

**SEPARATION OF TRACE ANTIMONY AND
ARSENIC PRIOR TO HYDRIDE GENERATION
ATOMIC ABSORPTION SPECTROMETRIC
DETERMINATION**

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ABSTRACT

A separation method utilizing a synthetic zeolite (mordenite) was developed in order to eliminate the gas phase interference of Sb(III) on As(III) during quartz furnace hydride generation atomic absorption spectrometric (HGAAS) determination. The efficiency of the proposed separation method in the reduction of suppression effects of several metal ions on As(III) signal was also investigated. Among the volatile hydride forming elements and their different oxidation states tested (Sb(III), Sb(V), Se(IV), Se(VI), Te(IV), and Te(VI)), only Sb(III) was found to have a signal depression effect even at low ($\mu\text{g l}^{-1}$) concentrations under the experimental conditions employed. It has been shown that mordenite adsorbs Sb(III) quantitatively, even at a concentration of $1000 \mu\text{g l}^{-1}$, at pHs greater than 2, and also, it reduces the initial concentrations of the metal ions to lower levels which can be tolerated in many studies. The adsorption of Sb(III) on mordenite follows the Freundlich isotherm and is endothermic in nature.

ÖZET

As(III)'ün kuvars tüp ısıtmalı hidrür oluşturmali atomik absorpsiyon spektrometri ile tayini sırasında, Sb(III)'ün gaz fazı-girişim etkisini gidermek için sentetik zeolit (mordenit) kullanımını içeren bir ayırma yöntemi geliştirilmiştir. Önerilen ayırma yönteminin, bazı metal iyonlarının As(III) sinyaline olan girişim etkilerini azaltıp azaltamayacağı da araştırılmıştır. Uygulanan deneysel koşullarda, uçucu hidrür oluşturan bazı elementler ve bunların farklı yükseltgenme basamaklarının (Sb(III), Sb(V), Se(IV), Se(VI), Te(IV) ve Te(VI)) etkisi incelenmiş ve sadece Sb(III)'ün düşük derişimlerde ($\mu\text{g l}^{-1}$) dahi As(III) sinyalini bastırıldığı gözlenmiştir. pH'nın 2'den yüksek olduğu durumlarda mordenitin, $1000 \mu\text{g l}^{-1}$ Sb(III) çözeltisindeki Sb(III)'ün tamamını tuttuğu, çözeltideki metal iyonlarının derişimini de kabul edilebilir seviyelere indirdiği gösterilmiştir. Sb(III)'ün mordenit üzerinde tutunmasının Freundlich izoterm modeline uyduğu ve adsorpsiyonun endotermik olduğu belirlenmiştir.

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CHAPTER 1

INTRODUCTION

1.1. Arsenic and Antimony in the Environment

1.1.1. Arsenic

Arsenic is a natural element in the environment. It can be found in soil and in many kinds of rock, especially in minerals and lead and copper ores. It may be released from wind-blown dust and may reach water from runoff and leaching, and during the mining and smelting of these ores. Arsenic is used as a preservative for wood to enhance its resistance to decay. Organic arsenicals are used as pesticides, largely on cotton. Small quantities of metallic arsenic are added to other metals forming alloys with improved properties. Another use of arsenic in alloys is in lead-acid batteries used in automobiles. Arsenic compounds are also applied in the production of semiconductors and light-emitting diodes (Chou and De Rosa 2003).

Arsenic is distributed in the environment in several oxidation states (-3, 0, +3 and +5) but mostly found in inorganic form as oxyanions of trivalent arsenite, As(III), or pentavalent arsenate, As(V), in natural waters. Organic As forms, such as monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), arsenocholine and arsenobetaine, may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important. Organic forms may however occur where waters are significantly impacted by industrial pollution.

Arsenic is a toxic element that is also a known carcinogen (WHO 2001). In general, organoarsenic compounds are reported to be less toxic than their corresponding oxyacids (Melamed 2005). The WHO guideline value for arsenic in drinking water is $10 \mu\text{g l}^{-1}$ (WHO 1993). The same concentration, $10 \mu\text{g l}^{-1}$, is given by USEPA as the maximum contamination level (USEPA 1999). The range of arsenic concentrations found in natural waters is wide, ranging from less than $0.5 \mu\text{g l}^{-1}$ to more than

5000 $\mu\text{g l}^{-1}$. Typical concentrations in freshwater are less than 10 $\mu\text{g l}^{-1}$ and some waters have concentrations smaller than 1 $\mu\text{g l}^{-1}$. Much higher concentrations are found, particularly in groundwater.

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidizing conditions, H_2AsO_4^- is dominant at low pH (less than about pH 6.9), whereas HAsO_4^{2-} becomes dominant at high pH (Figure 1.1). H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions, respectively. Under reducing conditions, the uncharged arsenite species H_3AsO_3 will predominate at pH values smaller than about 9.2 (Smedley and Kinniburgh 2002).

The distribution of the species as a function of pH is given in Figure 1.2. For arsenite, distribution is simple; for instance, at lower pH's H_3AsO_3 and at high pH's H_2AsO_3^- predominates. For arsenate, the percentage of the species (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}) changes in accordance with pH.

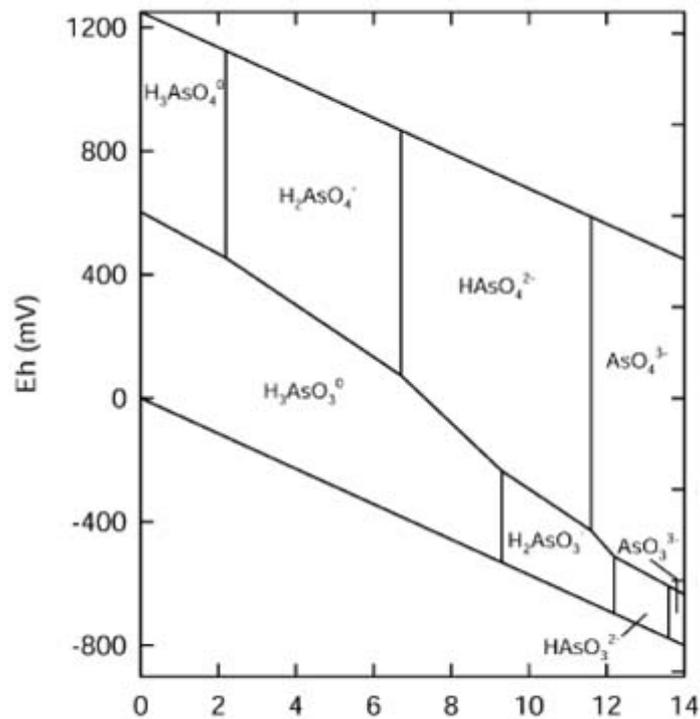


Figure 1.1. Eh-pH diagram for aqueous As species in the system As–O₂–H₂O at 25 °C and 1 bar total pressure (Smedley and Kinniburgh 2002).

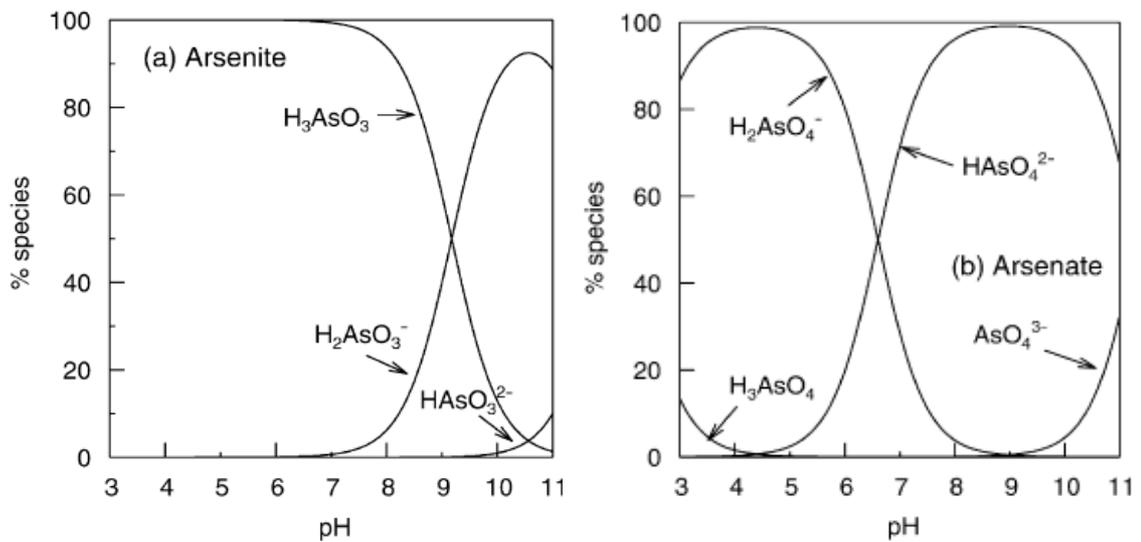


Figure 1.2. (a) Arsenite and (b) arsenate speciation as a function of pH (ionic strength of about 0.01M). Redox conditions have been chosen such that the indicated oxidation state dominates the speciation in both cases (Smedley and Kinniburgh 2002).

1.1.2. Antimony

Antimony occurs in nature as Sb_2S_3 (stibnite, antimonite) and Sb_2O_3 (valentinite), which is a transformation product of stibnite. These compounds are commonly released from the ores of copper, silver, and lead. Antimony is also a common component of coal and petroleum (Fiella et al. 2002a).

Antimony is used in semiconductor technology for making infrared detectors, diodes, and also in production of batteries, antifriction alloys, small arms and tracer bullets. Oxides/sulphides of antimony, sodium antimonate, and antimony trichloride are used in manufacturing flame-proofing compounds, paints, ceramic enamels, glass, and pottery. Tartar emetic (hydrated potassium antimonyltartrate) is used in medicine (WEB_1 (2005)).

Antimony can be present in four different oxidation states: -3, 0, 3, 5. However, in environmental samples it is mainly found in two oxidation states, III and V. Typical concentrations of antimony in environmental samples are reported to be very low, ranging from a few $ng\ l^{-1}$ in freshwaters to $200\ ng\ l^{-1}$ in oceans and of the order of a few $\mu g\ g^{-1}$ for sediments, soils and biota samples (Fiella et al. 2002a).

Antimony and its compounds are considered as pollutants. For drinking water, the maximum allowed concentrations are given as $6 \mu\text{g l}^{-1}$ (USEPA 1999) and $5 \mu\text{g l}^{-1}$ (Council of European Union 1998) by USEPA and Council of European Union, respectively. Chemical and toxicological properties of antimony are similar to arsenic and trivalent species are reported to be more toxic than pentavalent forms (Gebel 1997).

According to thermodynamic equilibrium, antimony exists as Sb(V) in oxic systems and as Sb(III) in anoxic ones (Fiella et al. 2002b). The redox behavior of antimony can be understood by its Eh-pH diagram, such as given for Sb-S-H₂O system at environmentally relevant concentrations for antimony and sulfur (Figure 1.3). According to this diagram, it is stated that antimony is present as soluble Sb(OH)_6^- in oxic systems and as soluble Sb(OH)_3 in anoxic ones at natural pH values. Under reducing conditions, and in the presence of sulfur, stibnite, $\text{Sb}_2\text{S}_3(\text{s})$, is formed at low to intermediate pH values. At higher pH values, the $\text{Sb}_2\text{S}_4^{2-}$ species replaces stibnite.

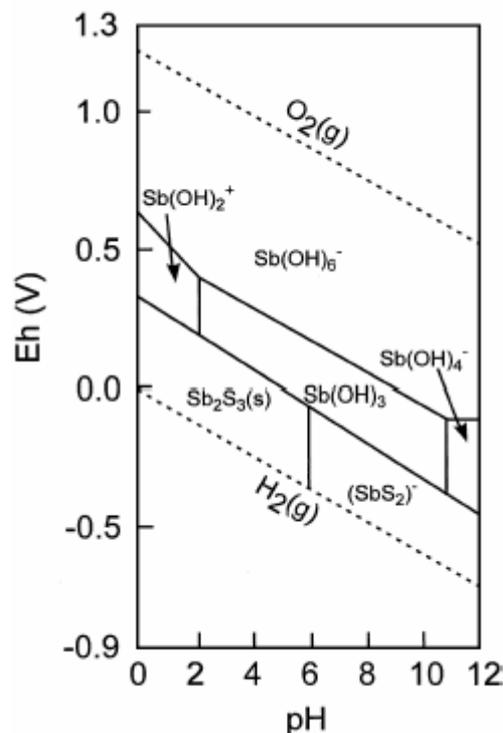


Figure 1.3. Eh-pH diagram of antimony in the Sb-S-H₂O system at a dissolved antimony concentration of 10^{-8} mol/L and a dissolved sulfur concentration of 10^{-3} mol/L (Fiella et al. 2002b).

1.2. Speciation

It is a well-known fact that the toxicity, bioavailability, and transport properties of an element are highly dependent on its chemical form. In the past, total quantification of an element was used to determine potential health hazards or benefits, but in recent years, it has been accepted that elemental quantification alone is not sufficient. To completely understand the ways in which particular elements will affect living organisms, it is necessary to determine and to quantify the chemical form of such elements in the sample, be they inorganic or organic forms (species).

Analysis performed to identify and quantify one or more distinct chemical species in a sample is known as “speciation analysis”. International Union of Pure and Applied Chemistry (IUPAC) states that speciation is “the process yielding evidence of the atomic or molecular form of an analyte” (Caroli 1996 p.1-2).

One of the important points of speciation analysis is to preserve the integrity of the sample and the species of interest during sampling, sample storage and pretreatment, such as dissolution, extraction and preconcentration. Any treatment that would result in a shift of equilibria or in a destruction or transformation of one species into another must be carefully avoided. Another important point is sensitivity as the elements of interest are usually trace constituents, and the individual species are obviously only a fraction of this trace (Welz 1998).

Selectivity and sensitivity are two important factors for a successful speciation analysis. These two issues can be achieved using on-line coupling of chromatographic or electrophoresis technique with an element selective detector (atomic absorption, emission, fluorescence, or mass spectrometry, inductively coupled plasma, or microwave induced plasma) (Kot and Namiesnik 2000).

1.2.1. Speciation of Arsenic Compounds

Arsenic is commonly found all over the environment in various chemical species that vary in toxicity and mobility. These species can be readily transformed by such events as biological activity, changes in redox potential, or pH. The actual toxicity levels for different arsenic compounds vary greatly. Arsenite, As(III), is more toxic than arsenate, As(V). In order to understand threat of arsenic in the environment for remedy

decisions, the analysis of environmental samples should include identifying and quantifying both the total amount and the different chemical forms of arsenic present. Speciation analysis of arsenic usually requires the coupling of proper sample preparation with two analytical techniques: first, a technique to separate the chemical forms of arsenic, and second, a sensitive detection. In order to identify and measure different arsenic species, numerous analytical methods of separation and detection have been proposed.

Some workers achieved speciation of arsenic by the principle of biosorption. Calzada et al. (1998) proposed the use of the alga *Chlorella vulgaris* for the separation of As(III) from the other arsenic species. The arsenic concentration is determined by hydride generation atomic absorption spectrometry (HGAAS). Koh et al. (2005) bonded *Saccharomyces cerevisiae* onto the controlled pore glass covalently, which showed selective preconcentration of As(V) over As(III). The effluent was directly connected to HG-ICP-AES. The optimum pH for the retainment of arsenic at the column was 7. As(V) and As(III) were completely separated in a few minutes with the flow rate of 1.5 ml min⁻¹. Nitric acid (3.0 M) was adequate for the elution of As(V).

An interesting approach is that suggested by Burguera et al. (1991), is based on the selective generation of arsine from As(III) through the use of the old Fleitman reaction with Al in NaOH. The method is reported to be suitable for on-line direct determination of As(III) and As(V) after on-line reduction with KI. A batch electrochemical hydride generation system was developed for the spectrophotometric determination of inorganic As(III) by silver diethyldithiocarbamate (Zavar and Hashemi 2000). This method was based on the electrochemical reduction of arsenic to arsine (AsH₃) in acidic media and on the subsequent reaction of AsH₃ with silver diethyldithiocarbamate to give an absorbing complex at 525 nm. Dambies et al. (2000) developed a new adsorption process for As(V) ion removal from an aqueous solution using molybdate-impregnated chitosan beads. The sorption mechanism is reported to be a complexation reaction between arsenate and molybdate ions. The arsenic concentration was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). Determination of ultratrace amounts of As(III) and As(V) in natural waters by inductively coupled plasma mass spectrometry (ICP-MS) coupled with flow injection (FI) online preconcentration and separation in a knotted reactor after forming APDC complex was reported by Yan et al. (1998). Detection limits were 21 ng l⁻¹ for As(III) and 29 ng l⁻¹ for total inorganic arsenic.

Several authors have also reported the separation and quantifying organo-arsenic species. Yalçın and Le (2001) used and tested the retention and elution characteristics of different sorbent materials for As(III) and As(V), MMA and DMA. The authors reported that alumina retained all four arsenic species whereas strong cation exchange resin was used for DMA (eluted with 1.0 M HCl) and a silica-based anion exchanger was used for MMA and As(V). MMA was eluted with 60 mM acetic acid and As(V) was eluted with 1.0 M HCl. As(III) remained in solution. They used flow injection hydride generation atomic fluorescence spectrometry (FI-HGAFS) and hydride generation atomic absorption spectrometry (HGAAS). Simon et al. (2004) described an on-line decomposition method based on UV photooxidation for the analysis of organoarsenic species by coupling cation exchange chromatography and atomic fluorescence spectrometry with hydride generation. In this study, aqueous pyridine solutions were used as mobile phase and fully compatible solutions, such as potassium nitrate, nitric acid and sodium hydroxide solutions were used in order to reduce the inhibition of signal by mobile phase. Tsalev et al. (2000) suggested on-line pre-reduction and complexation of As(V), methylarsonate and dimethylarsinate with L-cysteine at elevated temperature in a flow injection hydride generation atomic absorption spectrometry (FI-HGAAS) system and HPLC separation of these complexes on a strongly acidic cation-exchange column. Another study was about speciation of As(III), As(V), MMA, DMA, arsenobetaine and arsenocholine that was carried out in mineral water and soil leachate using capillary electrophoresis followed by ICPMS (Van-Holderbeke et al. 1999).

1.2.2. Speciation of Antimony Compounds

Antimony is mainly distributed as inorganic Sb(V) and Sb(III) in environmental, clinical and geochemical samples. However, some organic antimony compounds are also reported to be present in environmental samples. As mentioned earlier, the inorganic species of antimony are more toxic than methylated ones, and Sb(III) is more toxic than Sb(V). Because of the large differences regarding their toxic properties, speciation is required (Gebel 1997).

A high number of studies regarding the separation of Sb(III) and Sb(V) and determination of their concentrations with a subsequent detection system can be found

in literature. Yan et al. (1996) coupled a FI on-line sorption preconcentration system and electrothermal atomic absorption spectrometry (ETAAS) for the selective determination of Sb(III) in sea water where it was complexed with ammonium pyrrolidine dithiocarbamate (APDC), followed by sorption onto the inner walls of a knotted PTFE reactor and quantitative elution with ethanol. Speciation of antimony using HG-ICP-AES based on the pre-reduction kinetics of Sb(V) to Sb(III) with L-cysteine has also been reported by Feng et al. (1999) with detection limits of 1.2 and 4.5 ng ml⁻¹ for Sb(III) and Sb(V), respectively. Huang et al (1997) investigated different effects of micellar media on the absorption spectra of the complexes of bromopyrogallol red with Sb(III) and Sb(V). In this work, a mixed micellar medium composed of sodium dodecylsulfate and nonylphenoxypolyethoxyethanol at 80°C was used for the sensitive determination of Sb(III) in Sb(III)/Sb(V) binary mixtures. Garbos et al. (1999) used selective sorption of the Sb(III) chelate with APDC on a C₁₆-bonded silica gel microcolumn for the determination of Sb(III) and total inorganic antimony after reducing Sb(V) with L-cysteine. The microcolumn was connected to the tip of the ETAAS autosampler, and the sorbed antimony was directly eluted with ethanol; the detection limit was 0.007 ng ml⁻¹.

In recent years, hyphenated techniques have been reported in large number of research articles; i.e., the online combination with suitable element specific detectors of modern separation techniques such as GC, HPLC, CE. A procedure for the separation and determination of inorganic species of antimony based on the use of coupled HPLC-HG-atomic fluorescence spectrometry (AFS) is described. Sb(III) and Sb(V) were separated on a miniaturized anion-exchange column (Supelcosil LC-SAX) using a 0.06 mol l⁻¹ ammonium tartarate aqueous solution at pH 6.9 as eluent (Sayago et al. 2000). Zheng et al. (2000) explored the potential of size-exclusion chromatography (SEC) for the separation of both inorganic and organic antimony compounds, and demonstrated that Sb(III), Sb(V), and trimethylantimony dichloride (TMSbCl₂) could be separated on an Asahipak HG-520 SEC column with 50 mmol l⁻¹ Tris buffer (pH 7.4). Under these conditions, the sharp and symmetric peaks of Sb(V) and TMSbCl₂ could be baseline-separated. Krachler and Emons (2001) employed HPLC-ICP-MS for the speciation of Sb(III), Sb(V), and TMSbCl₂. The two inorganic Sb species Sb(III) and Sb(V) as well as TMSbCl₂ were separated by anion exchange chromatography. HPLC eluents were directly aspirated into the plasma of an ICP-MS using ultrasonic nebulization with membrane desolvation. GC-ICP-MS was employed by Feldmann et al. (1998) to study

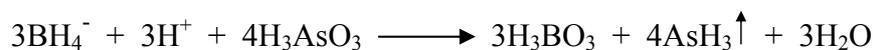
the presence of volatile antimony compounds in landfill and fermentation gases. Complementary capillary GC-MS (CGC-MS) determinations in the electron ionization mode were used to provide data about parent ions, fragmentation patterns, and isotopic ratios for the first time. Trimethylantimony (Me_3Sb) was the only volatile antimony species detected in the analyzed landfill and fermentation gases. Detection limits of 0.2 ng Me_3Sb and 0.3 pg Me_3Sb was achieved for GC-MS and CGC-ICPMS, respectively.

1.3. Hydride Generation Atomic Absorption Spectrometry (HGAAS)

As mentioned in the previous section, there are many methods for the determination of antimony and arsenic in various matrices such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic fluorescence spectrometry (AFS), inductively coupled plasma mass spectrometry (ICP-MS), UV-VIS spectrophotometry. Hydride generation atomic absorption spectrometry (HGAAS) is probably the most popular technique for the determination of arsenic and antimony, either directly or after a suitable pretreatment step. The elements Ge, Sn, Pb, As, Sb, Bi, Te, and Se form covalent gaseous hydrides. The generation of volatile hydrides enables a very efficient analyte introduction other than an efficient matrix removal in AAS. The basic design of a hydride generation system, with subsequent atomic absorption spectrometric detection may be considered as composed of four steps: generation of hydride, collection of the hydride (if necessary), transfer of the hydride to the atomizer, and atomization of hydride (Godden and Thomerson 1980). In order to increase the signal it is necessary to generate the hydride quickly or to collect it and then transfer it as quickly as possible to the atomizer. This minimizes dilution of the hydride by the carrier gas. Such a procedure enhances the detection limits by a factor of 10 to 100. Due to the high toxicity of these species, their determination at low concentration levels has significant importance.

Several reagents have been used to convert the analyte element into its hydride for analytical purposes. In most early work, a metal-acid reducing system was employed, such as $\text{SnCl}_2\text{-HCl-KI-Zn}$ and $\text{TiCl}_3\text{-HCl-Mg}$ (Godden and Thomerson 1980). However, the most convenient and currently used method is $\text{NaBH}_4\text{-acid}$ system.

A typical hydride generation reaction is given below with As(III) as the analyte and NaBH₄ as the reductant (Skoog et al. 1998 p.203).



After the hydride is evolved, it is transferred in two principal ways: either the hydride is conveyed directly into the atomizer as it is generated, or a trap is used before it is being transferred to the atomizer (Yan and Ni 1994).

For atomization of gaseous hydrides, the argon (or nitrogen)-hydrogen diffusion flame was initially used. Soon after the development of the hydride generation the use of electrically heated or flame heated quartz tubes were proposed for the atomization. Quartz tube atomizers offer the advantage of higher sensitivity and negligible background attenuation. The silica tube is mostly mounted in a holder and the analyte hydrides are normally introduced at the center of the heated quartz tube. The tube length and diameter have a complex influence on the analyte signal and on interferences due to contaminants (Dedina and Tsalev, 1995 p.91-117).

Popularity of HGAAS arises from the following advantages: separation of analyte from the sample matrix, high efficiency of sample introduction, good sensitivity, ease of automation, and possibility of chemical speciation.

1.3.1. Interferences in HGAAS

The interferences in HGAAS are very well outlined by Dedina and Tsalev (1995 p.91-117). As outlined in this monograph, these interferences are generally examined in two groups: spectral and nonspectral. Spectral interferences occur when the radiation is absorbed by species other than free atoms of the analyte. Nonspectral interferences are caused by the influence of sample components on the analyte signal.

Spectral interferences are usually of less important in this technique because of the separation of the analyte from the matrix. Line interferences are not seen but nonselective background absorption can be observed. Background absorption occurs more often when a collection device is used in conjunction with the argon-hydrogen

flame. When the collected hydride is released to the flame, the flame transparency decreases, and therefore a non specific absorption signal is obtained.

Nonspectral interferences are observed in both the liquid phase and the gas phase. The interferences which occur during hydride formation and its transfer from solution are the liquid phase interferences and the gas phase interferences which affect the analyte in the gaseous phase.

1.3.1.1. Gaseous Phase Interferences

As mentioned in the monograph by Dedina and Tsalev (1995 p.91-117), gaseous phase interferences are obviously caused by volatile species, most often by hydrides but also by other compounds or by liquid spray produced in a hydride generator. These interferences can take place on the surface or in the dead volume of generator, the connective tubing or the atomizer. Gaseous phase interferences could have either a direct effect if they are observed only simultaneously with generation of the interferent or a memory effect if they continue after the generation of the interferent ends. Gaseous phase interferences can be divided into two groups, according to their origin:

a) Transport interferences: They take place during passage of hydride from the sample solution to the atomizer. These interferences may cause delay or loss in collection devices of hydride collection generators. Transport interferences which cause delay are called transport kinetic interference and those causing loss of hydride are called transport efficiency interference. Similar to the case of liquid phase interferences, a process leading to transport efficiency interference may need not cause transport kinetics interference.

b) Interferences in the atomizer: They depend on the mechanism of hydride atomization and on analyte transfer in the atomizer. In principle, they might either reduce the integral atomization efficiency that is called atomization efficiency interference or they might delay analyte in the atomizer.

1.3.1.2. Liquid phase interferences

Liquid phase interferences can be seen according to the changes in the rate of hydride release from the liquid phase. This kind of liquid phase interferences are named release kinetics interference and when the liquid phase interferences are the result of the decrease in efficiency of hydride release they are called release efficiency interferences. They are caused by interfering species present in sample solutions.

There are many kinds of interferences in the liquid phase but all is observed into two basic groups: compound interferences and matrix interferences (Dedina and Tsalev 1995 p.91-117). If the characteristic of the analyte in the sample and in the standard solution are not the same, release of hydride may be different from the sample than from the standard, even if the standard is added to the sample. Therefore, the compound interferences arise. These interferences take place if organic bonds of analyte were not completely decomposed during sample pretreatment or if the analyte is in the elementary form or in a valency which is converted to hydride with lower efficiency or at a slower rate than the analyte valency in the standard. The compound interferences also occur when a different analyte form arises as a result of an irreversible reaction of analyte with a matrix component present in a sub-stoichiometric concentration.

If the concentration of the sample matrix is higher than the stoichiometric concentration, the added standard is influenced in the same way as analyte and as a result the matrix interference occurs. Matrix interferences take place when matrix components affect the hydride release efficiency. There are many sources of the matrix interference; every physical or chemical process preventing analyte being converted to hydride or formed hydride being released from the reaction mixture are some of the reasons of matrix interferences. Obviously, some interferences are element specific. The most common type of matrix interferences are the interferences of dissolved inorganic compounds. The inorganic interferences can be classified as:

(i) *Ion-ion interference*: Before the sodiumborohydride addition, the analyte in ionic form reacts with the interferent also in ionic form in the sample solution, and then the analyte is converted to a compound which is not reduced to hydride or which is reduced with lower efficiency. The compound, analyte and interferent are in equilibrium so that, in contrast to compound interferences, the same interference magnitude is observed for a standard added to the sample.

(ii) *Ion-product interference*: When the interferent reacts with sodium borohydride some species produces which captures the analyte in the ionic form resulting in a decrease in efficiency of the hydride release.

(iii) *Hydride ion interference*: Formed hydride is bonded by the dissolved interferent present in ionic form.

(iv) *Hydride-product interference*: Hydride is captured by species produced by the reaction of interferent with tetrahydroborate.

(v) *Sodiumborohydride depletion interference*: The reducing agent is consumed by the interferent.

Inorganic interferents can be divided into three groups; strong oxidants (Cutter 1983), ions of transition and noble metals, e.g. Ni, Cu, Co, Fe, Ag, Au, Pd, Pt, Rh (Bax et al. 1988, Welz and Sucmanova 1993, Campos et al. 2002, Welz and Melcher 1984), other species including ions of hydride forming elements (Ay and Henden 2000, Dedina 1982, Welz and Melcher 1981, Erdem and Henden 2004).

1.3.1.2.1. Reduction of Matrix Interferences

Many studies have been performed in order to reduce the interferences in HGAAS, especially caused by transition metal ions and volatile hydride forming elements. Welz and Jacobs (1986) studied the influence of acid and sodium borohydride concentrations to reduce the interference of transition metal ions in arsenic and selenium determination and concluded that higher acid-lower sodium borohydride concentrations improve the interference-free determination. Brindle and Le (1990) used thiol containing compounds and amino acids for the enhancement of signals. Moreover, reducing agents such as L-cysteine (Brindle and Le 1990), and thiourea (An et al. 1992) were also used for the reduction of transition metal ion interferences. Campos et al. (2002) suggested picolinic acid and L-cysteine mixture to eliminate Cu and Ni interferences and tolerable concentrations were found up to 4000 and 1000 mg l⁻¹ of nickel and copper, respectively.

Another important interfering group is volatile hydride forming elements that have mutual interferences during determination (Dedina and Tsalev 1995 p.98). Welz and Melcher (1981) removed the effect of Se(IV) on As(III) and As(V) adding copper to the sample solution. The authors explained the mechanism in a way that, selenium

hydride, which is formed first, reacts with copper ions in the solution to form insoluble selenides (CuSe) whereas copper arsenide (Cu_5As_2) is soluble in acids. Therefore, the evolution of selenium hydride from solution, and its interference on arsenic signal, is prevented. On the other hand graphite tube atomizers at temperatures $> 2000\text{ }^\circ\text{C}$ was suggested by Dittrich and Mandry (1986). The mechanism was explained as the formation of diatomic molecules between analyte and matrix elements such as AsSb. The effect of KI on the interferences by Bi, Se and Te on Sb signal and the interferences of Sb, As, Bi, Te, and Sn on the Se signal using oxygen and a mixture of ozone were examined by Barth et al (1992). In a study by Ay and Henden (2000), a separation procedure using a GC column was applied to eliminate the inter-element interference of arsenic and antimony. In the GC column, arsine is eluted first and separated from stibine. The authors suggest taking stibine outside the atomizer for arsenic determination. In the next study by Erdem and Henden (2004), a pyrex adsorption U-tube trap containing glass wool was placed between the drying tube and quartz tube atomizer and the mutual interference between arsenic and antimony was investigated by selective heat decomposition of arsine and stibine.

1.4. Aim of This Work

As can be seen from the previous section, there are many studies on the reduction of HGAAS interferences during determination. In the present study, a different approach is proposed for the elimination/reduction of interferences on arsenic HGAAS signal. For the separation of As(III) and Sb(III) before hydride generation step a synthetic zeolite (mordenite) was used. It has also been shown that the proposed separation method has the ability to reduce the extent of metal ion interferences to a tolerable level.

CHAPTER 2

EXPERIMENTAL

2.1. Chemicals and Reagents

All reagents were of analytical grade. 18 M Ω ultra pure water was used throughout the study. Glassware and plasticware were cleaned by soaking in 10 % (v/v) nitric acid and rinsed with distilled water prior to use.

1. Standard As(III) stock solution (200 ppm): prepared by dissolving 0.131 g of As₂O₃ (Fischer) in 10 ml of 1 mol l⁻¹ NaOH, adding 5 ml of 1 mol l⁻¹ H₂SO₄ (Merck) diluting to 500 ml with ultra pure water.
2. Standard As(V) stock solution (1000 ppm): prepared by dissolution of 0.1534 g of As₂O₅ (Fischer) in 500 ml ultra pure water, 1% (v/v) HCl.
3. Standard Sb(III) stock solution (1000 mg l⁻¹): Prepared by dissolution of 1.408 g of potassium antimony tartrate (C₄H₄KO₇Sb) (Sigma) in 500 ml ultra pure water.
4. Standard Sb(V) stock solution (1000 mg l⁻¹): Prepared by dissolving 1.116 g of potassium antimonate (KSb(OH)₆ ½ H₂O) (Riedel-de Haën) in 500 ml ultra pure water.
5. Calibration standards: Lower concentration standards were prepared daily from their stock standard solutions.
6. Sodium borohydride solution (1% m/v): Prepared from fine granuled product (Merck) and was stabilized by the addition of 0.1% (m/v) NaOH (Merck).
7. pH adjustment: NH₃ (Merck) (0.1-1.0 M) and HCl (Merck) (0.1-1.0 M) were used.

2.2. Instrumentation and Apparatus

An atomic absorption spectrometer, Thermo Elemental Solaar M6 Series with an air-acetylene burner was used in all the measurements. Antimony and arsenic determinations were performed by HGAAS using their hollow cathode lamps at the wavelengths of 217.6 nm and 193.7 nm, respectively. A deuterium hollow cathode lamp was used for background correction in all determinations. The monochromator bandpass was 0.2 nm for antimony and 1.0 nm for arsenic.

The quartz tube atomizer used in HGAAS measurements was 10 cm long, 8 mm in internal diameter and 10 mm in external diameter with a 4 mm bore inlet tube fused at the middle for sample introduction. Air-acetylene flame was used for heating the quartz tube externally and nitrogen was used as the carrier gas. The hydride generation system coupled with segmented flow injection unit (FI 90) was used in all measurements for antimony and arsenic determinations. A schematic representation of the hydride generation apparatus used is shown in Figure 2.1. It is a continuous hydride generation system segmented with air bubbles. Operating parameters for the HGAAS system are given in Table 2.1. In the determination of metals, flame atomic absorption spectrometry (FAAS) was applied. In batch sorption studies, Yellowline RS 10 (Staufen, Germany) reciprocating shaker was used to provide efficient mixing.

Table 2.1. Operating parameters of the Segmented Flow Injection (SFI-HGAAS) system used.

Carrier gas (N ₂) flow rate	200 ml min ⁻¹
HCl concentration	0.12 M
HCl flow rate	6.1 ml min ⁻¹
NaBH ₄ concentration	1% (w/v) stabilized with 0.1% (w/v) NaOH
NaBH ₄ flow rate	3.0 ml min ⁻¹

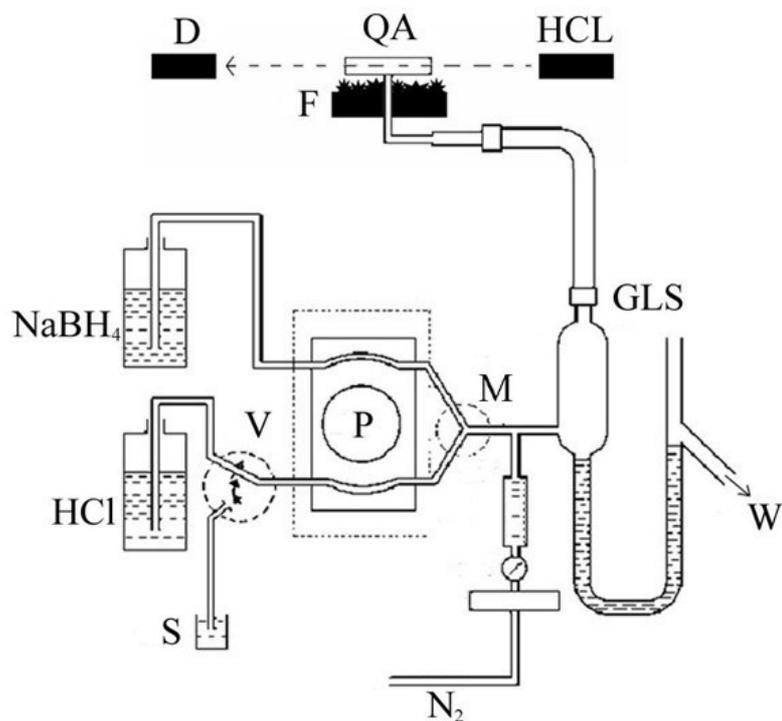


Figure 2.1. Segmented flow injection (SFI-HGAAS) system used in this study (taken from Operator's Manual of the instrument). D: detector, QA: quartz tube atomizer, HCL: hollowcathode lamp, F: air-acetylene flame, S: acidified sample, V: injection valve, P: two-channel peristaltic pump, M: mixing piece, GLS: gas/liquid separator, W: waste.

2.3. Interference Studies on As(III) Signal in HGAAS Measurements

2.3.1. Interference Effect of Several Metal Ions

The interference effect of several metal ions on As(III) signal was investigated in such a way that various concentrations of the metals were prepared and spiked with As(III). The change in HGAAS signals of As(III) as a function of metal concentration was obtained. For this purpose, 30.0 ml of separate metal ion solutions with the concentrations ranging from 0.1 mg l⁻¹ to 5.0 mg l⁻¹, were spiked with 25.0 µg l⁻¹ As(III). The corresponding metal ion/As(III) concentration ratios were of 4 to 200. The solutions were analyzed with HGAAS system for As(III).

2.3.2. Interference Effect of Other Hydride Forming Elements

In order to investigate the interference effect of other volatile hydride forming elements on As(III) signal, a similar strategy was followed with Se(IV), Te(IV), and Sb(III). As in the case of metal ions, 30.0 ml of hydride forming elements with concentrations 25.0 – 1000.0 $\mu\text{g l}^{-1}$ were prepared separately and spiked with 25.0 $\mu\text{g l}^{-1}$ As(III). The As signal from each solution was measured with HGAAS system.

2.4. Sorption Studies with Mordenite

2.4.1. Sorption of Metal Ions on Mordenite

Sorption characteristics of mordenite towards the selected metal ions and hydride forming elements were investigated through batch process. Mordenite ($\text{Na}(\text{AlSi}_5\text{O}_{12})\cdot 3\text{H}_2\text{O}$) used had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 20, percent Na_2O of 0.08 % (m/m), has a surface area of 500 m^2/g and its nominal cation form was ammonium.

The general strategy followed in the batch process was as follows: 30.0 ml of the related solution was prepared and 0.3 g of mordenite was added into this solution. The pH of the solution was always between 6 and 8. The mixture was shaken for 1-2 minutes manually and then placed on a reciprocating shaker for 15 minutes. After the shaking period, the mixture was centrifuged, the solid and the solution phases were separated and the supernatant solution was analyzed by HGAAS for As(III) and Sb(III) and FAAS for the metals.

The effect of initial concentrations of the metal ions on sorption on mordenite was investigated for the concentrations of 1.0, 10.0, 100.0, and 1000.0 mg l^{-1} . After the usual shaking and centrifugation steps, the supernatant solutions were analyzed to determine the concentrations of metal ions remaining in the solution. In addition, the supernatant solutions were spiked with 25.0 $\mu\text{g l}^{-1}$ As(III) in order to see whether the remaining concentrations of the metal ions had any interference on As(III) signal.

2.4.2. Sorption of Other Hydride Forming Elements on Mordenite

Similar sorption experiments were performed with some other volatile hydride forming elements; namely Se(IV), Se(VI), Te(IV), Te(VI), Sb(III), and Sb(V). The concentrations of all the species were $40.0 \mu\text{g l}^{-1}$.

Based on the results of the interference study related with hydride forming elements, a special attention was given to Sb(III) since it showed the most suppressive interference on As(III) signal. The effect of solution pH on the sorption of Sb(III) and As(III) was examined separately in the pH range 2.0-10.0, and also in 1.0 and 4.0 M HCl. The concentrations of both Sb(III) and As(III) were $40.0 \mu\text{g l}^{-1}$.

2.4.3. Sorption Isotherm Studies

In addition to the pH experiments, the equilibrium sorption isotherm studies were conducted in order to reveal the concentration-dependence of the partitioning of Sb species between liquid solutions and mordenite at a particular temperature. These studies were also performed through batch process. The accurately weighed amounts of mordenite (0.300 or 1.000 g) were added into 30.0 ml of solutions containing the specified concentrations of Sb(III) (ranging from 5.0 to 500.0 mg l^{-1}) and the mixtures were shaken in a thermostated water bath (30 or 50 °C) for an hour. At the end of the shaking period, the solid and solution phases were separated through centrifugation and the concentrations of Sb in the supernatant solutions were determined by HGAAS or FAAS. The sorbed amount of Sb per unit mass of mordenite was calculated from the mass balance.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Interference Studies

As mentioned in section 2.3, initial studies were concentrated on the observation of the change in HGAAS signal of As(III) in the presence of several metal ions and other hydride forming elements.

3.1.1. Effect of Metal Ions on As(III) Signal

It is known that several metal ions may interfere with the HGAAS determination of As and Sb, and this interference is generally observed as suppression of the hydride signal. In the present study, the effect of selected metal ions on As(III) signal was investigated in a way that varying concentrations of the metal ions (0.1 mg l^{-1} to 5.0 mg l^{-1}) were prepared and spiked with $25.0 \text{ } \mu\text{g l}^{-1}$ As(III). The details of the experimental procedure can be found in section 2.3.1. The results are shown in Figure 3.1.

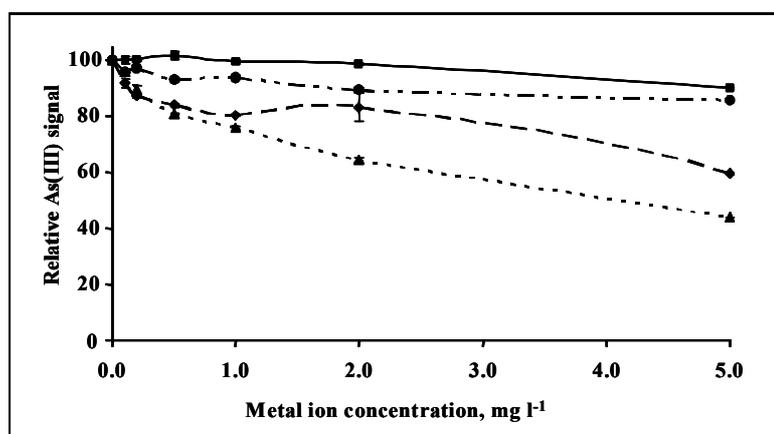


Figure 3.1. Effect of metal ion concentration on As(III) signal, (▲) Ni²⁺, (●) Ag⁺, (◆) Cu²⁺, (■) Pb²⁺. ($25.0 \text{ } \mu\text{g l}^{-1}$ As(III), 1% (m/v) NaBH₄, 0.12 M HCl).

As can be seen from the figure, the highest signal depression was observed for Ni^{2+} and Cu^{2+} whereas the As(III) signal was not significantly affected from Ag^+ and Pb^{2+} ; at least, under the experimental conditions employed (10-15 % depression for a metal concentration at 5.0 mg l^{-1}). These findings are in accordance with some studies in literature (Pohl and Zirnicki 2002). Higher concentrations ($> 5.0 \text{ mg l}^{-1}$) were not tried because of the reduction of metal ions to elemental state upon injection of NaBH_4 and thereby increasing the possibility of damaging and clogging of the pump tubings and narrow connection points of the SFI-HGAAS. Yet, the suppression effect is expected to be higher with increasing concentrations of metal ions.

3.1.2. Effect of Volatile Hydride Forming Elements on As(III) Signal

Volatile hydride forming elements can cause serious gas phase interferences in HGAAS system. These interferences can take place either during the transfer of the hydride from the sample solution to the atomizer, or in the atomizer (Dedina and Tsalev 1995). In order to test whether the selected volatile hydride forming elements had a suppression effect on As(III) signal, a $25.0 \text{ } \mu\text{g l}^{-1}$ As(III) standard in separate solutions of the selected species; namely, $250.0 \text{ } \mu\text{g l}^{-1}$ Sb(III), Se(IV) and Te(IV), in different HCl concentrations (0.12-3.0 M) was prepared. The relative As(III) signals are shown in Figure 3.2.

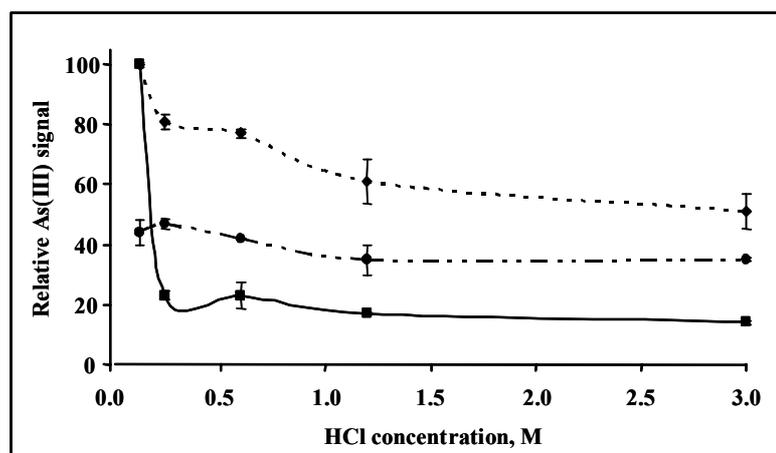


Figure 3.2. Suppression effect of $250.0 \text{ } \mu\text{g l}^{-1}$ of (●) Sb(III), (◆) Te(IV), (■) Se(IV) on $25.0 \text{ } \mu\text{g l}^{-1}$ As(III) signal as a function of HCl concentration ($n=3$).

As can be seen from the figure, Sb(III) exhibited almost a constant signal suppression (~60%) at all HCl concentrations studied whereas no signal suppression was observed from Se(IV) or Te(IV) in 0.12 M HCl. But, immediately after this HCl concentration (e.g. in 0.24 M HCl), a significant decrease in As(III) signal was obtained with Se(IV), almost 80% suppression, and about 20% decrease with Te(IV). These results show the strong dependence of hydride generation reaction on sample acidity.

After this finding, effect of interferent concentration on As(III) signal was investigated in two different HCl concentrations. For this purpose, 25.0 $\mu\text{g l}^{-1}$ As(III) standard was prepared in varying concentrations (25.0 - 1000 $\mu\text{g l}^{-1}$) of Sb(III), Se(IV) and Te(IV) in 0.12 M and 1.2 M HCl. The respective figures are shown in Figure 3.3 and Figure 3.4.

As seen in Figure 3.3, in 0.12 M HCl, Sb(III) suppressed the As(III) signal whereas no signal suppression was observed from Se(IV) and Te(IV). On the other hand, 1.2 M HCl created a more convenient environment for Se(IV) and Te(IV) to exhibit their interference effect on As(III) signal (Figure 3.4). Se(IV) was more effective and even no As(III) signal was obtained in presence of 500 $\mu\text{g l}^{-1}$ Se(IV) in 1.2 M HCl.

In addition, the pH of the reaction mixture after mixing the sample (in different HCl concentrations) and the reducing agent (1.0 % (m/v) NaBH_4 in 0.1 % (m/v) NaOH) was measured in the SFI-HGAAS system used. The results are listed in Table 3.1.

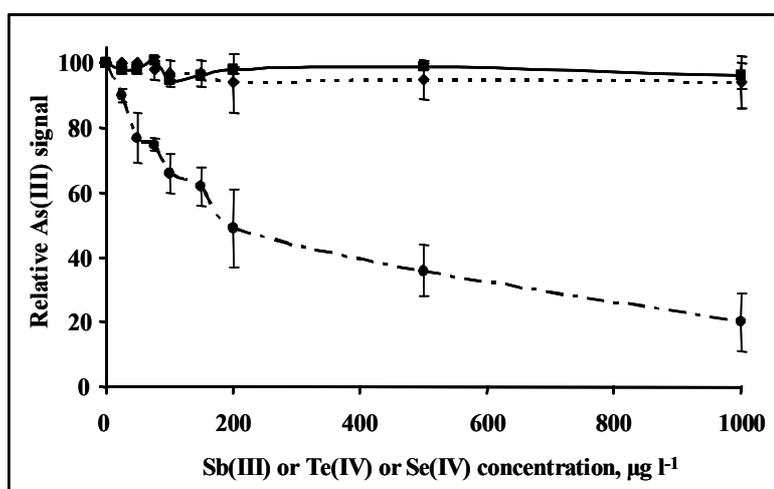


Figure 3.3. Effect of the concentrations of (●) Sb(III), (◆) Te(IV), (■) Se(IV) on As(III) signal in 0.12 M HCl (25.0 $\mu\text{g l}^{-1}$ As(III), 1% (m/v) NaBH_4) (n=3).

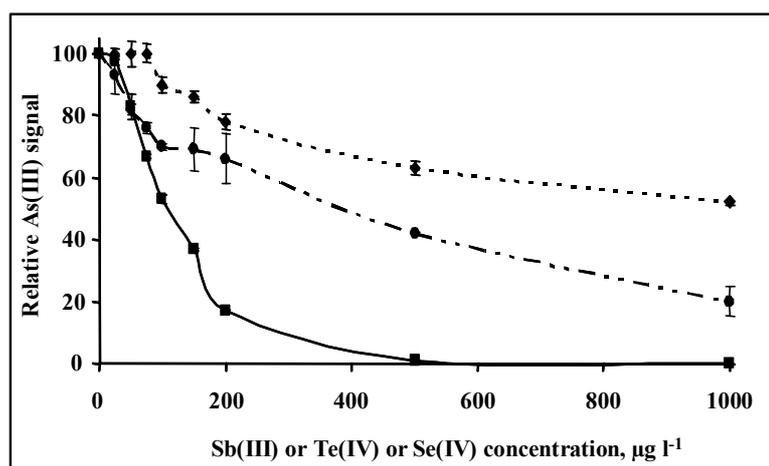


Figure 3.4. Effect of the concentrations of (●) Sb(III), (◆) Te(IV), (■) Se(IV) on As(III) signal in 1.2 M HCl ($25.0 \mu\text{g l}^{-1}$ As(III), 1% (m/v) NaBH_4) ($n=3$).

These results are in accordance with the results mentioned earlier by Belcher et al. (1980). According to the results, H_2Se and H_2Te could possibly not escape from the solution and not transferred into the gas phase when the initial concentration of HCl is 0.12 M (after mixing sample and reducing agent, pH of the solution was 6.6). On the other hand, when the initial HCl concentration was 1.2 M, pH of the solution changed to 1.0 after mixing; H_2Se and H_2Te could escape from the solution and therefore cause gas phase interference.

Table 3.1. pH values of the reaction mixture after mixing the sample (in different HCl concentrations) and the reducing agent (1.0 % (m/v) NaBH_4 in 0.1 % (m/v) NaOH) in the SFI-HGAAS system used.

HCl concentration, M	pH
0.012	9.8
0.060	9.0
0.12	6.6
0.18	1.4
0.24	1.0
0.6	0.5
1.2	0.1

3.2. Sorption Studies

Sorption studies were performed using potential adsorbents (Clinoptilolite, Zeolite Beta, Mordenite, Zeolite Y, Zeolite ZSM-5, Muromac A-1, Chelex 100, Amberlite IRC-718, Duolite GT-73) in two parts. Firstly, sorption of metal ions, and secondly, sorption of volatile hydride forming elements were studied. Among the materials investigated, mordenite (a synthetic zeolite) demonstrated a promising behaviour in reducing the interference effects of both metal ions and hydride forming elements; and therefore, was used in the subsequent experiments. Procedural details can be found in sections 2.4.1 and 2.4.2.

3.2.1. Sorption of Metal Ions

Use of zeolites including mordenite for the sorption of metal ions has been shown by many researchers (Misaelides et al. 1996, Farm 2002, Alvarez-Ayuso et al. 2003). In the present study, the initial experiments were planned to understand the sorption behaviour of mordenite towards metal ions as a function of solution pH. As shown in Figure 3.5, any pH between 4.0 and 8.0 can be used for the removal of all four metal ions from the solution quantitatively. An interesting observation in this figure is that Cu^{2+} and Ni^{2+} showed a similar behavior during sorption as seen in interference studies given in Figure 3.1. The reason for the decrease of % sorption of Cu^{2+} and Ni^{2+} at low pH's might be due to the competition between the metal and hydronium ions.

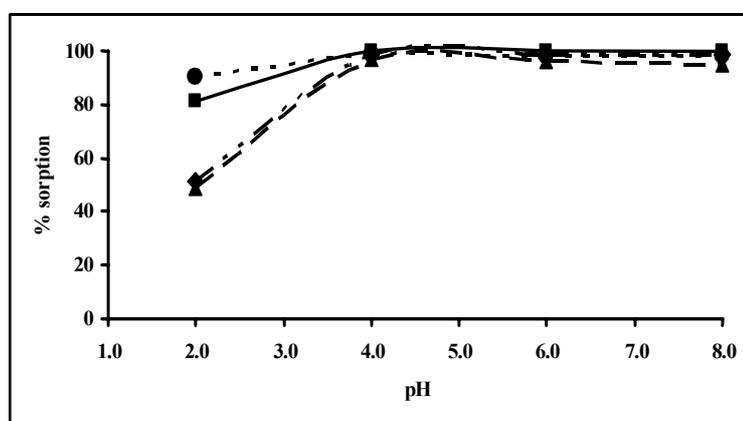


Figure 3.5. Percentage sorption of mordenite towards (\bullet) Ag^+ , (\blacksquare) Pb^{2+} , (\blacklozenge) Cu^{2+} and (\blacktriangle) Ni^{2+} as a function of pH. (Metal ion concentration : 5.00 mg l^{-1}) ($n=3$).

After determining the appropriate pH values, in order to have an idea about the capability of mordenite in removal of metals from the solution, the specified amount of the sorbent (0.3 g) was added into separate solutions of the four metal ions with different initial concentrations of 1.0, 10.0, 100.0, and 1000.0 mg l⁻¹. The concentrations of the metal ions that remained in the solution after sorption are given in Table 3.2. Also given in the table, the percent suppression of the As(III) signal when the supernatant solutions were spiked with 25.0 µg l⁻¹ As(III). As seen from the table, when the initial concentration of the metals is 1000.0 mg l⁻¹, mordenite can not decrease their concentration to a tolerable level. The percent suppression of the remaining concentration of metal ions was not examined due to the possibility that such high concentrations could have caused some uncontrollable problems such as the formation of dispersed metals in the solution and the clogging of connection points in the SFI-HGAAS system used. In the case of Ag⁺ and Pb²⁺, even an initial concentration of 100.0 mg l⁻¹ did not cause any suppression since the percent sorption was still 98% and 100%, respectively. The concentration of Ag⁺ remained in the solution was 2.0 mg l⁻¹ and this relatively low concentration caused only a 4(±3)% suppression in As(III) signal. This finding supports also the observations given in Figure 3.1.

Table 3.2. Percent sorption of Ag⁺, Ni²⁺, Cu²⁺, and Pb²⁺ on mordenite and the effect of their remaining concentrations in effluents on As(III) signal (a) Cu²⁺, (b) Ni²⁺, (c) Ag⁺, (d) Pb²⁺.

initial conc. (mg l ⁻¹)	conc. in effluent (mg l ⁻¹)	% sorption	% suppression in As signal
1	< 0.01	> 99	< 5
10	< 0.04	> 99	< 5
100	10 ± 1	90 ± 1	45 ± 4
1000	778 ± 33	22 ± 3	NA

(a)

initial conc. (mg l ⁻¹)	conc. in effluent (mg l ⁻¹)	% sorption	% suppression in As signal
1	< LOQ	> 99	< 5
10	0.03 ± 0	> 99	< 5
100	19 ± 1	81 ± 1	96 ± 1
1000	822 ± 5	18 ± 1	NA

(b)

initial conc. (mg l ⁻¹)	conc. in effluent (mg l ⁻¹)	% sorption	% suppression in As signal
1	0.023 ± 0	> 99	< 5
10	0.04 ± 0	> 99	< 5
100	2 ± 0	98 ± 0	< 5
1000	362 ± 7	64 ± 1	NA

(c)

initial conc. (mg l ⁻¹)	conc. in effluent (mg l ⁻¹)	% sorption	% suppression in As signal
1	< LOQ	> 99	< 5
10	< LOQ	> 99	< 5
100	0.4 ± 0	> 99	< 5
1000	301 ± 12	69 ± 0	NA

(d)

NA: Not Analysed; LOQ: limit of quantitation. (LOQ was calculated as 10 times the 3σ-based limit of detection as explained by Carre et al. (1997) and was equal to 0.04 mg l⁻¹ for the investigated metals).

The concentrations of Cu^{2+} and Ni^{2+} remained in the solution after the usual sorption procedure (100.0 mg l⁻¹ initial concentrations of the metal ions were mixed with mordenite and the mixture was filtered thereafter) were 10(±1) and 19(±1) mg l⁻¹, respectively. These concentrations of Cu^{2+} and Ni^{2+} were still very effective in suppression of As(III) signal. In both cases, the injection of NaBH_4 caused the metal ions to be converted to elemental state and be dispersed in the solution which possibly adsorbed AsH_3 as soon as it was formed. With the initial concentrations of 1.0 and 10.0 mg l⁻¹, mordenite decreased the concentrations of the metal ions below 0.04 mg l⁻¹, and this and lower concentrations of the metals had a very slight suppression on As(III) signal only in the case of Ni^{2+} . These results indicate clearly the potential of mordenite in reducing the interference effect of transition metal ions on As(III) signal.

3.2.2. Sorption of Volatile Hydride Forming Elements

The sorption of different oxidation states of Se, Te, and Sb on mordenite was investigated as explained in Section 2.4.2. At the end of the usual sorption procedure, the lower oxidation states of the volatile hydride forming elements, namely, Sb(III), Se(IV) and Te(IV) were determined by SFI-HGAAS directly after bringing the solutions to the required acidity for the hydride generation step. On the other hand, a prereduction step was applied to measure the higher oxidation states (Sb(V), Se(VI) and Te(VI)). Treatment of the supernatant solution with 0.5% (m/v) L-cysteine was sufficient for Sb(V) to Sb(III) reduction whereas heating the solution to 80 °C in 6 M HCl for half an hour served as an efficient prereduction step for Se(VI) (Şahin et al. 2003), and Te(VI) (Körez et al. 2000).

Among the elements and their oxidation states examined, mordenite showed selectivity only to Sb(III) as shown in Table 3.3. Except Sb(III), none of the volatile hydride forming elements investigated had a suppression effect on As(III) signal, under the experimental conditions employed (Figure 3.3). Different sorption behavior of mordenite towards Sb(III) necessitated a further investigation of the case. For this purpose, effect of solution pH and HCl concentration on the sorption of As(III), As(V), Sb(III), and Sb(V) on mordenite were examined more closely. The results are shown in Figure 3.6.

Table 3.3. Percentage uptake of Te(IV), Te(VI), Se(IV), Se(VI), Sb(III), and Sb(V) on mordenite. (All concentrations were $40.0 \mu\text{g l}^{-1}$)

	Concentration remained, $\mu\text{g l}^{-1}$	% Sorption
Te(IV)	32 ± 1	19 ± 2
Te(VI)	38 ± 1	4 ± 1
Se(IV)	36 ± 3	9 ± 8
Se(VI)	39 ± 1	1 ± 1
Sb(III)	2 ± 1	95 ± 2
Sb(V)	39 ± 1	2 ± 2

It can be said that mordenite shows high adsorption selectivity for Sb(III) at pH 4.0-6.0. The high selectivity of mordenite for Sb(III) among the hydride forming elements investigated may also lead to such applications as separation and preconcentration of Sb(III) from solutions containing the species with similar chemical properties like As(III).

Another set of experiments was also planned in order to reveal some of the physicochemical aspects of Sb(III) sorption on mordenite as explained in Section 2.4.3.

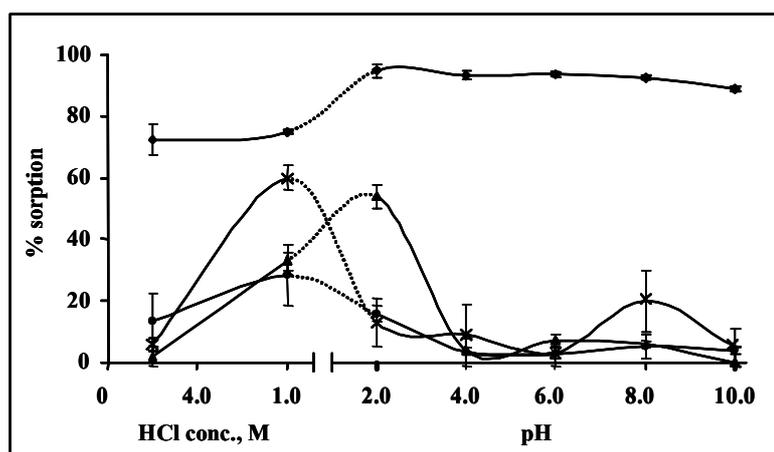


Figure 3.6. Percentage uptake of mordenite for (●) As(III), (×) As(V), (◆) Sb(III), (▲) Sb(V) as a function of pH and HCl concentration. (Species concentrations : $40.0 \mu\text{g l}^{-1}$, 1% (m/v) NaBH_4 , 0.12 M HCl).

3.2.3. Sorption Isotherm and Thermodynamic Relations in Sb(III) Uptake by Mordenite

The sorption experiments of Sb(III) were performed in the batch process. The equilibrium relationship between the amount of Sb(III) adsorbed per unit mass of mordenite ($[C]_s$) and the residual Sb(III) concentration ($[C]_l$) in solution phase were expressed using adsorption isotherms. The Sb(III) concentrations ranged from 5.00 to 500 mg l⁻¹ and two different amounts of solid (0.30 g and 1.0 g) and temperatures (30 °C and 50 °C) were examined. The applicability of the Freundlich sorption isotherm was tested under these specified conditions.

The general expression of Freundlich isotherm is given as:

$$[C]_s = k [C]_l^n \quad (1)$$

where;

$[C]_s$: equilibrium concentration of the sorbed species on the solid phase

$[C]_l$: equilibrium concentration of the sorbate at the liquid phase

k: a constant related to sorption affinity

n: a constant related to linearity of the sorption curve.

This expression can be linearized as:

$$\log [C]_s = \log k + n \log [C]_l \quad (2)$$

Thus, plotting $\log[C]_s$ versus $\log [C]_l$ would lead to linear behavior with 'n' being the slope and 'k' the intercept of the isotherms. Freundlich isotherm model allows for several kinds of adsorption sites on the solid, each kind having a different heat of adsorption. The Freundlich isotherm represents well the data at low and intermediate concentrations and is a good model for heterogeneous surfaces. When the value of Freundlich constant n is equal to unity, Freundlich equation becomes linear and the Freundlich constant k becomes equivalent to the distribution ratio, R_d which is an empirical constant usually used in the quantification of the sorption process (Shahwan and Erten 1999).

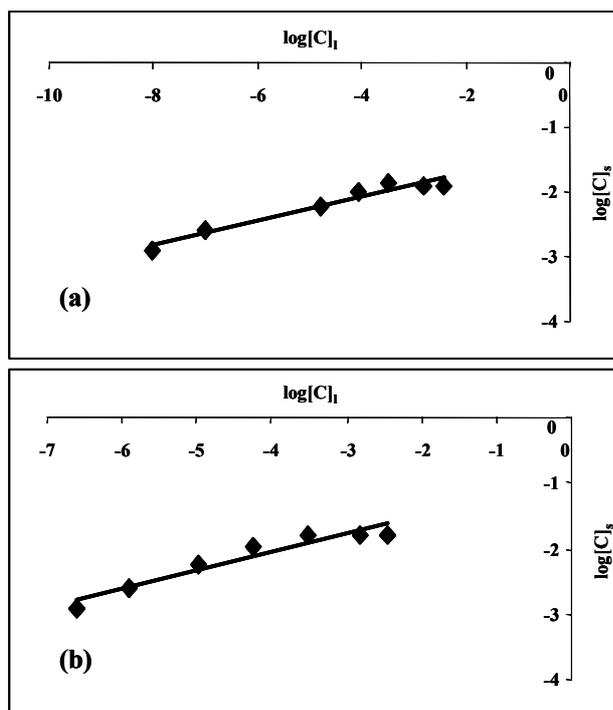


Figure 3.7. Freundlich isotherm model curves when plotted for the initial Sb(III) concentrations of 5.00 to 500 mg l⁻¹ (amount of mordenite: 1.0 g). (a) at 30 °C ($y = 0.1898x - 1.3217$, $R^2 = 0.951$), and (b) at 50 °C ($y = 0.2742x - 0.9684$, $R^2 = 0.9192$).

As can be seen from Figure 3.7, the adsorption data for Sb(III) on mordenite follow adequately the Freundlich isotherm. The characteristic Freundlich constants are given in Table 3.4. In batch adsorption processes, the adsorption reaction can be written as:



where C_l and C_s stand, respectively, for the equilibrium concentration of the sorbate species in the liquid and on the solid sorbent, and \underline{s} refers to the concentration of the sorption sites on the sorbent. The importance of \underline{s} stems from the fact that sorption sites can act as the limiting reactant when the sorption reaction takes place at higher loadings of the sorbate, the thing that leads to a plateau of saturation beyond a certain high initial concentration. For dilute solutions, the fractional coverage of the sorption sites can be assumed to be small enough to justify approximating the activity (or concentration) of the sorption sites to be constant, and the activity coefficients of the sorbate specie in liquid solution and at the solid to be equal to unity. Under these approximations, the equilibrium constant of the above reaction becomes equivalent to the distribution ratio,

R_d (ml g^{-1}), an empirical constant that is valid at a certain concentration for a particular set of experimental conditions, and defined as:

$$R_d = \frac{[C]_s}{[C]_l} \quad (4)$$

With the mentioned limitation in mind and under equilibrium conditions, the distribution ratio may be related to the change in Gibbs free energy, ΔG° , by the following equation:

$$\Delta G^\circ = -RT \ln R_d \quad (5)$$

Gibbs free energy can also be written in terms of enthalpy change, ΔH° , and the entropy change, ΔS° , as given below:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

Here, ΔH° can be calculated using the relation:

$$\Delta H^\circ = R \ln \frac{R_d(T_2)}{R_d(T_1)} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \quad (7)$$

As can be seen from Table 3.4, the calculated ΔG° values indicates that the sorption process is spontaneous in all cases. It is also obvious that spontaneity increases with increasing temperature leading to higher coverage at higher temperatures. The endothermic nature of sorption of Sb on mordenite is indicated by the positive values of the enthalpy change ΔH° . The positive sign of the ΔS° values indicate that sorption leads to more randomness/mobility in the system, possibly due to the dehydration steps and/or release of a larger number of ions or molecules by mordenite upon fixation of Sb specie.

Table 3.4. The calculated Freundlich isotherm constants, ΔG° , ΔH° , and ΔS° values from adsorption data.

m/V (g l^{-1})	n		k (meq g^{-1})		ΔG° (kJ mol^{-1})		ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$)
	303 K	323 K	303 K	323 K	303 K	323 K		
10	0.32	0.27	0.20	0.15	-8.2	-9.7	13.9	73.1
33.3	0.19	0.27	0.04	0.11	-8.8	-10.4	14.3	76.3

3.2.4. SEM, XRD and EDX Results

Uptake of Sb(III) species on mordenite was studied using XRD and SEM/EDX techniques. Typical SEM micrographs of mordenite before and after Sb(III) loading are shown in Figure 3.8. No change in the morphology or crystal size of mordenite particles was observed upon loading with Sb(III). This was also supported by XRD findings. XRD diagrams of mordenite before and after Sb(III) sorption are given in Figure 3.9. According to the diagrams, mordenite reflections were essentially unaffected in terms of peak positions and shapes. SEM and XRD results are, thus, indicative of structural stability of mordenite upon retention of Sb(III) within the employed experimental conditions.

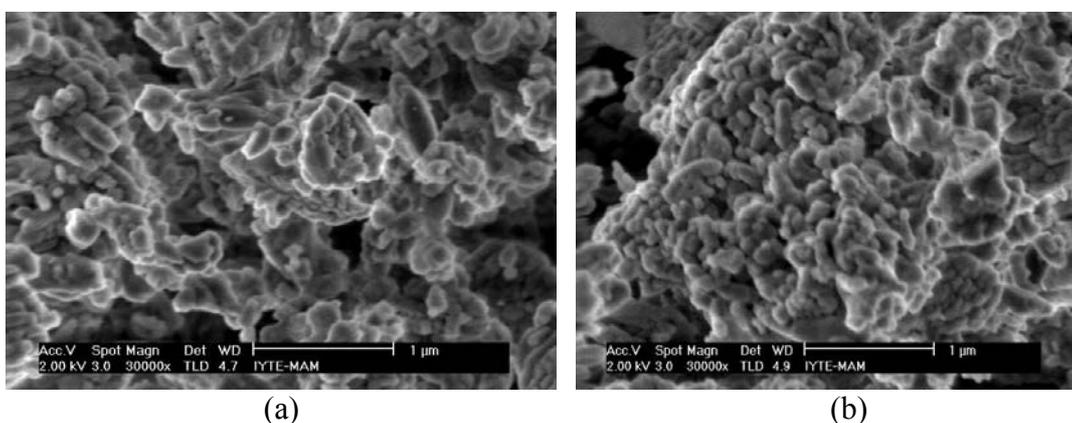


Figure 3.8. SEM microimages of (a) pure mordenite (30000X); (b) Sb(III)-loaded mordenite (30000X) (Sb(III) concentration : 500 mg l⁻¹)

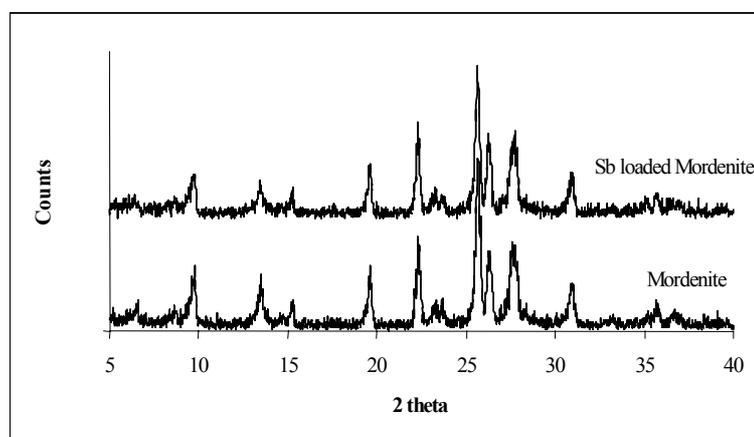


Figure 3.9. The XRD patterns of mordenite and Sb(III)-loaded mordenite.

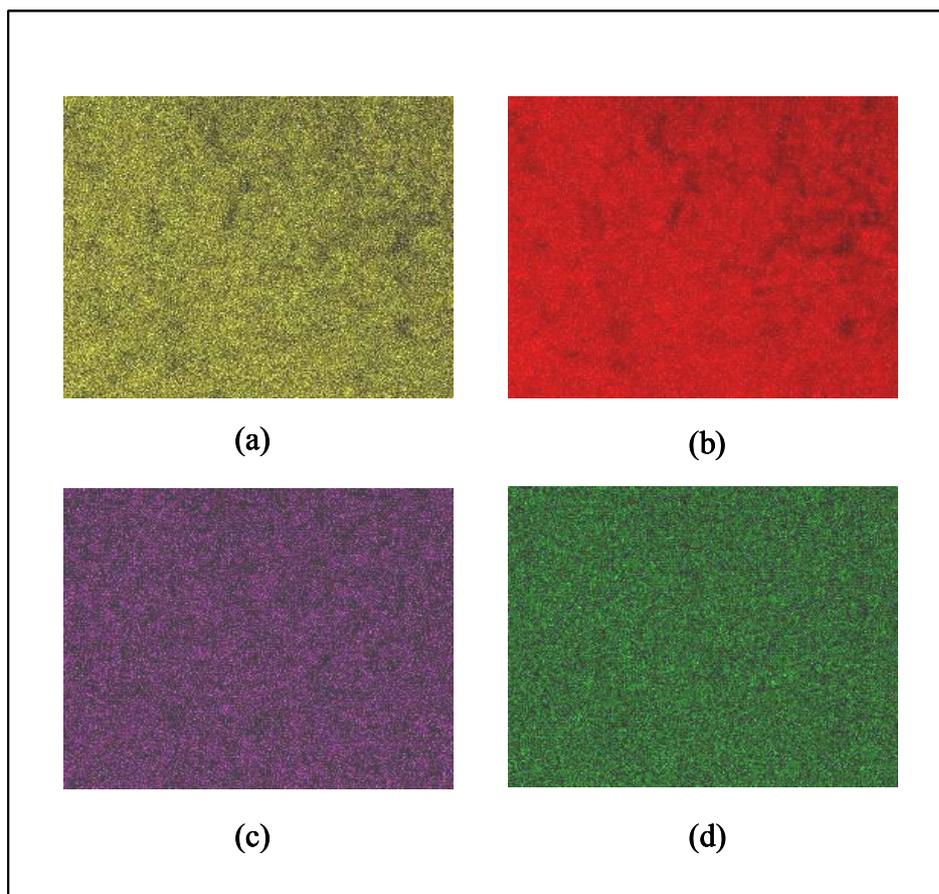


Figure 3.10. The EDX mapping of antimony-loaded mordenite; (a) Al (K-line), (b) Si (K-line), (c) Sb (L-line), (d) K (K-line)

The distribution of sorbed Sb on mordenite surface was revealed using energy dispersive X-ray spot analysis (EDX) in addition to EDX mapping. A typical map of Sb signals is given by Figure 3.10. The figure shows also Al and Si signals, in addition to K, with K possibly originating from $C_4H_4KO_7Sb$ used in preparing Sb(III) standards. The pictures demonstrate a uniform distribution of Sb on the surface of mordenite.

3.2.5. Reduction of Sb(III) Interference on As(III) Signal

As explained in Section 3.1.2, Se(IV) and Te(IV) did not cause any suppression on As(III) signal under the experimental conditions employed whereas Sb(III) had a serious suppression effect even at very low concentrations (Figure 3.3). Knowing this and the capability of mordenite in sorbing Sb(III), it was thought that the sample could be pretreated with mordenite which will guarantee the interference-free determination of

As(III) in the presence of the above-mentioned volatile hydride forming elements. This was confirmed as follows; $40.0 \mu\text{g l}^{-1}$ As(III) was prepared in varying concentrations of Sb(III), from 50.0 to $1000.0 \mu\text{g l}^{-1}$, and the solutions were analyzed both directly and after the proposed mordenite treatment. The pH of the solution was always between 6 and 8. The results are demonstrated in Figure.3.11. As can be seen from the figure, the presence of Sb(III) will affect the As(III) signal starting from very low concentrations. But, when the same solutions were processed by mordenite, the As(III) signal is regenerated and the interference of Sb(III) is reduced to a tolerable level. Even for a solution containing $1000.0 \mu\text{g l}^{-1}$ Sb(III), $87(\pm 2) \%$ of the $40.0 \mu\text{g l}^{-1}$ As(III) signal is regenerated.

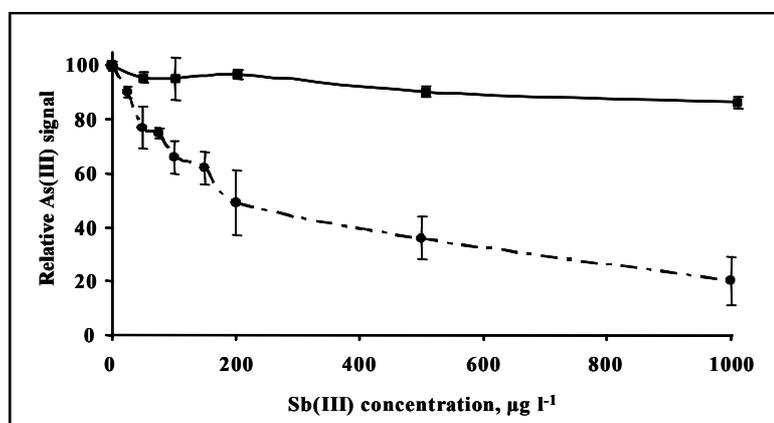


Figure 3.11. Effect of Sb(III) on As(III) signal (●) before and (■) after the proposed mordenite pretreatment. (As(III) concentration : $40.0 \mu\text{g l}^{-1}$).

CHAPTER 4

CONCLUSIONS

It has been demonstrated that a pretreatment method utilizing a synthetic zeolite, mordenite, offers an efficient new route for the interference-free determination of As(III) in the presence of Sb(III) which is one of the most suppressive interferences in As(III) determination by HGAAS. Mordenite exhibits high selectivity towards Sb(III) and the sorption was observed to be endothermic and followed Freundlich isotherm model. Several other hydride forming elements, such as Se(IV), Se(VI), Te(IV), Te(VI) were found not to interfere with As(III) determination with the experimental conditions employed. The proposed pretreatment method was also shown to be capable of reducing the interference effects of several metal ions (Ag^+ , Ni^{2+} , Cu^{2+} , and Pb^{2+}) in the reaction medium.

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