulfur ores. The element occurs in small amounts in minerals like the altaite (PbTe), the calaverite ($AuTe_2$), the coloradoite (HgTe), the ricardite

(Cu_4Te_3), the petzite (Ag_3AuTe_2), the silvanite ($(Ag,Au)Te_2$) and the tetradimite (Bi_2Te_2S). Tellurium can also be found in the native state and in the dioxide form (TeO_2). The main tellurium deposits are located in Canada, in the USA (Montana, Utah and Arizona) and in Peru.

Tellurium is most often recovered from the anode slimes of copper and from the mineral, nagyagite. These materials are usually decomposed by boiling with a mixture of concentrated hydrochloric acid and nitric acid. Tellurium is precipitated by help of sulphur dioxide. If selenium and tellurium are combined in a mixture, boiling the mixture with sulphuric acid is enough to separate these elements from each other. In these processes, tellurium is precipitated as TeO_2 and the selenium is changed to selenious acid, H_2SeO_3 that remains in the solution (1).

1.1.1. Metallic Tellurium

Crystalline tellurium has a silvery-white appearance, and exhibits a metallic luster when pure. It is brittle and easily pulverized. When tellurium is deposited from solution by the reduction of tellurous acid by means of sulphorous acid, it is obtained as a brown powder or 'amorphous' tellurium.

Metallic tellurium burns when it is heated in air, and it combines energetically with the halogens and many metals. The reactions are;

$Te\ (s) + 2O_2\ (g) \rightarrow TeO_2\ (s)$ (Tellurium burns in air to form the dioxide tellurium (IV) oxide, TeO_2)

$Te_8\ (s) + 24F_2\ (g) \rightarrow 8TeF_6\ (l)$ [orange]

(Tellurium reacts with fluorine, F_2, and burns to form the hexafluoride, tellurium (VI) fluoride.)

Although it can be reduced to its hydride by a reductant such as sodium borohydride, it does not combine directly with hydrogen. It does not dissolve in nonoxidizing acids, but it is soluble in concentrated sulphuric acids, nitric acid and caustic alkalis (1).

1.1.2. The Compounds of Tellurium

In compounds of tellurium, the most common oxidation state of tellurium are: -2, +2, +4, and +4. A +2 oxide of tellurium, TeO, exists and forms in cold hydrochloric acid. However, when it is heated, it decomposes into free tellurium and a +4 complex chloride of tellurium, $TeCl_4$. In his book, Latimer (2) reports the following oxidation – reduction potentials for tellurium (Volt) for tellurium in acidic and basic solutions;

In Acidic Solution:

$$H_2Te \xrightarrow{0.72} Te \xrightarrow{-0.529} TeO_2 \xrightarrow{-1.02} H_6TeO_6$$

In Basic Solution:

$$Te^{-2} \xrightarrow{1.14} Te \xrightarrow{-0.57} TeO_3^{-2} \xrightarrow{>-0.4} TeO_4^{-2}$$

Tellurium reacts with other elements similar to oxygen. But, it does not combine directly with selenium and / or sulphur but forms crystals with both of them. The most stable compounds of tellurium are the oxides, the chlorides and the fluorides of tellurium. Its acids and salts that are derived from dioxides are also stable.

Tellurium is electronegatively bivalent towards hydrogen and the metals. In its compound formation with the most elements tellurium is in +4 oxidation state.

However, in its fluorine compounds, tellurium is in +6 oxidation state. The most important compounds that are formed by Te include oxides, oxyacids, oxyhalides, halide compounds and alkyls (3)

I.2. Applications of Tellurium in Industry

Tellurium has become widely used since World War II. Its metallurgical additive property and its semiconducting property have been of considerable interest. Particular attention has been focused on tellurium as a free – machining agent in steels and as a constituent in compounds and alloys for thermoelectric power generation and refrigeration. In addition, a continuing interest has been shown in the applications of tellurium in such diverse areas as rubber and plastics, petrochemicals, solid lubricants, pharmaceuticals, metal finishes, explosives, glasses and semiconductor devices (4).

The main part of tellurium production has been used in semiconductor and instrument manufacture and in chemical and metallurgical industries. An electric lamp with liquid Te emits light with a continuous spectrum approaching that of solar. As an alloy component, it is used in selenium photoreceptors for copiers and printers. The cadmium-mercury-telluride compound is used as the major photosensitive material employed in infrared detector systems. It is used as an alloy component in bismuth telluride cooling devices.

Tellurium is used in rubber manufacture to accelerate the vulcanization and the increase the strength. It is used in manufacture of pipe and protective sheathing for electrical cables. Tellurium improves machinability without materially decreasing conductivity. If it is added to lead, Te improves resistance to vibration and fatigue. Addition of the small quantities of tellurium improves the grain uniformity and enhances the hardness, toughness and corrosion resistance of metals.

Tellurium improves the properties of carbon and alloy steels. When added in a small quantity, it increases the depth of chill in steel. Tellurium is a carbide stabilizer in cast iron and its small quantity accelerates graphitisation. Addition of tellurium decreases somewhat the supercooling in eutectic hardening. Addition of 0.003 % tellurium increases the tensile strength and the hardness. Its addition impairs the fluidity. The limiting tellurium concentration is 0.05 percent. Addition of smaller than 0.015 percent of tellurium has little effect on the structure. A 0.02 percent tellurium concentration provides eutectic structure, and 0.05 percent perlite – cementite structure.

Tellurium oxides, tellurites and tellurates are used in glass manufacture. Sodium tellurite and potassium tellurite have vitreous property. Colorless transparent glasses can be prepared from fused tetratellurites of alkali – metals and barium. Tellurite glasses have higher indeces of refraction than the corresponding silicate, borate, phosphate and germenate glasses. A glass of formula $BaO.5TeO_2$ has a linear coefficient of thermal expansion and a deformation temperature of 325 °C, differing from the constants of ordinary glasses such as and 700 °C. The index of refraction of prisms made by such a glass is 2.08 for long wavelengths (5780 A°). The dielectric permeability at 50 Hz is about 25. In infrared radiation, tellurium glasses have low absorption at low wavelengths down to 5.5 µm.

Some tellurium isotopes are used in medicine in the treatment of thyroid gland diseases. The largest outlets with prospects of further increase in consumption of tellurium compounds are the growing semiconductor thermoelectric cells, photoreceivers, hall data units, filters and other devices in automation, radio electronics and remote control (1).

1.3. Toxicity of Tellurium and Its Compounds

Relatively little information has been published about the toxicity of tellurium and its derivatives. In view of the fact that there are a lot of misconceptions regarding the toxicity of tellurium and its compounds, it is appropriate to present data on this subject that will serve to guide those working with these metals. The effect of tellurium and its compounds on the organism is similar to the effect of the inorganic compounds of selenium and arsenic.

Tellurium has not been found to be a very dangerous element in industrial use although it can cause a pronounced garlic odor of the breath lasting for a considerable time after exposure. Garlic smell of $(CH_3)_2Te$ is detected on the workers with exposure to Te dust, TeO_2 fumes and gaseous TeH_2 (1).

The signs of poisoning with tellurium and its derivatives are headache, increased respiratory rate and pulse rate, premature fatigue and vertigo. Neusea, garlic odor of breath and sweat, vomiting, renal colic, cyanosis and hematurea are observed in poisoning with sodium tellurite.

Garlic odor is one of the unfailing signs of the introduction of tellurium into an organism. In human investigations the smell appeared in 75 minutes after ingestion of 0.5 g TeO_2 and persisted for 30 hours with an ingestion of 15 mg, the odor could be detected for 8 months. When garlic odor appears, the necessary measures should be taken to inspect the storage of materials and the cleanliness of working areas.

Tellurium dioxide is toxic. When it is introduced into an organism, it has a harmful effect on growth and the general condition of animals. Hydrogen telluride is the most toxic tellurium derivative. The gaseous hydrogen telluride provokes intravascular hemolysis and respiratory and cardiac failure, as do arsine and selenium hydride.

In one bizarre accident, three human subjects received sodium tellurite instead of sodium iodide directly into the ureter. In two of the cases, the dosage was about 2 grams. Garlic breath was noticed after a short time. Vomiting, renal pain at the site of injection, loss of consciousness, irregular breathing, cyanosis and finally death occurred. These two patients died within 6 hours, but the other, who was given a lower dose, survived (5).

The minimum fatal doses (doses fatal to at least 75 % of young rats within after 48 hours intraperitoneal injection) are shown on Table 1.1 (5). These results indicate that tellurite is more toxic than selenite or arsenite, both of which are well recognized for their harmful properties. Also, tellurite has an approximately ten fold greater effect than does tellurate.

Table 1.1. Minimum fatal doses associated with Te, Se and As compounds

Compound	**Fatal Dose (mg element / body weight)**
Sodium tellurite, Na_2TeO_3	2.25 – 2.50
Sodium tellurate, Na_2TeO_4	20.0 – 30
Sodium selenite, Na_2SeO_3	3.25 – 3.50
Sodium selenate, Na_2SeO_4	5.25 – 5.75
Sodium arsenite, Na_2HAsO_3	4.25 – 4.75
Sodium arsenate, Na_2HAsO_4	14.0 – 18.0

Together with hydrogen telluride (TeH_2) and tellurium hexaflouride, tellurium oxide, tellurites are among the more toxic tellurium compounds. In view of the lack of effective therapy in combating tellurium intoxication and its socially offensive nature, adequate precautions should be taken when handling tellurium bearing materials through the use of protective clothing and suitable ventilation to prevent the absorption of tellurium into the body.

1.4. Tellurium Determination Methods

The emission of inorganic tellurium compound or this element in the environment may create serious problems because of the toxicity of these compounds. Therefore, a lot of studies have been made to detect tellurium in varying sensitivities.

Tellurium is still assumed only as a rare, toxic and nonessential element (6, 7) therefore only a few articles on the determination of tellurium in the environment have been published. The reasons for lack of information may be the instability of its organo compounds towards air and light, and rarity of tellurium in nature, with consequent necessity for high sensitivity and sophistication in analytical procedures for its determination (8).

The main problem in the study of tellurium appears to be the analytical difficulty stemming from the poor sensitivities of most of the analytical methods (9).

In electrothermal atomic absorption spectrometry (ETAAS) technique, liquid sample is directly injected into graphite furnace for total element determination. The use of background correction systems is required. Use of chemical modifiers is mandatory to reduce volatilization losses of tellurium and for better control of matrix interferences. (eg. sulphates, chlorides, phosphates and iron). Limit of detection (LOD) for tellurium by using this technique is 0.5 – 2 ng/mL or 10 – 30 pg (10 - 12).

In hydride generation atomic absorption spectrometry (HGAAS) technique, hydride generation with on–line atomization is made mostly with silica tube atomizer. For total tellurium determination LOD is 0.05 – 0.1 ng/mL. Magnitude of liquid – phase interferences depend on hydride generation technique (batch, continuous flow, flow injection). The other hydride forming elements may generate serious interferences in the silica tube atomizer. Modification of silica tube surfaces suprasses analytical performance (13, 14).

In flow injection (FI)–HG–ETAAS technique, hydride is generated by flow injection technique and followed by in situ trapping in a graphite furnace or in a carbon rod atomizer. LOD for tellurium determination is 2- 40 pg or in low ng/mL range. Another alternative is inductively coupled plasma atomic emission spectrometry (ICP–AES) with various HG techniques. LOD for tellurium determination with HG–ICP–AES is 1 ng/mL (15, 16, 17).

Atomic fluorescence spectrometry which contains hydride generation coupled with a non – dispersive apparatus (HG–ND–AFS) is another technique for determination of tellurium. Miniature flame is used mostly for atomizer. By using this technique, atomization interferences are controlled very well. LOD for tellurium is in the range of 17 – 100 pg and a few ng/mL depending on HG technique that is applied (18). Also by using graphite furnace atomization coupled with laser excited atomic fluorescence spectrometry (LEAFS) technique, better LOD result for tellurium, which is 0.02 pg can be obtained.

In inductively coupled plasma mass spectrometry technique, detection limits for tellurium determination depend on solution nebulization. Matrix interferences are important for tellurium (19). Various HG techniques, which are coupled on – line ICP MS are applied for tellurium determination. LOD is 0.5 pg for tellurium (20). In addition, for simultaneous qualitative and semi quantitative determination of several hydride forming elements and their volatile compounds (eg. Me_2Te) HG – GC – ICP – MS technique is applied (21).

For tellurium determination gas chromatography can also be applied. Gas chromatography with flame ionization technique (GC-FID) is used for determination of volatile alkyl tellurides (eg. MeTeCN) and in the direct determination of Te-methionine. Although LOD of this technique for tellurium determination is good (5 pg), selectivity is poor (22). In gas chromatography with flame photometric detection technique (GC-FPD), neither selectivity nor detection limit is good for tellurium determination (23). In gas chromatography with fluorine-induced chemiluminescence detection (GC-FCD) technique, simultaneous detection of sulphur and tellurium alkyl compounds can be possible. LOD for tellurium is 6 – 22 pg (24).

Several electrochemical methods have been applied for tellurium determination. Various differential pulse polagraphic such as differential pulse polagraphy (DPP), voltammetric such as differential pulse voltammetry (DPV) and stripping voltammetric techniques such as cathodic stripping voltammetry (CSV), and differential pulse cathodic stripping voltammetry (DPCSV) can be used for determination of electroactive species Te (IV). There are serious interferences because of organic substances, surface-active substances and concomitant elements. LOD of DPP and DPV techniques is 20 ng/mL and of CVS and DPCSV is 100 pg/mL for Te (IV) (25).

In flame atomic absorption technique, it has recently been reported that FAAS sensitivity depends on oxidation state of Tellurium [Te (IV); Te (VI)] (26). Te (IV) species is more sensitive than Te (VI) species at FAAS.

1.5. Flame Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) is based on the measurement of the absorption of optical radiation by atoms in gas phase. The analytical process involves the conversion of molecules or ions into free atoms and the measurement of absorption of radiation by these free atoms (27). Australian scientist Walsh (28) gave major and important contributions in converting the principle of atomic absorption into an analytical technique by introducing hollow cathode light sources, flame atomizers, photomultipliers and a modulated system. The system that was demonstrated by him was applied as a quantitative analytical tool. Atomic absorption with flame atomizers was rapidly distributed as a simple technique, which gave high sensitivity, accuracy and precision (29).

In flame atomic absorption spectrometry, the sample solution is introduced as an aerosol into the flame, by nebulizer where the analyte ions are changed into free atoms. Only a little of the nebulized analyte solution reaches the burner therefore, the system wastes the sample. The residence time of free analyte atoms in the portion of the flame where they absorb radiation from the external source is about 0.1 ms. FAAS is one of the two techniques used in this thesis.

Various methods have been described to improve the sensitivity of conventional flame AAS. Atom trapping technique using silica tube is one of them.

1.6. Atom Traps for FAAS

Atom traps stemmed from the desire of introducing a higher sensitivity for flame spectrometry technique. Improved sensitivity, easy application, not requiring expensive equipment and short analysis time are the advantages of this technique. The principle of the traps is to collect the analyte atoms within the body of the flame. This type of preconcentration in the flame achieved prevents the usage of additional chemicals that may cause contamination. It is possible to analyze samples without time consuming preconcentrating procedures and potentially contaminating handling procedures. Various traps have been developed.

1.6.1. Slotted Silica Tube

Watling designed the use of a slotted silica tube to improve sensitivity of FAAS (30). The tube was placed on conventional burner head. This design improved the sensitivity 2 – 5 fold for volatile elements like Pb, Cd, Bi, Co, Mn, Ag, As, Sb, Cu, and Se. The reasons of improved sensitivity using a slotted silica tube are the reduction of flame speed, a longer optical path length and the increasing mean lifetime of free atoms in this optical path. The application examples of this technique are the determination of Pb in whole blood (31), Cu and Zn in serum and urine (32) and Bi in pharmaceutical formulations (33).

1.6.2. Water-cooled Silica Trap

Lau et al. (34) used a silica tube whose outer diameter was 4mm and inner diameter was 3 mm, in an air – acetylene flame that was cooled by the continuous flow of water. The flame was centered below the trap and sample solution was aspirated for a fixed time interval for trapping the analyte. In atomization of the collected analyte, analyte aspiration was stopped; water was flushed from the trap by air before it could boil. With the water supply cut off the flame brought the trap to red heat in about 6 s, thereby releasing the trapped material.

Water-cooled atom trap provides 8-40 fold sensitivity increase for volatile elements (35). Cd and Pb in soil (36) and in potable water (37), Pb in alcoholic drinks (38), trace elements in seawater and bovine liver (39) are some examples of applications of this technique.

1.6.3. Water-Cooled Silica Trap Combined with Slotted Silica Tube

A turkish scientist N. Ertaş (40) designed water-cooled trapping system with a slotted silica tube. He improved the sensitivity of Pb and Cd further by using a slotted silica tube and double slotted silica tube through which the light beam of hollow cathode lamp was passed. The slotted silica tubes were put on the water-cooled atom trap. By using this technique 50 – 200 times sensitivity enhancement was obtained and this was attributed to the increased residence time of the neutral atoms in the optical path of the spectrometer.

1.6.4. Slotted Silica Tube Trap

Huang et al. (41) introduced the usage of slotted silica tube trap. When it is compared to the other traps, slotted silica tube trap is simpler and easier. In this technique, trap provides an increase both in the residence time of the atoms in the optical path and as a preconcentrator. Sample solution was aspirated for a fixed collection time. Then flame conditions are altered for atomizing preconcentrated atoms. This technique is very convenient for determination of volatile elements. Sensitivity of slotted silica trap technique is 70 – 270 times more than that of conventional flame AAS.

1.7. Atomization Techniques

Two techniques, namely Flame Alteration and Organic Solvent Atomization are used for atomizing the trapped species.

1.7.1. Flame Alteration Technique

Ertaş et al. (40) described and developed this technique. The purpose is to use different flame conditions for the collection and atomization cycles. While the analyte is being collected, some part of the fuel is sent to waste. After a fixed time aspiration is stopped and the all fuel is sent to the flame. Because of this, fuel becomes stoichiometric or fuel rich. The blue zone of the fuel reaches to lower slot of slotted silica tube and atomization takes place.

1.7.2. Organic Solvent Atomization Technique

Another turkish scientist S. Kumser (42) showed the effect of usage of organic solvents such as methylisobuthyl ketone, methyl ketone, acetonitrile and n – hexane to the atomization. After the collection procedure, a small amount of (10 – 50 μL) organic solvent is aspirated to the flame for atomization. The signal which is the same as obtained for flame alteration technique is observed. It is understood that the atomization is effected by the changed properties of the flame caused by the introduction of the organic solvent. This technique is simple and adaptable for automation.

1.8. Interferences in Flame AAS

Interferences in FAAS contain three types. They are spectral, physical and chemical interferences.

1.8.1 Spectral Interferences

Lajunen et al. (43) indicated that the selective nature of the absorption process in AAS and the use of modulated light sources result in somewhat greater freedom from spectral interference from concomitant elements. Absorption spectral profile of the analyte with one or more such profiles because of the concomitants in the sample an overlap within the monitored wavelength range of the emission, luminescence, scattering cause a spectral interference. Atomic line interferences are not usually observed in atomic absorption spectroscopy with narrow line sources because the source width effectively determines the spectral resolution. However, line sources in atomic absorption emit more than just the desired analyte line. These lines may come from emission of metallic impurities and the filler gas. Such lines cause spectral interferences if they absorb and not separated from the analyte line by the wavelength selection device. Multielement line sources are employed in atomic absorption and can increase the problem of spectral interferences. Continuum source atomic absorption depends on the spectral resolution of wavelength selection device for selectivity (44). Because of usage of modulation and ac detection to separate it, background emission is not normally a problem. However, absorption by molecular species and scattering of the source radiation by nonvolatile salt particles or oxides can occur and give rise to a blank interference (45).

1.8.2. Physical Interferences

Differing physical properties of the sample and reference material, such as varying viscosity, surface tension, and density of the solution cause a physical interference. The physical properties effect the nebulization of the sample and the transport of the aerosol into the flame. Therefore, these interferences are also called transport interferences. It may cause signal enhancement as well as depression. Transport interferences occur more or less predominantly in the flame owing to pneumatic nebulizer and premix burner (46).

1.8.3. Chemical Interferences

Any reaction between concomitant and analyte in the sample that occurs in the solid and vapor phase to effect the population of free analyte atoms in the atom cell is called a chemical interferences. Chemical interferences occur in either vapor or solid (condensed) phase.

1.8.3.1. Chemical Interferences in Solid Phase

Non-specific interferences in the solid phase that means no compounds form between analyte and concomitant material in the flame in the solid phase may occur for any element. The occlusion of analyte within solid particles of salts of the matrix element in the flame can be accepted as an example of non-specific solid phase interference. In contrast, specific solid phase interferences are reason of reaction of the analyte element or one of its compounds with concomitant material to form a different compound with different thermocouple properties.

1.8.3.2. Chemical Interferences in Vapor Phase

Suppression or enhancement of the absorption signal may be caused by the effect of concomitant elements on the dissociation and ionization equilibrium which control the concentration of atoms of the element in the flame after vaporization of dissolved solid in a sample (47).

1.9. Atomization Mechanism

It is claimed that the use of slotted silica tube increases the sensitivity due to the increased residence time of analyte atoms in the light path of the hollow cathode lamp. The elements that show sensitivity improvements are the volatile ones that decompose thermally in the primary reaction zone of an air – acetylene flame. The alkali metals reduce the tube lifetime because devitrification of silica tube occurs. The metals other than volatile ones and the alkali metals show no sensitivity improvement using the slotted silica tube.

In the water-cooled silica trap, the analyte atoms are collected on the surface of the trap in the collection cycle. If the heating up the tube surface is done by replacing the water with air, trapped analyte will be revolatilized. Therefore, the heat causes the atomization of analyte. Lau et al. (34) indicated that during the collection time some of the analyte was swept away from the trap surface. Therefore, flame sputtering is needed more than thermal volatilization to remove atom from the silica surface during the trapping cycle.

Ertaş (40) used different flame conditions for collection and atomization cycles while the water was circulating continuously. The surface of the collector tube should not be changing dramatically in the atomization cycle. It is understood that sputtering and scouring action of the flames gases were playing an important role in this technique as well as heating effect.

Organic solvent aspiration to effect atomization was used and nature of atomization was investigated by Kumser (42); it was suggested that a chemical effect could be predominant factor rather than a temperature effect in atomization. Because, organic solvent aspiration was changing the chemistry of the flame by changing the combustion characteristics of the flame forming free radicals. The presence of a conventional thermal effect was searched by measuring the temperature of the flamed during organic solvent aspiration. After measuring the temperature of flame, it was seen that acetonitrile caused the highest increase in temperature. Although acetonitrile was expected to give the highest atomization signal, it gave smallest signals compared to the other solvents. In addition, n-hexane gave higher atomization signals in spite of its cooling effect. The reason of atomization by organic solvent aspiration for trapped Bi, Au and Mn species could be explained as three major effects:

i) Contribution of the slight increase in temperature;

ii) Reduction of the oxide species, trapped at the surface of the collector tube by organic solvent aspiration, which supplies the critical C/O ratio in the flame as well as resulting an easier atomization;

iii) Providing the most suitable chemical environment to the flame, together with the suitable temperature which could be a kind of unknown catalytic effect of free radicals in the flame or probably, the flame gases removed the analyte species from the surface of the silica tube.

The nature of Au species collected on a silica tube was with the use of X–ray photoelectron spectroscopy (XPS) by Süzer et al. (48). An XPS spectrum of gold deposited on atom trapping silica tubes reveals a Au peak with a binding energy of 84.8±0.2 eV, which falls in the middle of binding energies corresponding to zero oxidation state of Au at 84.0 eV and that of monovalent Au (I) at 85.2 eV. By comparison with other compounds of gold on silica it was understood that gold is trapped on atom trapping silica surface as zero oxidation state of Au (0) with a 0.8 eV matrix shift. In Süzer's another study (49), the chemical state of Bi and Mn collected on water – cooled silica were investigated with XPS both after deposition and atomization stages. Bi was trapped as Bi (III) but additional zero oxidation state of Bi was also observed after atomization stage. Mn was in the oxidized state, as Mn (II), both before and after the atomization stages. It was said that mechanism(s) of atomization into the flame, deposition onto the water–cooled silica surfaces during preconcentration and later atomization from the surface of the reheated silica back into the flame were relatively complex and were believed to involve active participation of both flame constituents and silica surfaces. It was concluded both flame constituents and silica surface were playing role in the mechanism(s) of atomization and deposition onto the water-cooled surfaces during preconcentration and these roles were different for each element.

1.10. Aim of this Study

It has been reported that FAAS sensitivity depends on oxidation state of Tellurium [Te (IV); Te (VI)] (26). One of the aims the study is speciation of Te in the sample using sensitivity differences in the FAAS depending on the oxidation state. In addition tellurium is present in a wide variety of materials at ultra trace levels. To apply trap method for tellurium to increase sensitivity is the other aim of the study. Organic solvent atomization is used to effect atomization. Besides an extensive interference study will be carried out for organic solvent atomization technique. Solid phase interferences of the ions Na^+, K^+, Mg^{2+}, PO_4^{3-}, SO_4^{2-}, CO_3^{2-} and NO_3^- with tellurium are investigated.

CHAPTER 2

EXPERIMENTAL

2.1. Reagents

1. Hydrochloric acid, Merck (37%), density = 1.19 g/mL
2. Nitric Acid, Merck (65%), density = 1.41 g/mL
3. Perchloric acid, Merck (60%), density = 1.53 g/mL
4. Sulphuric acid, Merck (95%), density = 1.84 g/mL
5. Te (VI) stock solution: prepared from telluric acid, $H_2TeO_4.2H_2O$, 229 g/mol, > 99.5% BDH Chemicals Ltd.
6. Te (IV) stock solution: prepared from tellurium dioxide, TeO_2, 159.6 g/mol, Fisher Chemicals
7. Ammonium Sulphate, $(NH_4)_2SO_4$, Merck
8. Ammonium Dihydrogen Phosphate, $(NH_4)H_2PO_4$, Merck
9. Potassium Chloride, KCl, Merck
10. Magnessium Sulphate Heptahydrate, $MgSO_4.7H_2O$, Fisher Chemicals
11. Sodium Chloride, NaCl, BDH Chemicals Ltd.
12. Calcium Nitrate Tetrahydrate, $Ca(NO_3)_2.4H_2O$, Riedel De Haén
13. Magnesium Chloride Hexahydrate, $MgCl_2.6H_2O$, Merck

14. Ammonium Nitrate, NH_4NO_3, Merck
15. Sodium Nitrate, $NaNO_3$, Merck
16. Ammonium Carbonate, $(NH_4)_2CO_3$, Merck
17. Calcium Chloride, $CaCl_2$, Riedel De Haén
18. Methyl Isobuthyl Ketone, Carlo Erba Reagents

2.2. Preparation of Standard Solutions

A 896.3mg/L Te (IV) solution was prepared by dissolving tellurium dioxide, TeO_2, in 2 M hydrochloric acid. Further dilutions were made with deionized water or 1% (v/v) nitric acid.

A 844.0 mg/L Te (VI) solution was prepared by dissolving telluric acid, $H_2TeO_4.2H_2O$, in deionize water. Further dilutions were made with deionized water or 1% (v/v) nitric acid to prevent precipitation at microlevel in deionized water. Deionized water from Milli – Q Water Purification System was used throughout the studies.

2.3. Apparatus and Materials

100 mL DuPont polyethylene containers were used for the storage and preparation of the solutions. Transferpipette adjustable micro pipettes (5 – 50 μL, 50 – 250 μL and 100 – 1000 μL) with disposable polyethylene tips were used to dispense reagents.

Silica tubes that have 12 mm outer diameter and 10 mm inner diameter were supplied from Quartz Sceintific Inc., Fairport Hairbour, Ohio. The slotted silica tubes were 120 mm in length with two 1 mm slots. The slots are 40 mm and 60 mm in length. They are angled at 180° to each other (Figure 2.1.).

2.4. Instrumentation

An atomic absorption spectrometer, Philips, Pye Unicam PU 9200 was used with air–acetylene flame. It has 50mm burner slot, deuterium hollow cathode lamp for background correction. A Photron tellurium hollow cathode lamp with a maximum current of 7mA was used; at awavelength of 214.3 nm spectral bandpass was 0.5 nm. Air was supplied through a Pye-Unicam 9003 air compressor.

2.4.1. Flame Conditions

The acetylene flow for flame AAS technique was 1.1 L/min and for slotted silica tube trap technique it was 0.8 L/min. The sensitivity of slotted silica trap technique depends higly on the flame condition. The most suitable flame conditions for this technique were adjusted by increasing the air pressure. Oxidizing flames performed best collecting the analytes where the primary reaction zone became small and right blue.The air pressure was about >30 psi. The pressure for acetylene was 10 psi. Airflow was 5 L/min.

2.4.2 Organic Solvent Atomization Technique

Organic solvent atomization technique was used to atomize trapped species. Very small volume of methyl isobuthyl ketone (50 μL) was used to affect atomization, which was sent to the flame with the use of micro sampling accessory.

2.5. Experiments with Hydride Generation AAS Technique

It is observed that in the acidic media the sensitivities of Te (VI) and Te (IV) species were equal with flame AAS. Therefore it was investigated whether any oxidation or reduction takes place in the presence of HNO_3 or HCl. In order to understand any possible change in oxidation state, experiments using Hydride Generation Atomic Absorption Spectrometry (HGAAS) technique were performed.

The optimized conditions were made for batch type HGAAS as suggested by Dedina (51). 100 ng / mL Te (VI) and Te (IV) solutions were prepared by dilution with both 2 M HNO_3 and 2 M HCl. A 1.0 % (w / v) $NaBH_4$ solution as a reductant was used with argon flow rate of 1 L/min.

2.6. Interference Studies

The interference of the ions Na^+, K^+, NO_3^-, SO_4^{2-}, CO_3^{2-}, Ca^{2+} and Mg^{2+} on the Te signals was investigated. All the interferences effects were studied using 1, 10, 100 mg/L of the interfering ion concentration. Counter ions for cation interferants were chloride, nitrate or sulphate. For anion interferants either the sodium or ammonium salts were used.

The interference can take place in solid phase and / or in vapor phase. The method used in our study for interferences was like the method used by Helles (50). Two experimental procedures were followed to decide in which phase the interference was present. First of all, both analyte and the interferant were in the solution. This solution was collected and atomized by means of organic solvent atomization technique. If an interfering effect was seen, another experiment was done to understand if the interference was in solid or gas phase. In the second experiment, analyte and interferant were in separate solutions. After collection of the analyte, interferant solution was aspirated to the flame through the capillary while the analyte was being atomized. If the same interfering effect as in the first experiment was seen, it was concluded that the interference was in gas phase. We can reach to thic conclusion as in atomization cycle the analyte atoms and interferant was released together from the slotted silica tube surface. However, due to the reactions in gas phase, interference takes place. On the other hand, if the interference had been in solid phase, the surface of the slotted silica tube would have been affected through providing a better or worse trapping surface. To allow the introduction of organic solvent, a special part was adjusted to the air entrance of the burner in the interference studies (figure 2.2.). If the solution containing both analyte and interferant gives no significant effect on the absorbance signal, then the second experiment explained above was not performed.

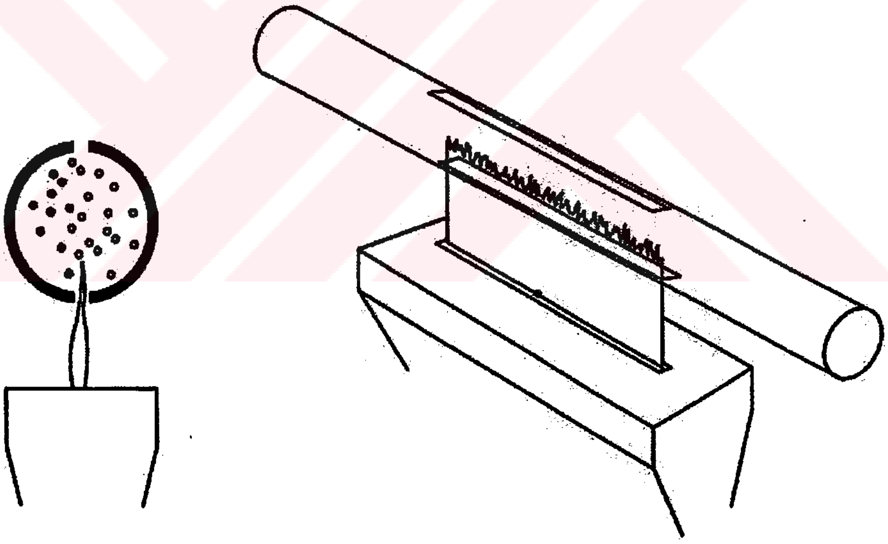

Figure 2.1. The trapping System Used For Organic Solvent Atomization Techniques

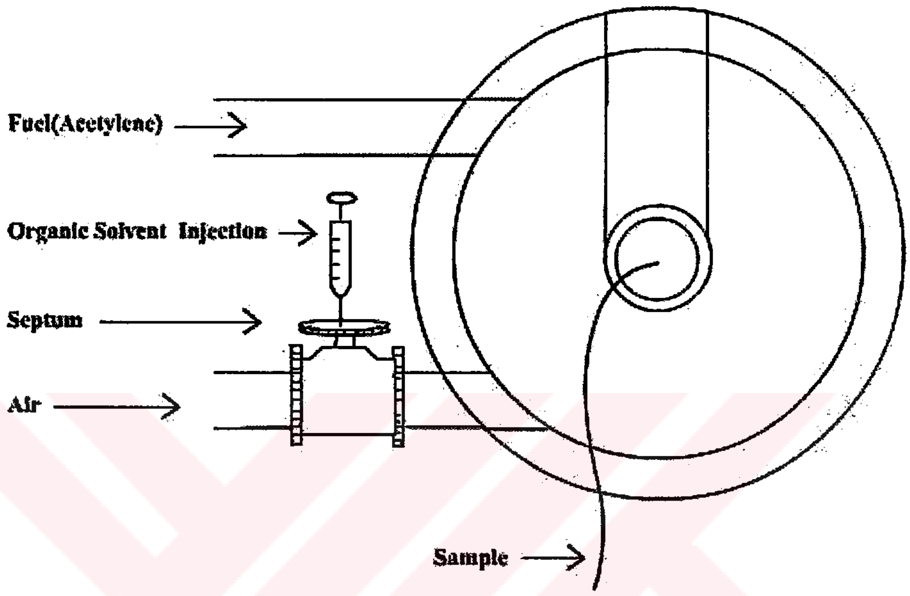

Figure 2.2. System Used for Introduction of Organic Solvent in Interference Studies

CHAPTER 3

RESULTS AND DISCUSSION

There are two main contributions in this study. First is the attemps for a speciation study for Te (VI) and Te (IV) using FAAS technique and the consequential observations. The second is the use and optimization of a fairly novel atom trap, slotted silica tube for determination of Te with organic solvent atomization technique. In addition, speciation study for Te (VI) and Te (IV) was repeated for slotted silica tube trap technique. Besides an extensive study was carried out for organic solvent atomization techniques to understand if the interference was in solid and / or in gas phase, using trap technique.

3.1. Speciation Studies using Flame AAS

3.1.1. Sensitivities of Te species by Dilution with Deionized Water

Willis et al. recently (26) have stated that the Flame AAS sensitivity depends on oxidation state of Tellurium [Te (IV) and Te (VI)]. Te (IV) gave a significantly greater absorbance (by a factor of about 1.66) as compared to Te (VI) using flame AAS when prepared deionized water. In this study, when the Te (VI) and Te (IV) solutions were prepared by dilution with deionized water, using the same concentrations, it was observed that Te (IV) have higher sensitivity than Te (VI) have, supporting the results by Willis et al. (26) (Figures 3.1. and 3.2.) In high (more than 1 M) acidity the sensitivity of both species decreased.

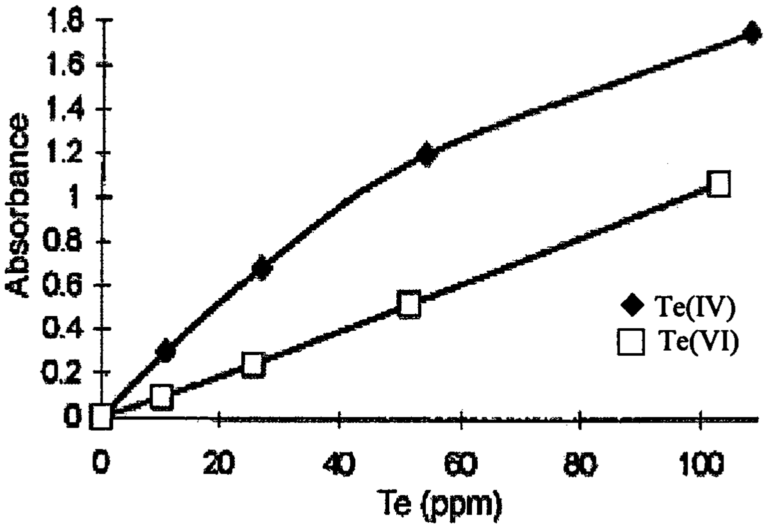

Figure 3.1. Calibration Curve for Te (IV) and Te (VI) in an optimized air – acetylene flame (Willis et al.).

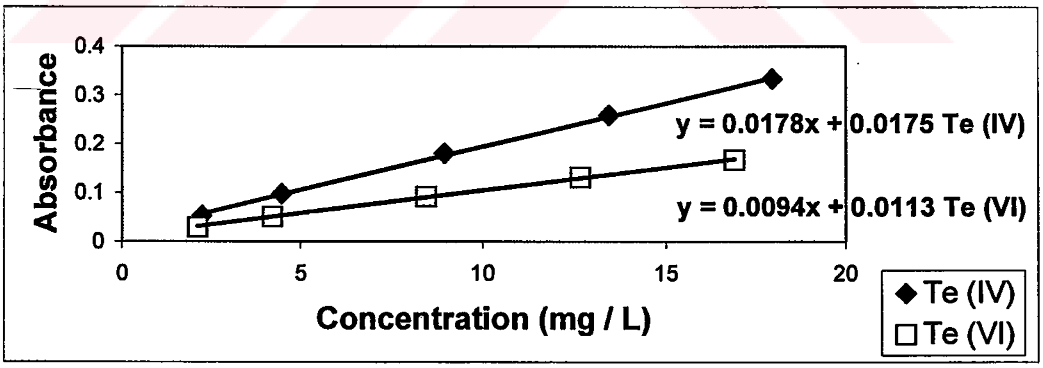

Figure 3.2. Calibration curve for Te (VI) and Te (IV) diluted with DW in an optimized air – acetylene flame.

3.1.2. Acidity Effect for Sensitivities of Tellurium Species

In this part of the study, Te solutions were prepared in different kinds of acid. It is observed that when Te (VI) solutions were prepared with deionized water, sensitivity of Te (IV) was greater than that of Te (VI) in deionized water. In addition to these, if the Te solutions were prepared in acidic medium, sensitivity of Te (VI) would be equal to sensitivity of Te (IV) (Table 3.1.). It was seen that even very small concentration of acid (HNO_3 or HCl) is enough for increasing sensitivity of Te (VI) species to the same level as Te (IV). In very high acidity the sensitivity of both species decreased because high acidity prevents the efficient nebulizing the Te atoms to the flame. (Figures 3.3., 3.4., 3.5., 3.6.)

Table 3.1. Effect of several types of acids to the signal of Te (VI) and Te (IV) species.

Dilution Medium	Absorbance of Te (VI) (8.44 mg / L) by FAAS	Absorbance of Te (IV) (8.96 mg / L) by FAAS
Deionized Water	0.164 ± 0.002	0.224 ± 0.004
(1 % v / v) HNO_3	0.225 ± 0.001	0.225 ± 0.003
(1 % v / v) HCl	0.224 ± 0.004	0.225 ± 0.005
(1 % v / v) H_2SO_4	0.226 ± 0.002	0.224 ± 0.004
(1 % v / v) $HClO_4$	0.226 ± 0.005	0.222 ± 0.008

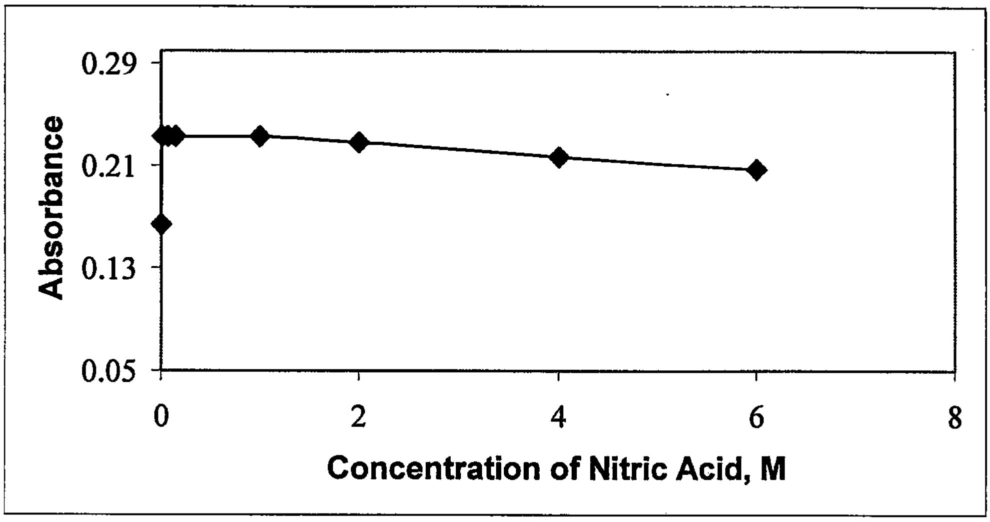

Figure 3.3. Effect of HNO_3 concentration on the sensitivitiy of (8.44 mg / L) Te (VI) , flame AAS.

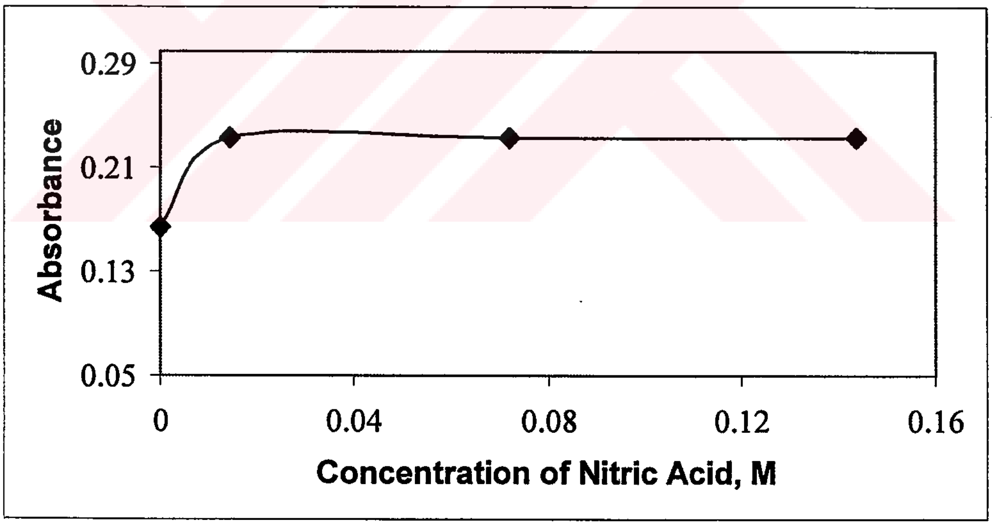

Figure 3.3.1. The part of Figure 3.3. showing the effect of HNO_3 in low concentration range to Te (VI) sensitivity; flame AAS.

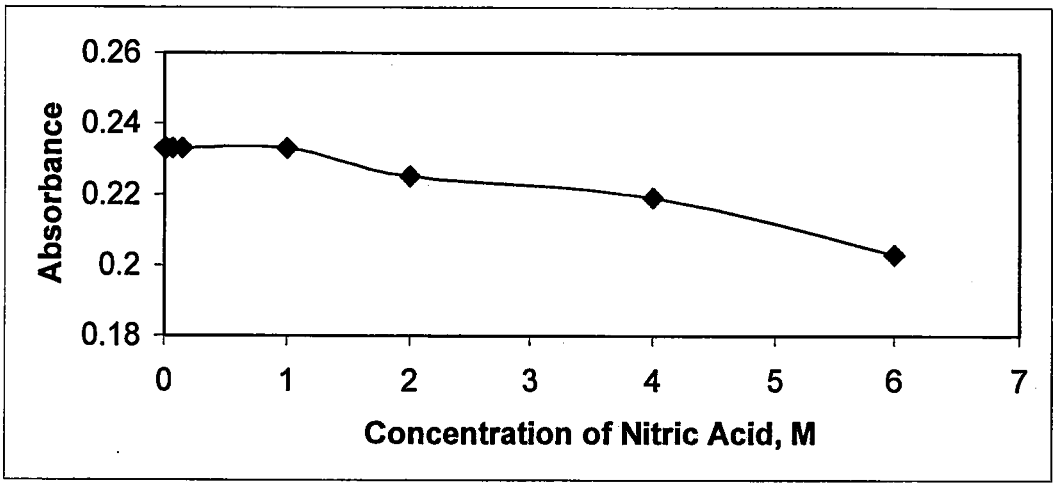

Figure 3.4. Effect of HNO_3 concentration on the sensitivitiy of (8.96 mg / L) Te (IV), flame AAS

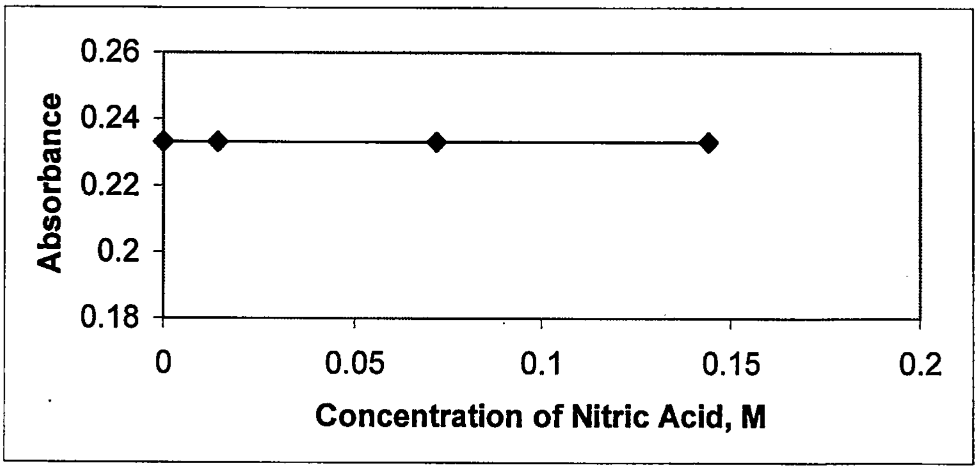

Figure 3.4.1. The part of Figure 3.4. showing the effect of HNO_3 in low concentration range to Te (IV) sensitivity; flame AAS.

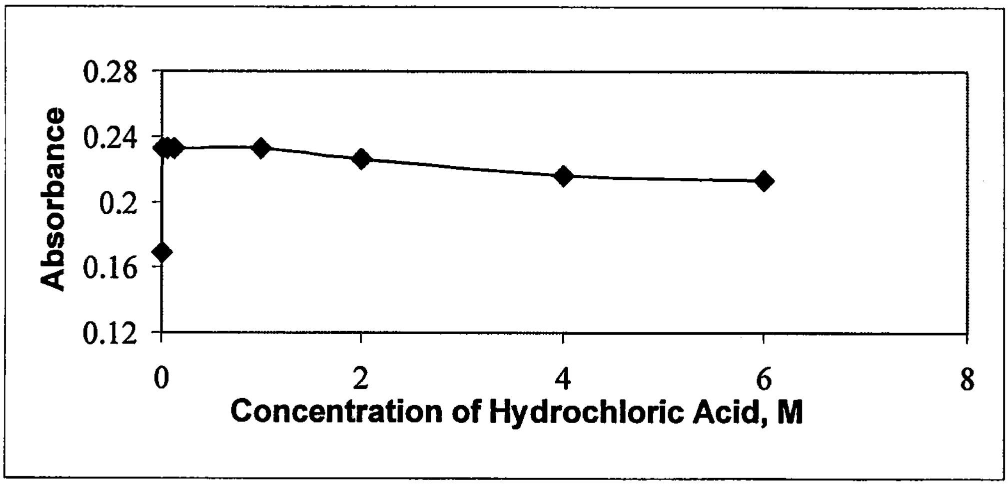

Figure 3.5. Effect of HCl concentration on the sensitivitiy of (8.44 mg / L) Te (VI), flame AAS

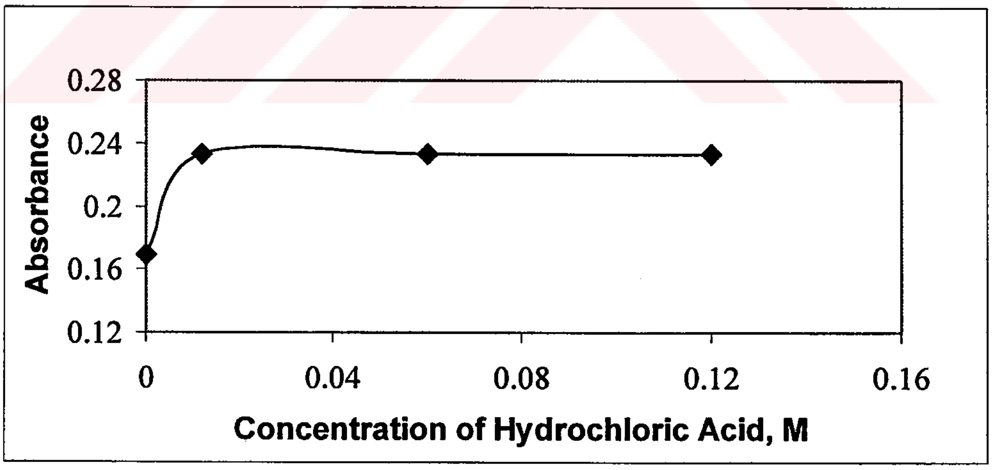

Figure 3.5.1. The part of Figure 3.5. showing the effect of HCl in low concentration range to Te (VI) sensitivity; flame AAS.

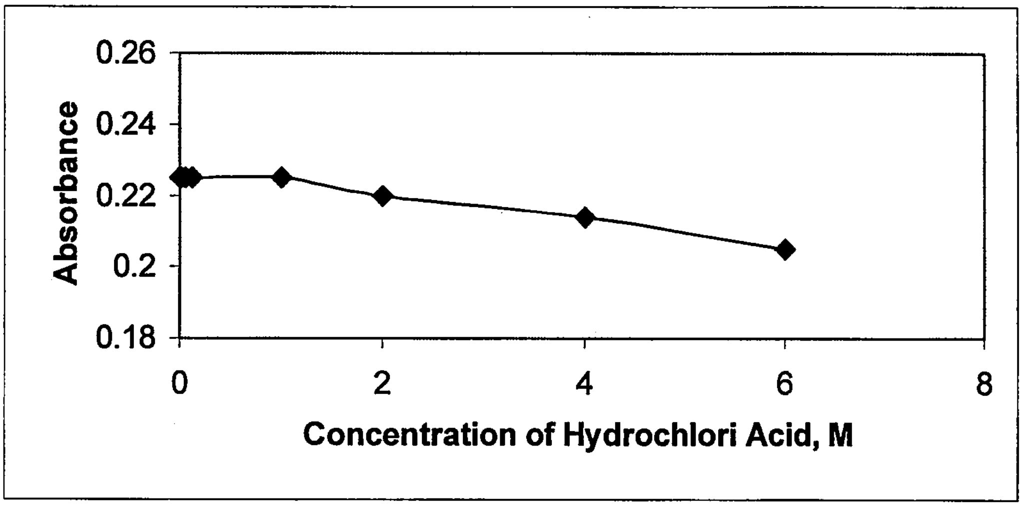

Figure 3.6. Effect of HCl concentration on the sensitivitiy of (8.96 mg / L) Te (IV), flame AAS

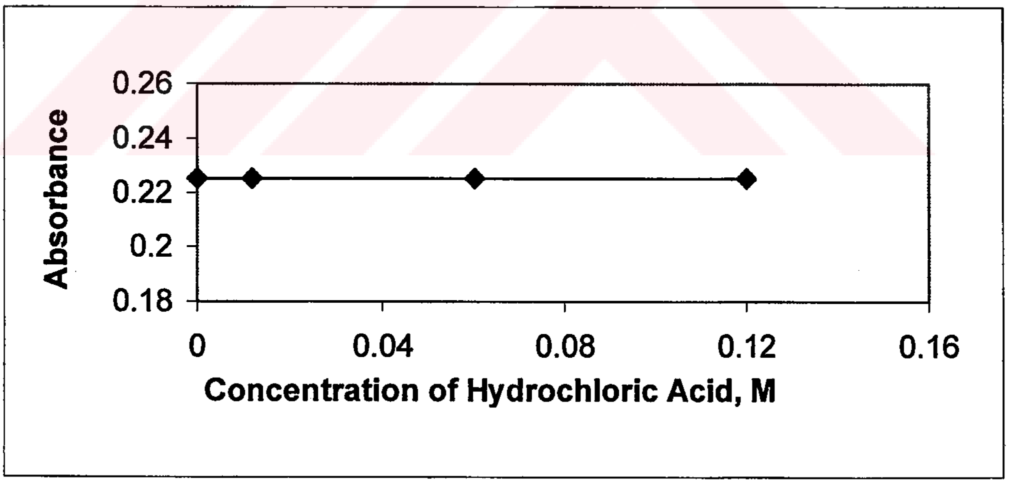

Figure 3.6.1 The part of Figure 3.6. showing the effect of HCl in low concentration range to Te (IV) sensitivity; flame AAS.

It was observed that in highly acidic medium sensitivities of both Te (VI) and Te (IV) species decreased. It was probable that higly acidic medium prevents the efficient nebulization of the solutions. Throughout this experiment both Te (VI) and Te (IV) solutions were prepared by dilution with 1 % (v/v) HNO_3. When the calibration curves were plotted for both Te (VI) and Te (IV) solutions diluted with 1 % (v/v) HNO_3, calculated detection limits were 0.38 mg / L for Te (VI) and 0.45 mg / L for Te (IV). Figure III.7. contains the calibration plots of Te species with 1 % HNO_3 (v/v) dilution in an air acteylene flame.

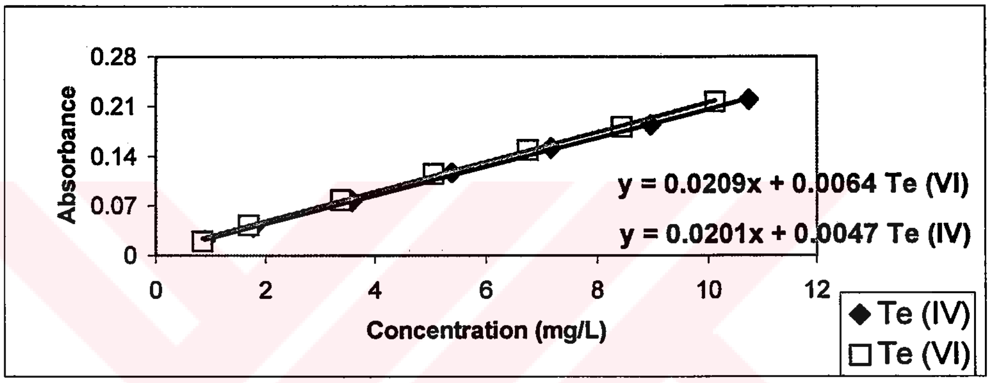

Figure 3.7. Calibration Curve for Te (IV) and Te (VI) by dilution with 1% (v/v) HNO_3 in an optimized air – acetylene flame

Both calibration graphs showed very good linearity with correlation coefficients of 0.9993 and 0.9991 for Te (IV) and Te (VI) respectively.

3.1.3. Te Species in the Same Matrix

In this part, first of all 1.69, 3.38, 4.22, 5.06, 6.75, 8.44 mg/L Te (VI) solutions were prepared by dilution with 1 % (v/v) HNO_3 and analysed at FAAS. Then 1.79, 3.58, 4.48, 5.38, 7.17, 8.96 mg/L Te (IV) solutions were prepared by dilution with 1 % (v/v) HNO_3 and analysed at FAAS. Last of all, in various ratios of Te (VI) + Te (IV) mixtures were prepared by dilution with 1 % (v/v) HNO_3 and analysed at FAAS. The results showed us that although there is no possibility to make speciation for Te element in the same matrix, the accurate determination in the sample, which contains whatever Te species in acidic medium, could be done. Table 3.2., Table 3.3. and Table 3.4. show the results of these expriments.

Table 3.2. Analysis of various concentrations of Te (VI) and Te (IV) solutions at FAAS.

Conc. of Te (IV) in 1 % (v/v) HNO_3	Absorbance	Conc. of Te (VI) in 1 % (v/v) HNO_3	Absorbance
1.79 mg / L	0.047 ± 0.002	1.69 mg / L	0.048 ± 0.002
3.58 mg / L	0.084 ± 0.004	3.38 mg / L	0.088 ± 0.002
4.48 mg / L	0.106 ± 0.003	4.22 mg / L	0.108 ± 0.004
5.38 mg / L	0.125 ± 0.006	5.06 mg / L	0.128 ± 0.003
7.17 mg / L	0.170 ± 0.003	6.75 mg / L	0.175 ± 0.004
8.96 mg / L	0.205 ± 0.004	8.44 mg / L	0.206 ± 0.002

Table 3.3. The mixture of Te (VI) + Te (VI) solutions in 1% (v/v) HNO_3

Conc. of Te (IV) + Te (VI) (mg / L)	**Absorbance**
8.96 + 0	0.207 ± 0.004
7.17 + 1.69	0.207 ± 0.004
5.38 + 3.38	0.208 ± 0.003
4.48 + 4.22	0.204 ± 0.005
3.58 + 5.06	0.206 ± 0.002
1.79 + 6.75	0.206 ± 0.004
0 + 8.44	0.204 ± 0.005

Table 3.4. Presentation of Table III.3. as percentage for the mixture

% Te (IV) + % Te (VI)	**Absorbance / 1 mg/L Te**
100 .0 + 0.0	0.0231 ± 0.0004
81.0 + 19.0	0.0234 ± 0.0004
61.4 + 38.6	0.0237 ± 0.0003
51.5 + 48.5	0.0235 ± 0.0006
41.4 + 58.6	0.0238 ± 0.0003
21.0 + 79.0	0.0241 ± 0.0005
0.0 + 100.0	0.0241 ± 0.0006

3.1.4. The Proof Experiment About Te Species

When it was observed that the sensitivities for Te (IV) and Te (VI) species were equal in the acidic media, it was questioned whether any oxidation or reduction takes place in presence of HNO_3 and HCl, respectively. In order to explain any possible change in oxidation state, the following experiments were performed by using Hydride Generation Atomic Absorption Spectrometry (HGAAS) technique.

In HGAAS technique, Te (IV) species give response by forming TeH_4, tellurium hydride in the acidic medium but Te (VI) does not. The optimized conditions were made for batch type HGAAS as suggested by Dedina (51). 100 ng / mL Te (VI) and Te (IV) solutions were prepared by dilution with both 2 M HNO_3 and 2 M HCl. 1.0 % (w / v) $NaBH_4$ solution as a reductant was used. Argon flow rate was 1 L/min. Results of this experiment are shown at Table 3.4. for this experiment.

Table 3.5. Results of HGAAS analysis

In (2M) HNO_3	Absorbance	In (2M) HCl	Absorbance
Blank	0.014 ± 0.001	Blank	0.019 ± 0.004
Te (VI)	0.018 ± 0.003	Te (VI)	0.026 ± 0.003
Te (IV)	0.443 ± 0.007	Te (IV)	0.390 ± 0.005

From these results it was understood that there is no oxidation from Te (IV) to Te (VI) when Te (IV) solution was prepared by dilution with 2M HNO_3 and there is no reduction from Te (VI) to Te (IV) when Te (VI) was prepared by dilution with 2 M HCl.

It may be concluded that, the presence of either acids, HNO_3 or HCl, does not affect oxidation states. It must be remembered that Te (IV) stock solution was prepared by dissolving TeO_2 in 1 M HCl; Te (VI) stock solution was prepared by $H_2TeO_4.2H_2O$ in H_2O. It may be suggested that Te (VI) stock solution may involve some part of the analyte in form of precipitated hydroxide H_6TeO_6 . Disolution with any acid assumes a complete dissolution therefore the sensitivities of Te (IV) and Te (VI) solutions gave same sensitivity both in our study and that by Willis (26); plasma is a more efficient atomizer than flame.

3.2. Slotted Silica Tube Technique

In this part of the study the use and optimization of slotted silica tube trap for determination of Te (VI) and Te (IV) with organic solvent atomization technique were performed. In addition, an interference study was done for this atomization technique to understand whether the inteference was solid and / or in gas phase. Conditions were optimized to achieve the best detection limits.

3.2.1. Optimization Parameters

3.2.1.1. Flame Conditions

Flame conditions were optimized to find the most suitable flame for trapping stage. The sensitivity of slotted silica trap method depended higly on the flame conditions. As explained at the experimental part (section 2), oxidizing flames provided best collecting conditions for the analytes where the primary reaction zone became small and blue. A fuel rich flame was used to affect atomization of the trapped species.

3.2.1.2. Volume of Organic Solvent

It was found only 50 µL of organic solvent (methylisobutylketone, MIBK) was found for both species of tellurium to be enough for the atomization of all the trapped analyte species. When high volumes of organic solvent was aspirated, almost no detectable change in the flame appearance was observed. Figure 3.8. and 3.9. show the optimization of volume of organic solvent.

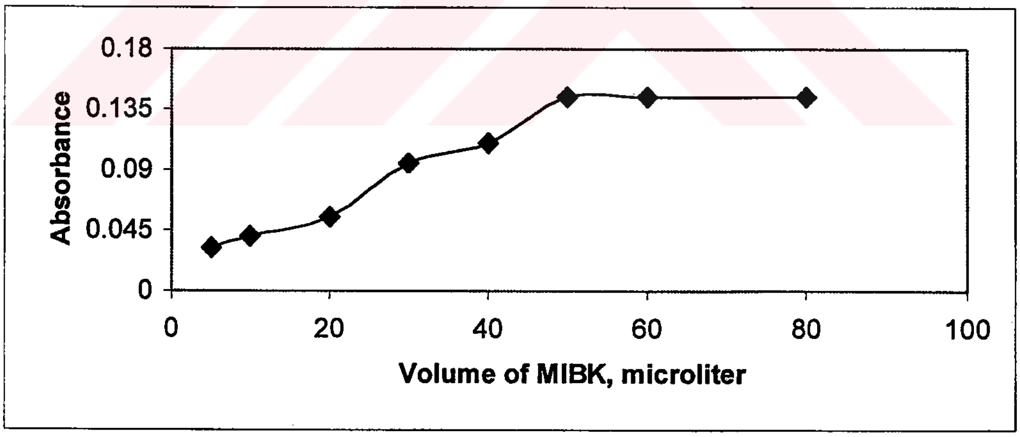

Figure 3.8. Optimization of MIBK volume for Te (IV) in slotted silica trap technique(dilution with 1 % HNO_3. 89.6 ng / mL Te (IV) 1.0 minute collection, 6.0 mL / min. suction rate)

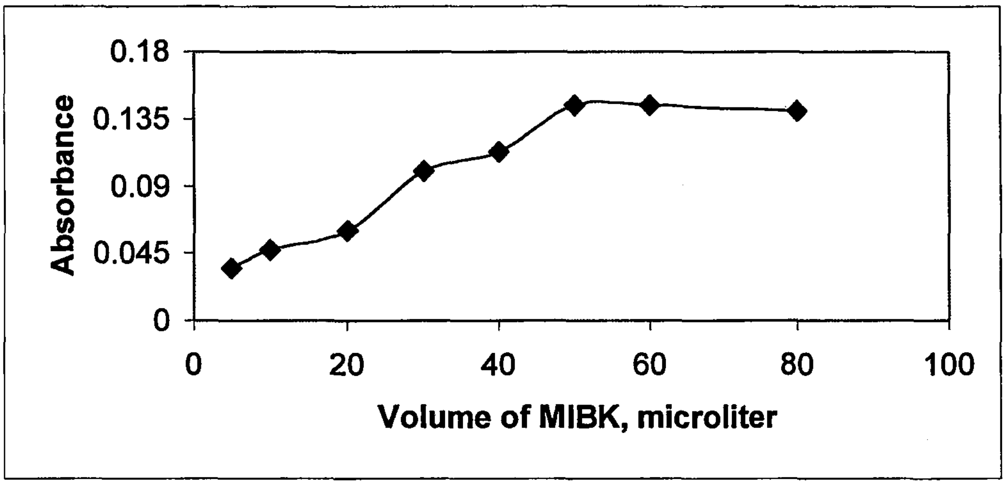

Figure 3.9. Optimization of MIBK volume for Te (VI) in slotted silica trap technique (dilution with 1 % HNO_3. 84.4 ng / mL Te (VI) 1.0 minute collection, 6.0 mL / min. suction rate).

3.2.1.3. Suction Rate and Collection Time

The collection time and the suction rate are important for the analysis of samples. Two different experiments were performed at a period of the effect of these parameters. Firstly, the collection time was kept constant at one minute and the suction rate of the nebulizer was increased. When the suction rate was increased more analyte was collected and because of this, absorbance signal increased (Figure 3.10., 3.11.). In the second set of experiments, the analyte volume was kept constant at 3 mL and suction rate was increased. Increasing the suction rate caused a corresponding decrease in the absorbance signal (Figure 3.12., 3.13.). The reason for this behavior is that the low suction rates, nebulization efficiency is better.

It was understood from these results that, for real analyses, if the sample volume is limited it will be better to collect a constant volume with a low suction rate on the other hand if there is no limitation to sample volume, it will be better to have a fixed the collection time with a high suction rate.

Throughout this study, suction rate used for all experiments was 6.0 mL / min and one minute collection period of 1.0 minute was used.

The calibration plots for Te (VI) and Te (IV) were constructed for the optimum parameters for the atomization technique (Figure III.13.). When the calibration curves were plotted for both Te (VI) and Te (IV) solutions diluted with 1 % (v/v) HNO_3, calculated detection limits were 6.79 ng / mL for Te (IV) and 5.34 ng / mL for Te (VI).

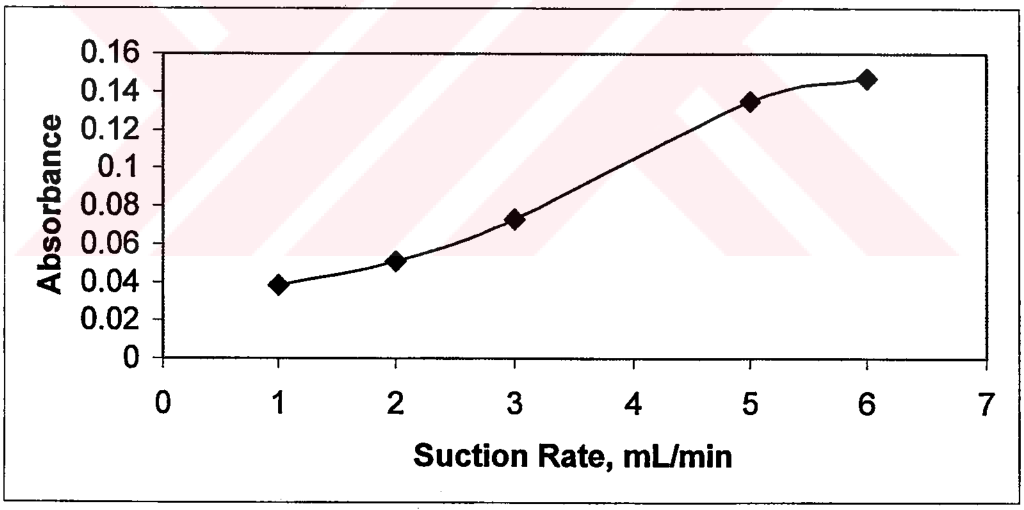

Figure 3.10. Optimization of suction rate at fixed collection time for slotted silica trap technique (84.4 ng / mL Te (VI) by dilution with 1 % HNO_3, 1.0 min. collection time).

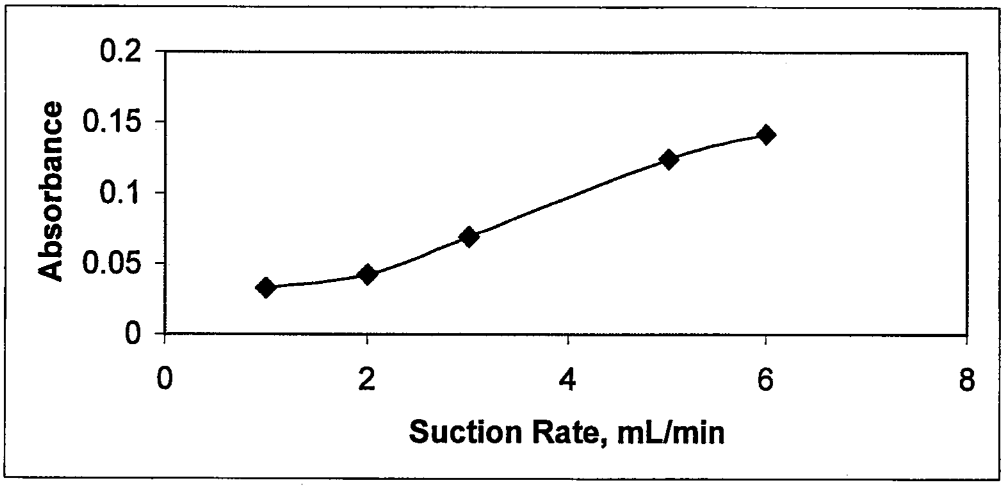

Figure 3.11. Optimization of suction rate at fixed collection time for slotted silica trap technique. [89.6 ng / mL Te (IV) by dilution with 1 % HNO_3, 1.0 min. collection time]

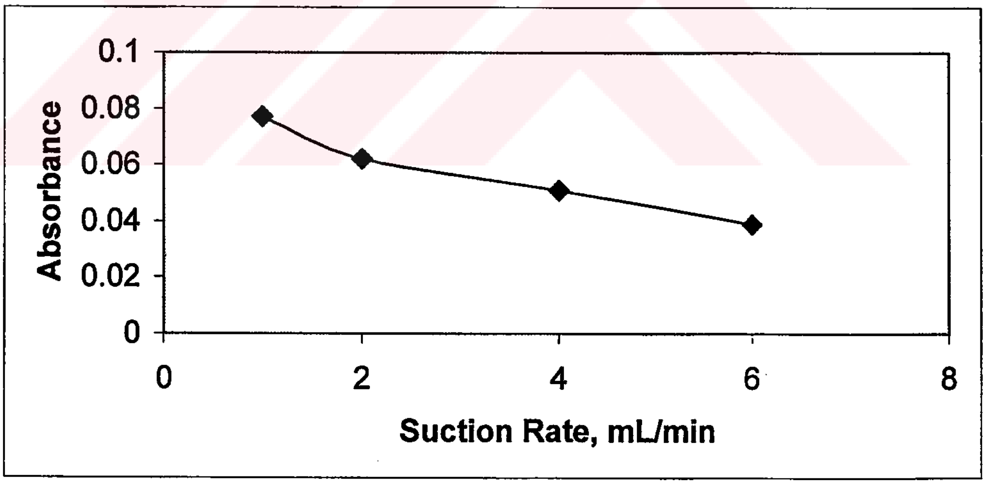

Figure 3.12. Optimization of suction rate at constant volume for slotted silica trap technique. [84.4 ng / mL Te (VI) by dilution with 1 % (v/v) HNO_3, 3.0 mL collection volume]

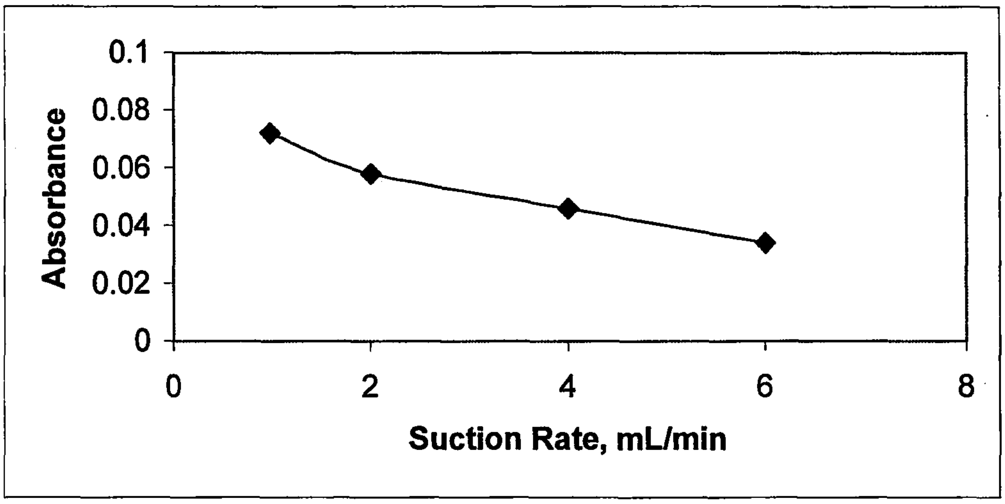

Figure 3.13. Optimization of suction rate at constant volume slotted silica trap technique. [89.6 ng / mL Te (IV) by dilution with 1 % HNO_3, 3.0 mL collection volume]

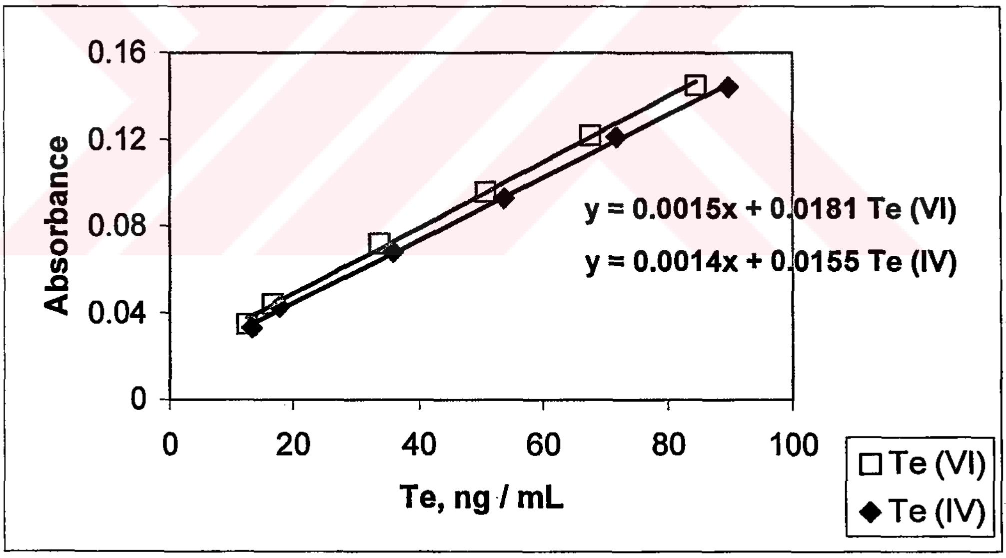

Figure 3.14. Calibration plots for Te (VI) and Te (IV) diluted with 1 % (v/v) HNO_3. 1 minute collection, 6.0 mL / min suction rate; slotted silica trap technique.

Both calibration graphs showed very good linearity with correlation coefficients of 0.9996 and 0.9993 for Te (IV) and Te (VI) respectively.

It has been suggested that the sensitivity enhancement achieved by using a slotted silica tube in conventional Flame AAS is because of the increased residence time of the analyte atoms in the light beam of the hollow cathode lamp (44). It is also known that this technique works well only for volatile elements. Alkali and alkaline earth metals causes devitrification of silica tube so they give unwanted results. Common use of slotted silica tube does not involve any trapping; just a momentary improvement is obtained for flam AAS. It must be noted that the trap used in this study involves preconcentration

.

3.2.2. Atomization Mechanism

The suggestion for atomization mechanism is the presence of a dynamic equilibrium that is supposed species in close environment of atomization take place between the walls of the slotted silica tube and the free analyte. This equilibrium should be easily reached for the volatile metals whereas it should be reached in a very slow manner or cannot be reached at all for nonvolatile metals because they are permanently and irreversibly retained on the surface. Therefore, slotted silica tube itself may be serving as a trap which delays the free atoms so that they can spend more time in the optical path even if it is used for momentary sensitivity enhancement in Flame AAS.

3.3. Speciation Studies Using Slotted Silica Tube Trap Technique

3.3.1. Sensitivities of Te species by Dilution with Deionized Water

In this part of the study, when the standard solutions were prepared diluting with deionized water, using slotted silica tube trap technique Te (VI) and Te (IV) gave responses in a similar way to that by Flame AAS. The sensitivity of Te (IV) is higher than the sensitivity of Te (VI) at the optimized conditions. These results were parallel to the Willis' results (26). Figure III.15. shows the sensitivity differences between Te (VI) and Te (IV) species using slotted silica tube trap technique.

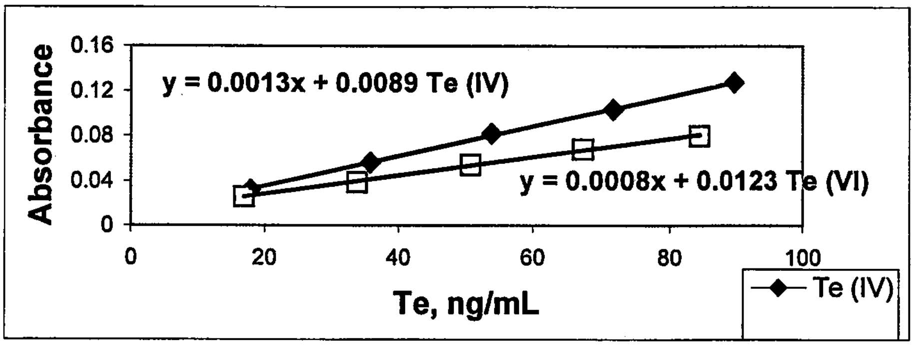

Figure 3.15. Calibration plots of Te (VI) and Te (IV) solution diluted by deionized water; slotted silica trap technique

3.3.2 Effect of Acidity on Sensitivities of Tellurium Species

In this part of this study, using slotted silica tube technique the same responses were obtained as the results obtained at Flame AAS.Te solutions were prepared by dilution with acid. It is observed that when Te solution were prepared by dilution with acid, sensitivity of Te (VI) was greater than that of Te (VI) by dilution by deionized water but there was no difference observed for sensitivities between Te (IV) and Te (VI) (Figure 3.15., 3.16.) In addition to these, if the Te solutions were prepared with acid, sensitivity of Te (VI) would be equal to sensitivity of Te (IV) (Figure 3.13.). It was searched the effect of concentration range of hydrochloric acid for both Te species and it was seen that even very small concentration of acid is enough for increasing sensitivity of Te (VI) species but there was no effect of acidity for Te (IV) species. In addition, in high acidity the sensitivity decrease for both species occurred using slotted silica tube trap technique. From these results, our suggestion, which was microlevel precipitation of Te (VI) sloution prepared with deionized water, was proved.

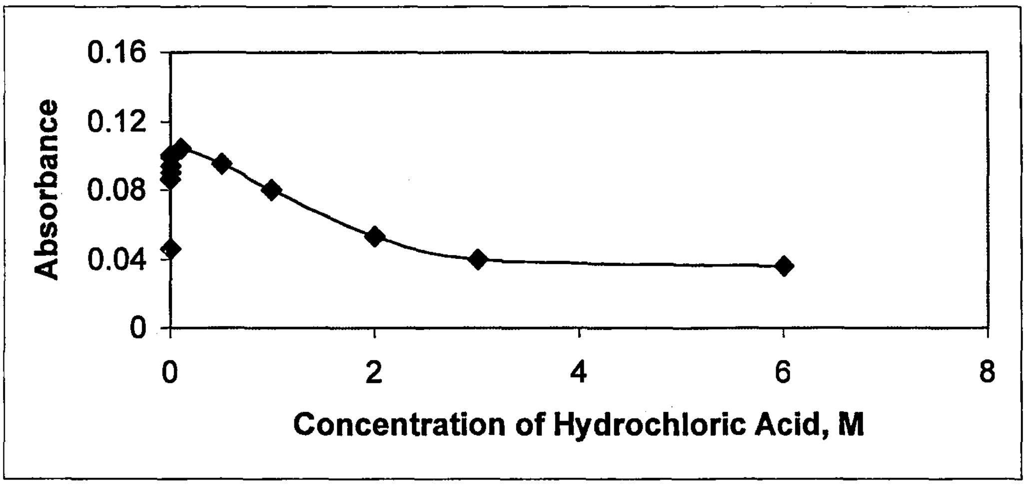

Figure 3.16. Effect of HCl concentration to the sensitivitiy of Te (VI) (84.4 ng / mL); slotted silica trap technique.

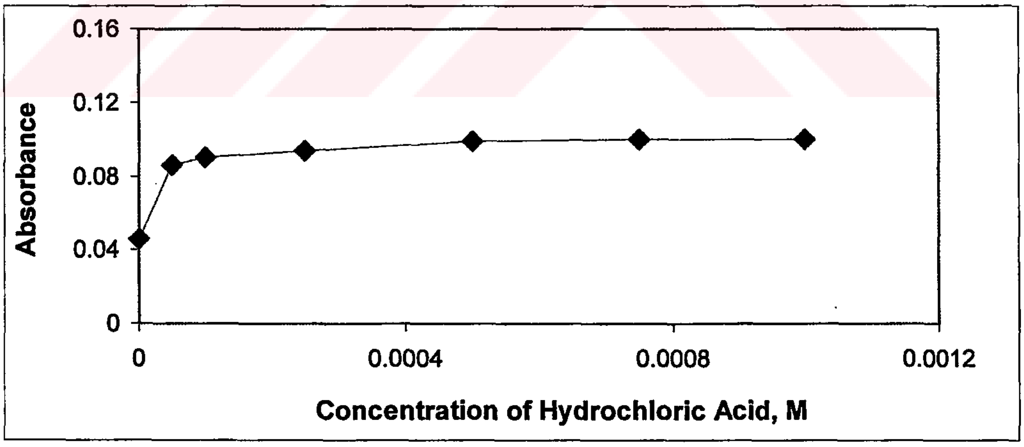

Figure 3.16.1. showing the effect of HNO_3 in low concentration range to Te (VI) (84.4 ng / mL) sensitivity; slotted silica trap technique

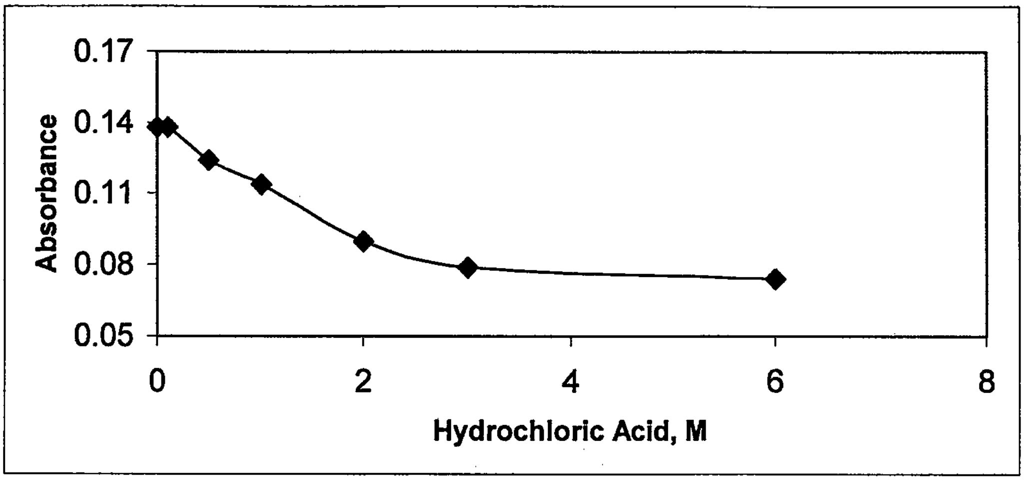

Figure 3.17. Effect of HCl concentration to the sensitivity of Te (IV) (89.6 ng / L); slotted silica trap technique.

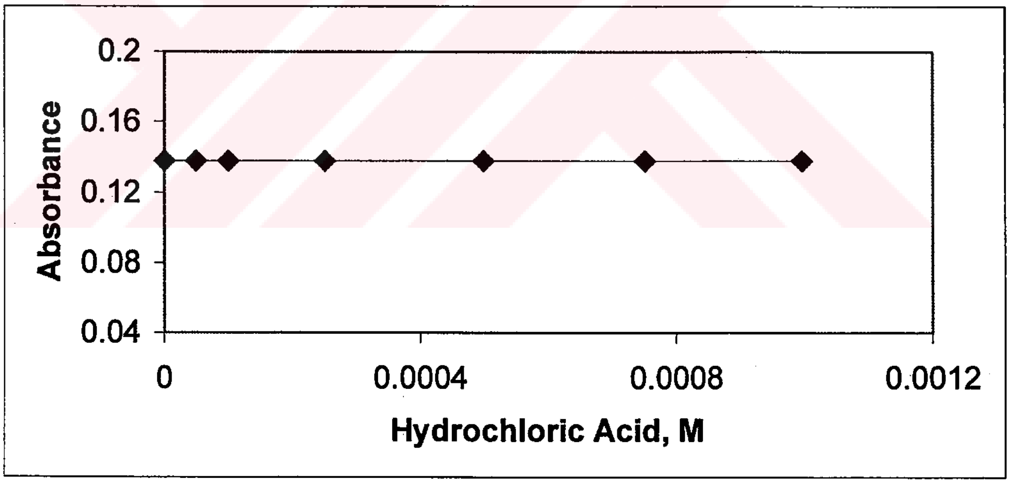

Figure 3.17.1. Showing the effect of HCl concentration in low concentration range to Te (VI) sensitivity ; slotted silica trap technique

3.4. Interference Studies for Te (IV) and Te (IV)

The interference studies for Te (VI) and Te (IV) were performed using slotted tube atom trap with organic solvent atomization. The absorbance signals of pure analyte solutions were normalized to 100 and the absorbance signals for analyte and interferant solutions were calculated by using this. If a ± 5 % change in the absorbance signal was observed, it was stated that the interference was present. The of all the interfering effects were depressing. No enhancement of the signal was observed. Most of interferences were solid phase interferences. Devitrification of the silica tube had been a serious problem, in presence of high alkali metal concentrations.

The results of the interference studies are shown in the Table III.5. and Table III.6. for Te (IV) and for Te (VI) respectively. Calcium nitrate, ammonium carbonate, ammounium sulphate, and ammonium dihydrogen phosphate exhibited no effect on both Te (VI) and Te (IV) signals in solid and / or in gas phase.

All other interferants interfered with the analyte in solid and / or in gas phase. Calcium chloride and ammonium nitrate made depression of the analyte quantitative signal, especially at high interferant concentrations. Magnesium sulphate, magnesium chloride, potassium chloride, sodium chloride depressed the signal even at a concentration level of 1 mg / L. Sodium nitrate also resulted in interference in solid phase when sodium was present at a concentration of 10 mg / L or higher. For the interferants of chloride compounds, chloride may have more interference effect than metals have because of making stable compounds of chloride with tellurium element.

Table III.6. Interference Studies for Te (VI) [84.4 ng / mL Te (VI) 30 sec. Collection]

		Relative Signal of the Analyte ± SD	
		Organic Solvent Atomization	
Interferant	**Conc.of Interferant (mg / L)**	**Solid Phase**	**Gas Phase**
$(NH_4)_2SO_4$ (SO_4^{2-})	1	100.1 ± 0.2	-
	10	99.6 ± 0.5	-
	100	99.6 ± 0.4	-
$(NH_4)_2CO_3$ (CO_3^{2-})	1	100.2 ± 0.3	-
	10	98.4 ± 0.2	-
	100	100.5 ± 0.1	-
$Ca(NO_3)_2$ (Ca^{2+})	1	100.1 ± 0.6	-
	10	99.9 ± 02	-
	100	98.7 ± 0.7	-
$CaCl_2$ (Ca^{2+})	1	100.2 ± 0.2	-
	10	99.1 ± 0.2	-
	100	59.4 ± 03	98.5 ± 0.2
$MgSO_4$ (Mg^{2+})	1	86.4 ± 0.1	99.1 ± 0.1
	10	86.9 ± 0.4	99.8 ± 0.2
	100	59.2 ± 02	97.4 ± 0.3

Table III.6. Continued

		Relative Signal of the Analyte ± SD	
		Organic Solvent Atomization	
Interferant	**Conc.of Interferant (mg / L)**	**Solid Phase**	**Gas Phase**
NaCl	1	88.9 ± 0.8	96.1 ± 0.1
(Na$^+$)	10	88.4 ± 0.3	94.3 ± 0.1
	100	87.6 ± 0.1	94.5 ± 0.5
$NaNO_3$	1	100.1 ± 0.5	-
(Na$^+$)	10	88.5 ± 0.2	100.2 ± 0.2
	100	88.1 ± 0.3	98.0 ± 0.7
KCl	1	91.1 ± 0.1	100.0 ± 0.2
(K$^+$)	10	90.0 ± 0.2	100.0 ± 0.1
	100	90.3 ± 0.1	100.1 ± 0.3
$NH_4H_2PO_4$	1	99.8 ± 0.4	-
(PO_4^{3-})	10	99.9 ± 0.2	-
	100	100.0 ± 0.1	-
NH_4NO_3	1	100.0 ± 0.3	-
(NO_3^-)	10	100.1 ± 0.1	-
	100	92.3 ± 0.1	99.7 ± 0.1
$MgCl_2$	1	92.3 ± 0.1	100.1 ± 0.2
(Mg^{+2})	10	76.4 ± 0.2	100.0 ± 0.3
	100	74.3 ± 0.1	100.2 ± 0.1

Table III.7. Interference Studies for Te (IV) [89.6 ng / mL Te (IV) 30 sec. Collection]

Interferant	Conc.of Interferant (mg / L)	Relative Signal of the Analyte ± SD	
		Organic Solvent Atomization	
		Solid Phase	**Gas Phase**
$(NH_4)_2SO4$ (SO_4^{2-})	1	100.1 ± 0.1	-
	10	98.2 ± 0.3	-
	100	98.6 ± 0.1	-
$(NH_4)_2CO_3$ (CO_3^{2-})	1	100.1 ± 0.1	-
	10	100.0 ± 0.1	-
	100	99.6 ± 0.2	-
$Ca(NO_3)_2$ (Ca^{2+})	1	100.2 ± 0.4	-
	10	99.9 ± 0.1	-
	100	99.2 ± 0.2	-
$CaCl_2$ (Ca^{2+})	1	100.1 ± 0.2	-
	10	100.0 ± 0.3	-
	100	57.6 ± 0.1	98.6 ± 0.2
$MgSO_4$ (Mg^{2+})	1	78.5 ± 0.2	100.1 ± 0.2
	10	76.9 ± 0.5	98.6 ± 0.3
	100	58.5 ± 0.8	98.4 ± 0.4

Table III.7. Continued

Interferant	Conc.of Interferant (mg / L)	Relative Signal of the Analyte ± SD	
		Organic Solvent Atomization	
		Solid Phase	Gas Phase
NaCl **(Na^+)**	1	92.2 ± 0.1	98.2 ± 0.8
	10	91.4 ± 0.3	97.5 ± 0.1
	100	89.8 ± 0.1	93.1 ± 0.2
$NaNO_3$ **(Na^+)**	1	100.0 ± 0.6	-
	10	88.3 ± 0.1	100.0 ± 0.7
	100	86.7 ± 0.2	99.6 ± 0.2
KCl **(K^+)**	1	91.3 ± 0.2	100.1 ± 0.1
	10	90.9 ± 0.5	100.0 ± 0.3
	100	90.1 ± 0.4	100.3 ± 0.2
$NH_4H_2PO_4$ **(PO_4^{3-})**	1	99.8 ± 0.3	-
	10	100.1 ± 0.3	-
	100	98.4 ± 0.4	-
NH_4NO_3 **(NO_3^-)**	1	100.0 ± 0.1	-
	10	100.3 ± 0.7	-
	100	93.6 ± 0.2	99.9 ± 0.1
$MgCl_2$ **(Mg^{+2})**	1	87.3 ± 0.5	100.1 ± 0.1
	10	78.6 ± 0.3	100.0 ± 0.2
	100	75.8 ± 0.3	99.9 ± 0.6

3.5. Analytical Figures of Merit

Using slotted silica tube trap technique with organic solven t atomization, considreable enhancements in sensitivities and detection limits were obtained compared to conventional Flame AAS. (Tables 3.8., 3.9.,3.10., 3.11.)

The sensitivities obtained for three techniques under optimum conditions are listed in Table 3.10., where the sensitivity is defined as the concentration of analyte that produces a peak absorbance of 0.0044.

Table 3.8. Detection Limits for 1.0 min. collection, 6 mL / min. suction rate (n = 15) (Te solutions were in 1 % (v/v) Nitric Acid.)

	Detection Limit, ng / mL		
	Flame AAS	Water – Cooled Atom Trap (52)	Slotted Silica Tube Trap
Te (IV)	450	150	6.79
Te (VI)	380	-	5.34

Table 3.9. Detection Limit Improvement Factors. 1.0 min collection, 6.0 ml / min suction rate. [Te solutions were diluted with 1 % (v/v) Nitric Acid]

	Detection Limit Improvement Factor		
	Flame AAS	Water – Cooled Atom Trap (52)	Slotted Silica Tube Trap
Te (IV)	1	10	66
Te (VI)	1	-	71

Table 3.10. Sensitivities in terms of characteristic concentration (for 1 % absorption). 1.0 min collection, 6.0 ml / min suction rate. [Te solutions were diluted with 1 % (v/v) Nitric Acid]

	Sensitivities in Terms of Charateristic Concentration, ng / mL		
	Flame AAS	Water – Cooled Atom Trap (52)	Slotted Silica Tube Trap
Te (IV) ng / mL	194	40	2.73
Te (VI) ng / mL	198	-	2.60

Table 3.11. Sensitivity Improvement Factors. 1.0 min collection, 6.0 ml / min suction rate. [Te solutions were diluted with 1 % (v/v) Nitric Acid]

	Sensitivity Improvement Factor		
	Flame AAS	Water – Cooled Atom Trap (52)	Slotted Silica Tube Trap
Te (IV) ng / mL	1	15	71
Te (VI) ng / mL	1	-	76

* Calik (52)

When the comparison was made between peak areas of Flame AAS and for Slotted silica tube trap technique for Te solutions, 25.3 % area efficiency was obtained. (See appendix C)

The precision of slotted silica tube trap method was not good. RSD values (for ten runs) were 12.3 %, 13 % for Te (IV) and Te (IV) respectively. The reason of bad RSD values for this tecnique is because of flame conditions. The sensitivity of this tecnique is highly dependent on the flame conditions. Continuity of the best flame conditions, during the experiment, is very difficult and not always the best flame conditions was found.

CHAPTER IV

CONCLUSION

In this study, Slotted Silica Tube Trap conditions were optimized for Te (VI) and Te (IV) species. For atomization, Organic Solvent Atomization method was used. At the optimized conditions, by using this atomizaiton method, enhancement factor for 71 and 66 were obtained in sensitivity for Te (VI) and Te (IV) respectively, compared to the conventional flame AAS.

An extensive interference study was done for Te species. A new method was used to understand whether the interference was in solid or in gas phase.

Low cost, simple instrumentation, ease of application, short analysis time and improved sensitivity that is close to sensitivity of ETAAS are advantages of slotted silica tube trapping technique. It is an alternative attractive alternative for other flame methods and traps presently used with the high sensitivity it offers. The atomization technique used is readily adaptable for automation.

In addition, when Te (VI) and Te (IV) species are prepared by deionized water they give diffferent absorbances for FAAS and Slotted Silica Tube Trapping techniques. However, if these species are prepared in acidic media, they have equal sensitivity for both Flame AAS and Slotted Silica Tube Trap Technique. The reason of sensitivity differences for both techniques is the precipitation at micro level that occurred in the Te (VI) solution when the dilution is made by H_2O.

Equilibrating the sensitivities of Te (IV) and Te (VI) allows an accurate calibration and analysis for total Te.

For the future work, the accuracy test will be done if a standard reference material is found. By means of accuracy test, for Te element, the slotted silica tube atom trap method coulde be validated for application to real samples.

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APPENDICES

APPENDIX A. GRAPHICAL REPRESENTATIONS OF INTERFERENCES FOR TE (VI)

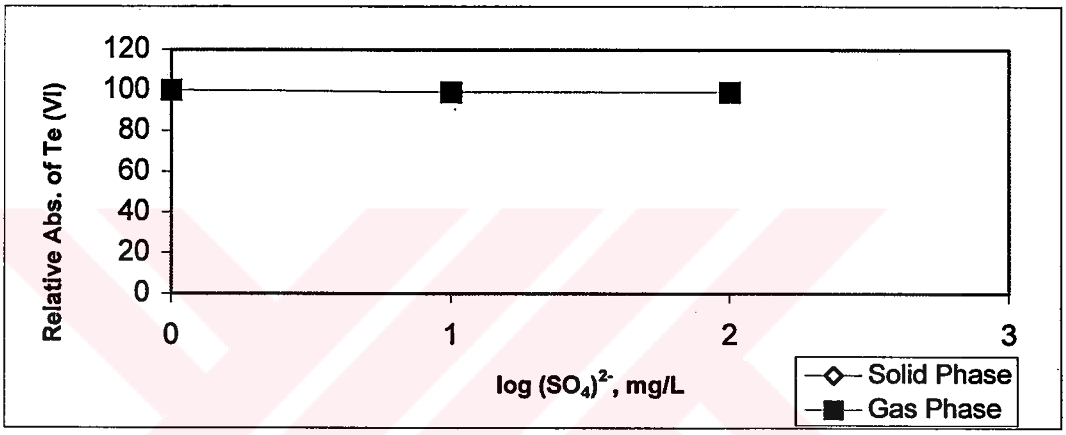

Figure A.1. Effect of $(NH_4)_2SO_4$

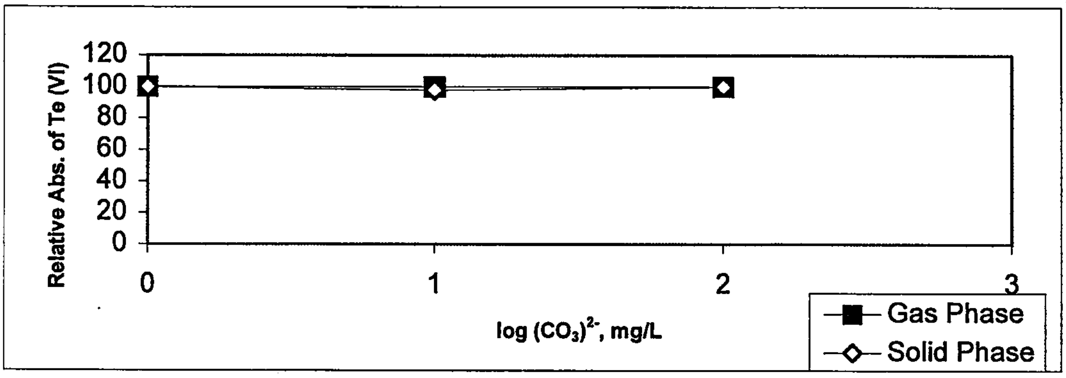

Figure A.2. Effect of $(NH_4)_2CO_3$

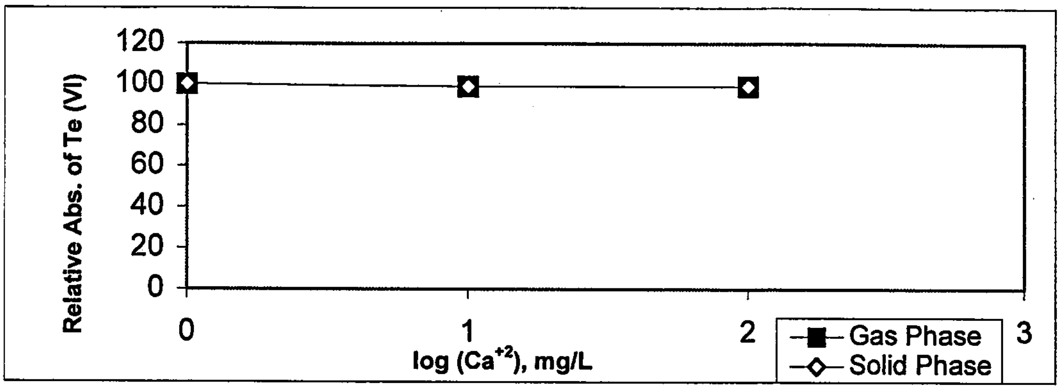

Figure A.3. Effect of $Ca(NO_3)_2$

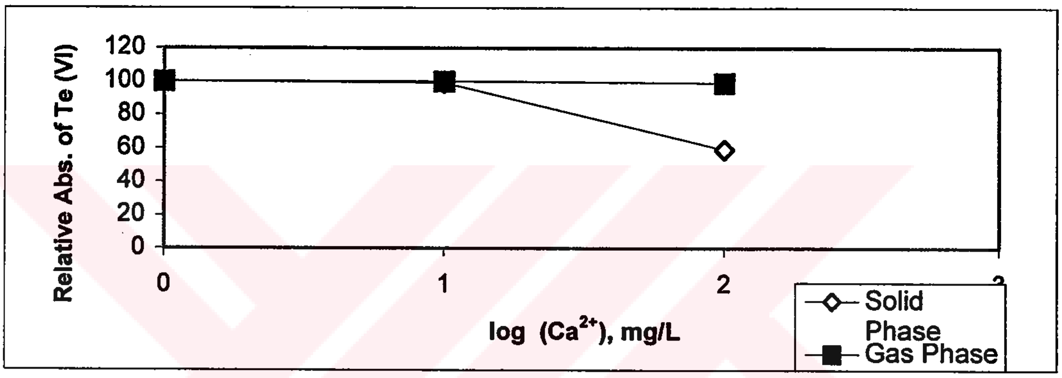

Figure A.4. Effect of $CaCl_2$

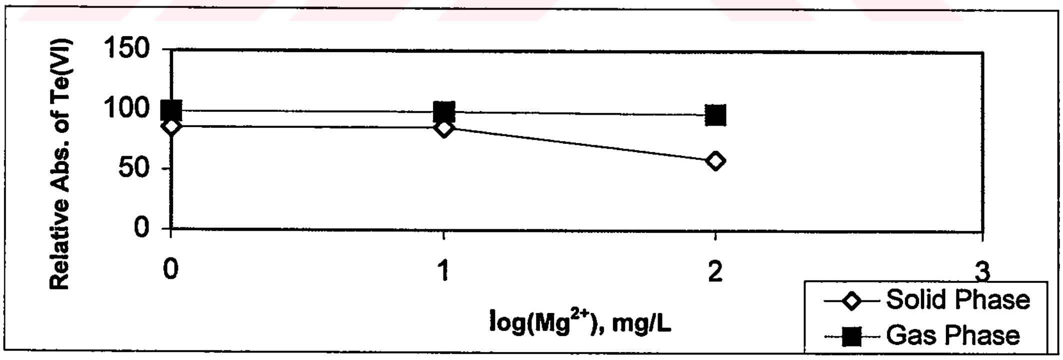

Figure A.5. Effect of $MgSO_4$

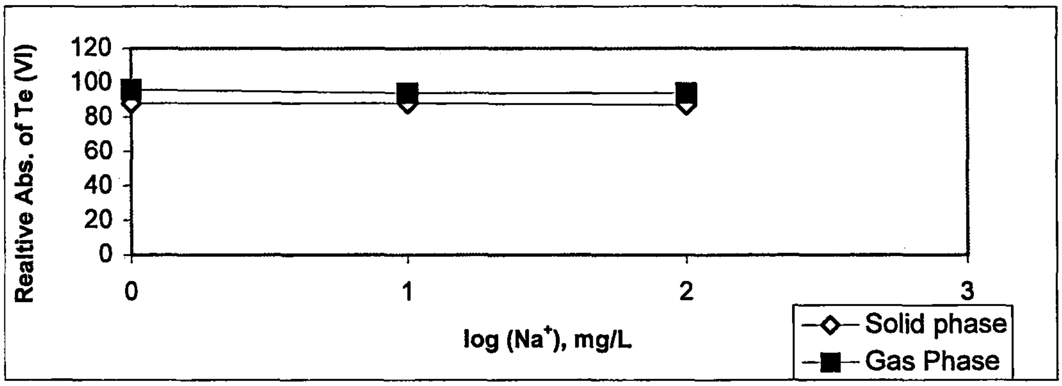

Figure A.6. Effect of NaCl

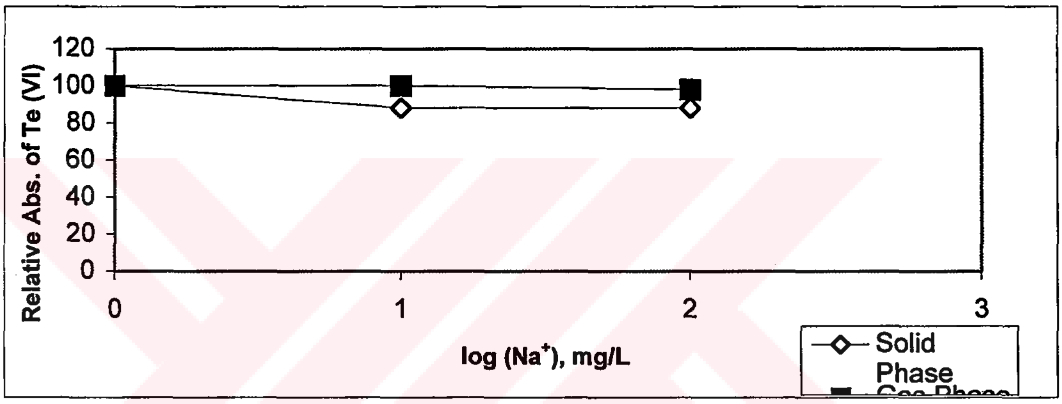

Figure A.7. Effect of $NaNO_3$

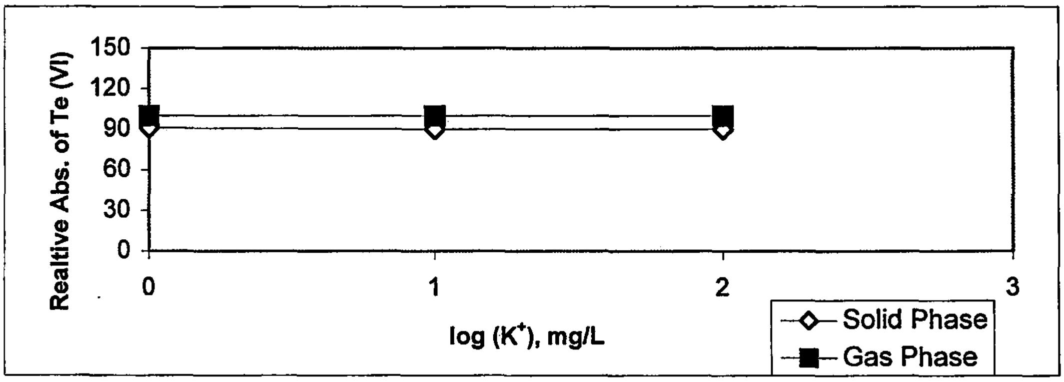

Figure A.8. Effect of KCl

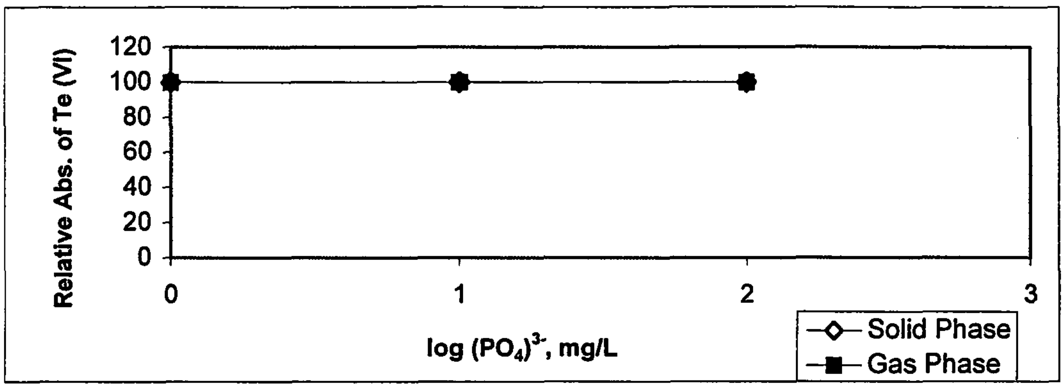

Figure A.9. Effect of $NH_4H_2PO_4$

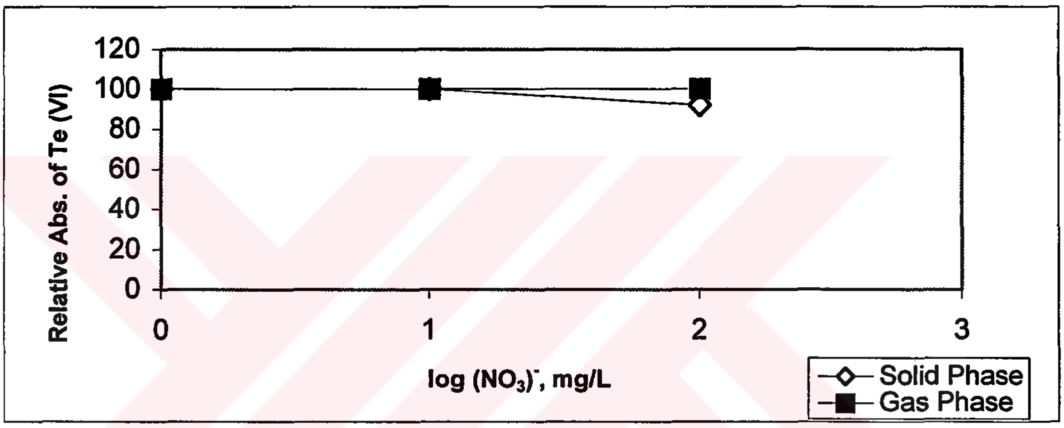

Figure A.10. Effect of NH_4NO_3

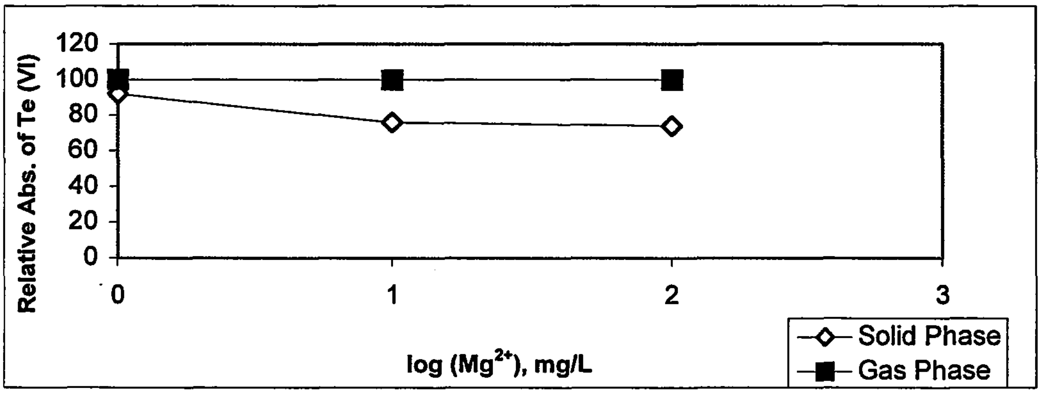

Figure A.11. Effect of $MgCl_2$

APPENDIX B. GRAPHICAL REPRESENTATIONS OF INTERFERENCES FOR TE (IV)

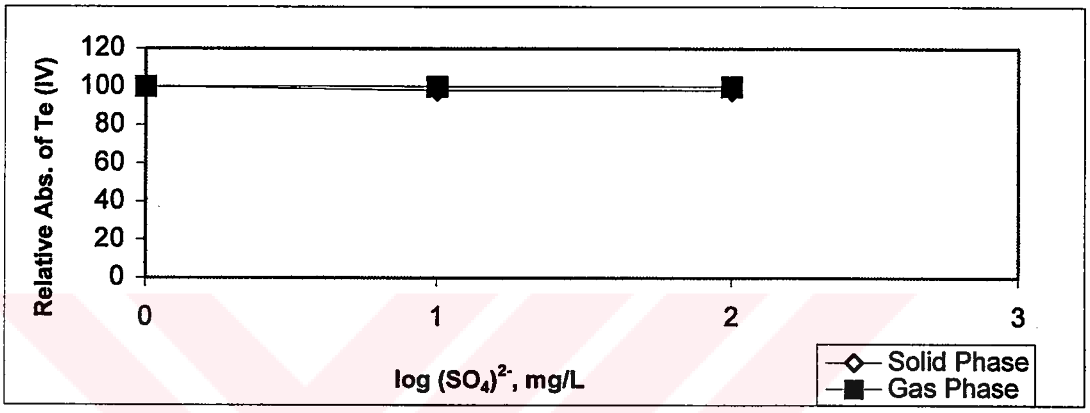

Figure B.1. Effect of $(NH_4)_2SO_4$

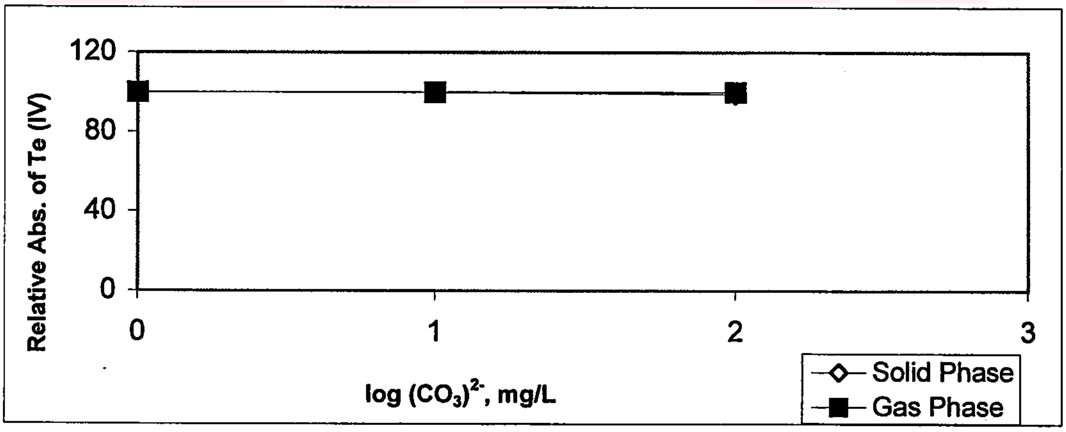

Figure B.2. Effect of $(NH_4)_2CO_3$

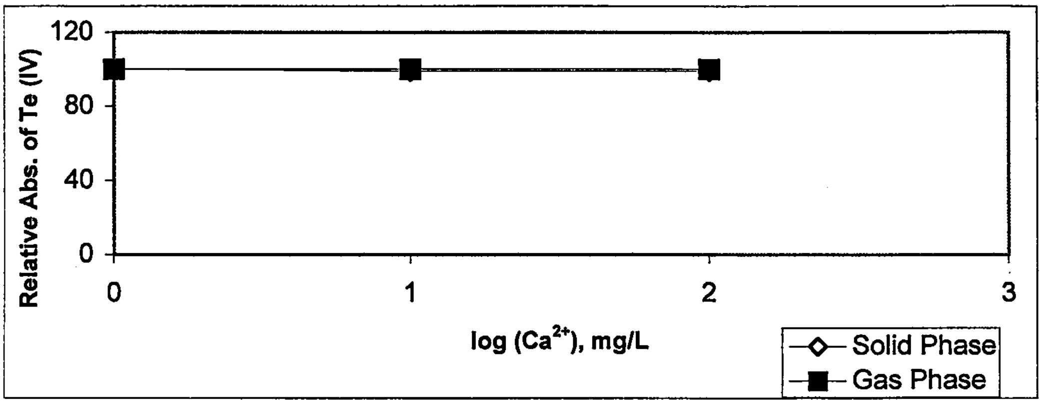

Figure B.3. Effect of $Ca(NO_3)_2$

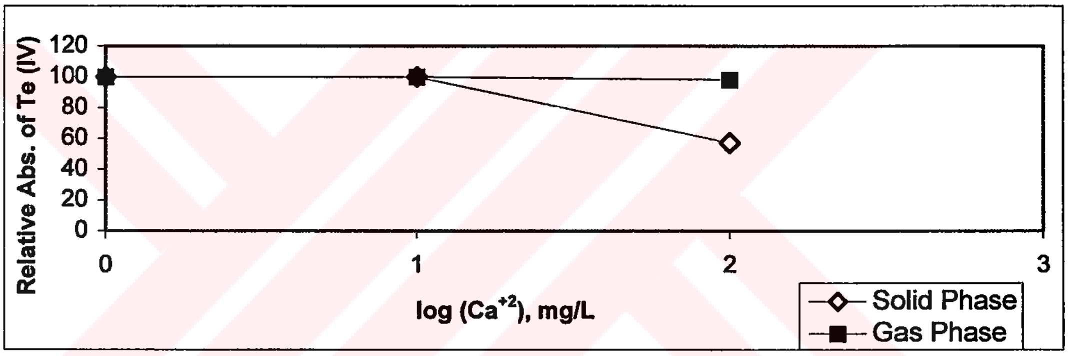

Figure B.4. Effect of $CaCl_2$

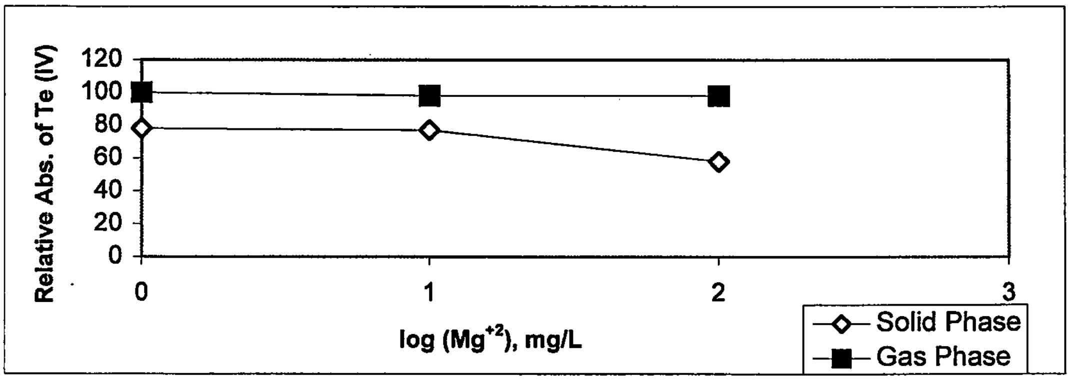

Figure B.5. Effect of $MgSO_4$

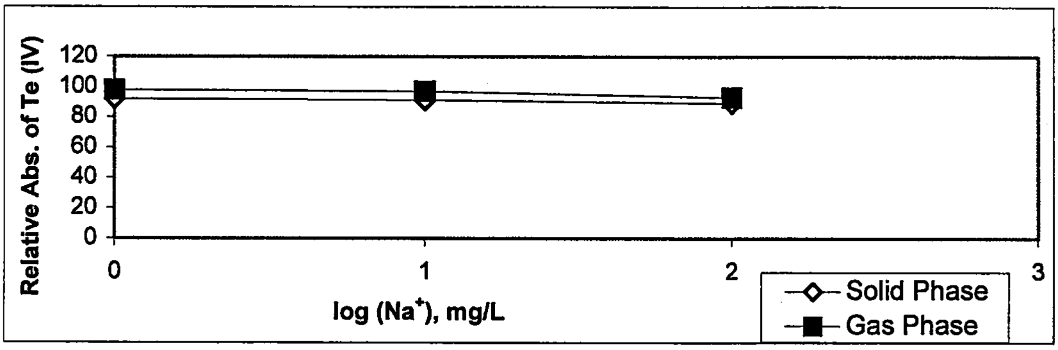

Figure B.6. Effect of NaCl

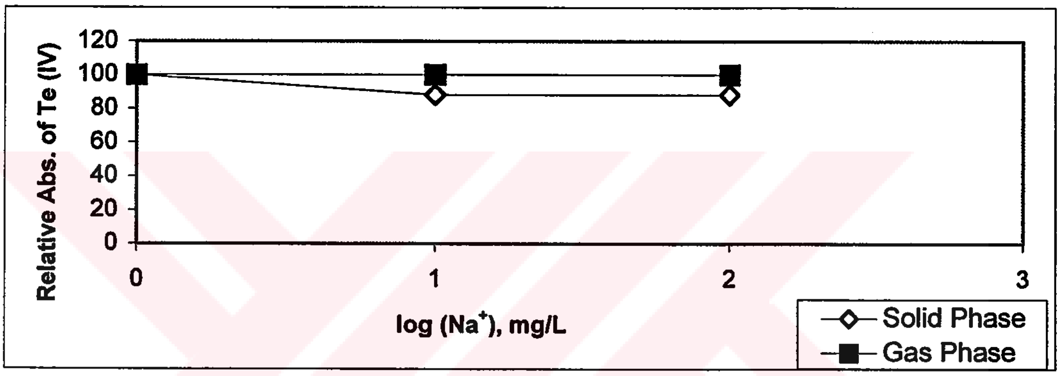

Figure B.7. Effect of $NaNO_3$

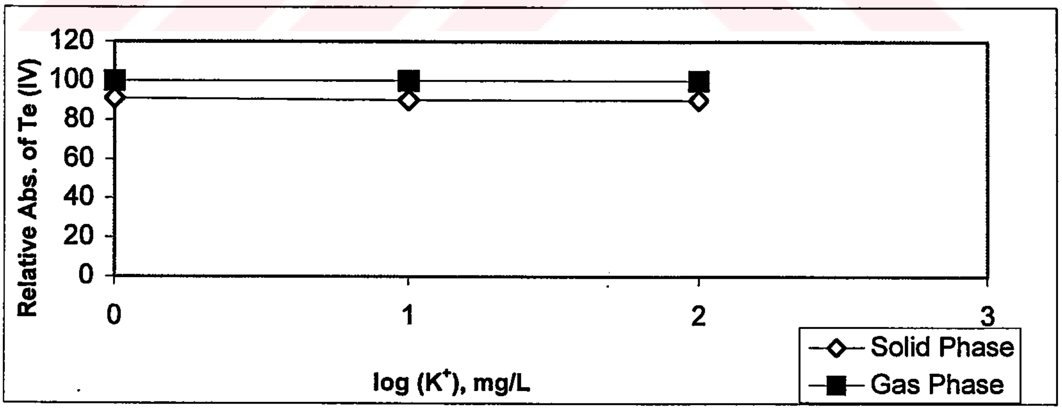

Figure B.8. Effect of KCl

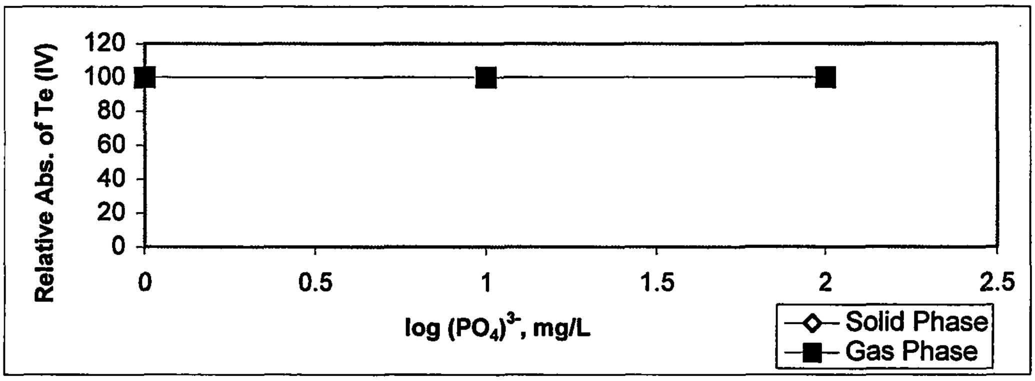

Figure B.9. Effect of $NH_4H_2PO_4$

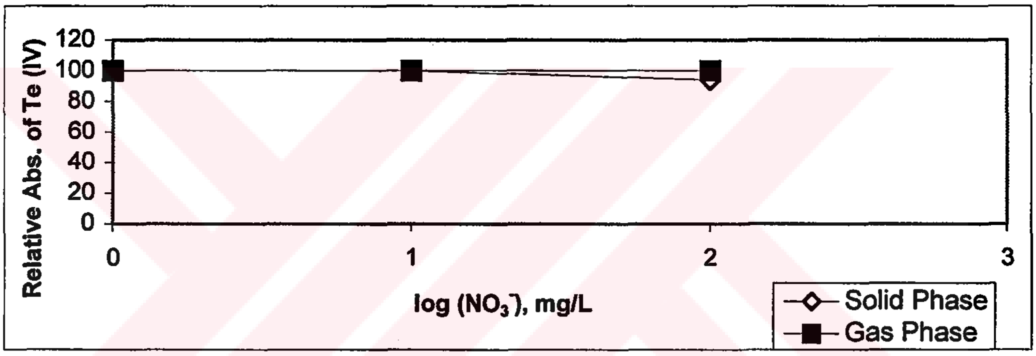

Figure B.10. Effect of NH_4NO_3

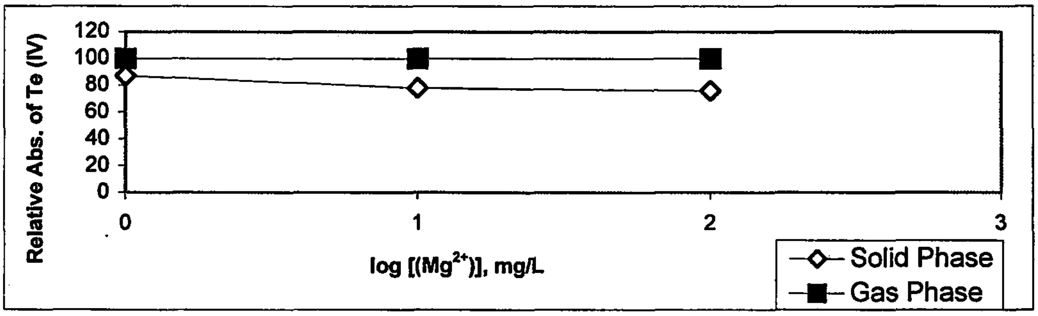

Figure B.11. Effect of $MgCl_2$

APPENDIX C. CALCULATION OF COLLECTION EFFICIENCY

A) On flame AAS

Concentration : 8.96 mg/L = 8960 ng/mL

Aspiration time : 5 s

Absorbance of the peak : 0.218

Area of the Peak (a) : 5 * 0.218 = 1.09 abs*s

B) Using Slotted Silica Trap Technique

Concentration : 89.6 ng/mL

Aspiration time : 60 s

Absorbance of the peak : 0.183

Bottom Length of the Peak (in tems of the s unit) : 0.36 s

Area of the peak (b) : (0.36 * 0.36) / 2 = 0.03312 abs.s

Efficiency : (b / a) * [Conc.of Te (IV) at FAAS / Conc. of Te (IV) Slotted S.T.] * [Aspiration time of FAAS / Aspiration time of Slotted S.T.] * 100

Efficiency : (0.03312 abs.s / 1.09 abs.s) * (8960 ng/mL / 89.60 ng/mL) * (5 s / 60 s) * 100 = 25.3 %