EGE UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

M.Sc.

METHOD DEVELOPMENT FOR THE DETERMINATION OF TRACE ARSENIC

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Yasemin İŞLEK tarafından yüksek lisans tezi olarak sunulan "**Method Development for The Determination of Trace Arsenic**" başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve **18.08.2010** tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET

ESER DÜZEYDE ARSENİK TAYİNİ İÇİN METOT GELİŞTİRME

İŞLEK, Yasemin

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Bu tezde HG-AAS yöntemi ile sularda eser arsenik tayini için Ni^0 / Ni_xB sorbenti kullanılarak ön-deriştirme yöntemi geliştirilmiştir.

Bu amaçla $Ni(NO_3)_2.6H_2O$ çözeltisi uygun indirgen ile ($NaBH_4$), sorpsiyon özelliğine sahip metal yapısına dönüştürülerek sorbent hazırlanmıştır. Bu sorbentin sulu çözeltilerden arsenik ön-deriştirilmesinde uygulanması optimize edilmiştir. Arsenik tayinleri uçucu hidrür oluşturmaya dayalı olarak Atomik Absorpsiyon Spektroskopisi ile yapılmıştır.

Hazırlanan sorbentin As(III) ve As(V) için sorpsiyon verimi ve kapasitesi çalışılan pH aralığında (pH 4-10) yüksektir. Kapasite 2.19 g As(III)/ 1 g sorbent olarak bulunmuştur. As(III) ve As(V) için sorpsiyon kinetiği hızlıdır. Çalışılan koşullarda iki kat deriştirilerek 5 ng/mL düzeydeki As(III) tayini için bağıl standart sapma % 3.35 (n=7) olarak bulunmuştur.

Anahtar sözcükler: Arsenik, Ön-deriştirme, Nikel Bazlı Sorbent , Hidrür Sistem Atomik Absorpsiyon Spektroskopisi.

ABSTRACT

METHOD DEVELOPMENT FOR THE DETERMINATION OF TRACE ARSENIC

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This study aims to develop a novel preconcentration method for trace arsenic determination in waters by using Ni^0 / Ni_xB as a sorbent.

$Ni(NO_3)_2.6H_2O$ solution was reducted using an appropriate reductant ($NaBH_4$) to form nickel based sorbent. Working conditions for sorbent have been optimized. Hydride Generation Atomic Absorption Spectrometry (HG-AAS) was used for the determination of arsenic.

This newly prepared sorbent has high sorption efficiency and capacity for As(III) and As(V) in the working range of pH 4-10. The sorption capacity was found to be 2.19 g As(III)/ 1 g sorbent. The sorbent possesses fast sorption kinetic for both As(III) and As(V). Under the optimized conditions, the relative standard deviation for the determination of 5 ng/mL As(III) after two times concentration was found to be 3.35% (n=7).

Keywords: Arsenic, Preconcentration, Nickel Based Sorbent, Hydride Generation-Atomic Absorption Spectrometry.

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SYMBOLS and ABBREVIATIONS

Abbreviations	Explanations
AAS	Atomic absorption spectrometry.
AES	Atomic emission spectrometry.
AFS	Atomic fluorescence spectrometry.
AMD	Acid mine drainage.
CCA	Chromated copper arsenate.
DMA	Dimethylarsinic acid.
HG-AAS	Hydride generation Atomic absorption spectrometry.
FI	Flow injection.
MLC	Maximum contaminant level.
MMA	Monomethylarsonic acid.
TMAsO	Trimethylarsine oxide.
USEPA	U.S. Environmental Protection Agency.
WHO	World Health Organization.

1. INTRODUCTION

1.1 History of Arsenic

Arsenic has been found in nature since antiquity. Arsenic compounds were mined by the early Chinese, Greek and Egyptian civilizations. During the Bronze Age, arsenic was often included in the bronze (mostly as an impurity), which made the alloy harder (Mohan and Pittman Jr., 2007).

Aristotle makes reference to sandarach (arsenic trisulfide) in the 4th century B.C. In the 1st century A.D., Pliny stated that *sandarach* is found in gold and silver mines and arsenic (arsenic trioxide) is composed of the same matter as *sandarach*. By the 11th century three species of arsenic were known, the white, yellow and red - since then recognized as arsenic trioxide, arsenic trisulfide (orpiment) and arsenic disulfide (realgar), respectively.

Albertus Magnus is reputed in the 13th century to be the discoverer of metallic arsenic. He isolated arsenic when he heated soap and orpiment (arsenic trisulphide, As_2S_3). However, his documentation is considered vague. It was not until 1649 that J. Schroder clearly reported the preparation of metallic arsenic by reducing arsenic trioxide with charcoal. Thirty-four years later, N. Lemery also observed that metallic arsenic was produced by heating arsenic trioxide with soap and potash. By the 18th century the properties of metallic arsenic were sufficiently known to classify it as semimetal (History magazine, 2001).

Arsenic was used in a compound called Paris Green developed around 1775 by Carl Scheele, which was used as a pigment in paints, wallpaper and fabrics. Throughout the 1800s, there were reports of people becoming ill from living in houses decorated with the poisonous wallpaper, however, Paris Green was not recognized as a health hazard until the end of the century. When Napoleon died in 1821, his doctors recorded the official cause of death as stomach cancer (Ball, 2002). Although trace amounts of arsenic were found in Napoleon's hair, the amount could have been absorbed naturally and not intentionally administered. Napoleon could have absorbed arsenic through eating a seafood meal, as it appears naturally in sea water and in sea dwellers. Towards the end of Napoleon's life, he spent increasing amounts of time indoors, where his home was decorated with Paris Green wallpaper.

In the 1830s, British chemist James Marsh developed a method for arsenic detection that was so sensitive it could detect the residue of fruit spray containing arsenic on food and in stomach contents. Marsh was the first to use arsenic detection in a jury trial. However, arsenic was often untraceable as the liver metabolizes it into naturally occurring chemicals. Arsenic lingers in urine, nails and hair. 'Marsh Test', which worked by adding zinc metal and sulphuric acid to the sample suspected of containing arsenic. If arsenic is present, the resulting chemical reaction converts the arsenic into arsine (each arsenic atom has three hydrogen atoms attached) which is a (very poisonous) gas. This gas is then passed along a heated glass tube, which causes the arsine gas to decompose, and the arsenic metal is deposited as a silvery-black film on the sides of the tube. The tube can then be sealed, and kept as evidence. Not only could minute amounts of arsenic be detected, but the test was very specific, since virtually no other element behaves in this way. With a chemical test this good, the age of the arsenic poisoners was drawing to a close. The only problem with the chemical test is that your arsenic-containing sample is used up in the course of the test - in that sense it is a destructive test and the Marsh Test is not sensitive enough to be able to detect arsenic in hair samples. In the 20th Century, techniques such as X-ray fluorescence spectroscopy replaced the Marsh Test. These non-destructive tests are incredibly sensitive, and can detect really tiny quantities of elements (History magazine, 2001).

Arsenic was an ingredient in Victorian fly papers. When soaked in water, it would combine with the water to create a deadly liquid that was easily disguisable in beverages and food. Arsenic was also popular due to its easy availability in rat poison and insecticides. Some even called it "inheritance powder".

In the 1890s, medical authorities in Italy were concerned about the unexplained deaths of over a thousand children. A chemist, E. Gosio, was consulted. Gosio did not examine the children, but the rooms where the deaths occurred. He discovered the deaths had two common factors: Paris Green wallpaper in the rooms and a presence of mildew. The children, being shorter and playing on the floor, inhaled the heavy arsine, the byproduct of arsenic and dampness. The removal of Paris Green from wallpaper prevented further deaths.

Up to the 1940s, arsenic was successfully used to treat syphilis; it was a key ingredient in a compound named Salvarsan. It has also been given to leprosy victims and sufferers of yaws (a contagious tropical skin disease).

Arsenic probably reached its greatest popularity in the golden age of murder-mysteries. When not in the hands of writers, arsenic is used today to remove color from glass, as a growth promoter for livestock, as a metal alloy and as a preservative in taxidermy.

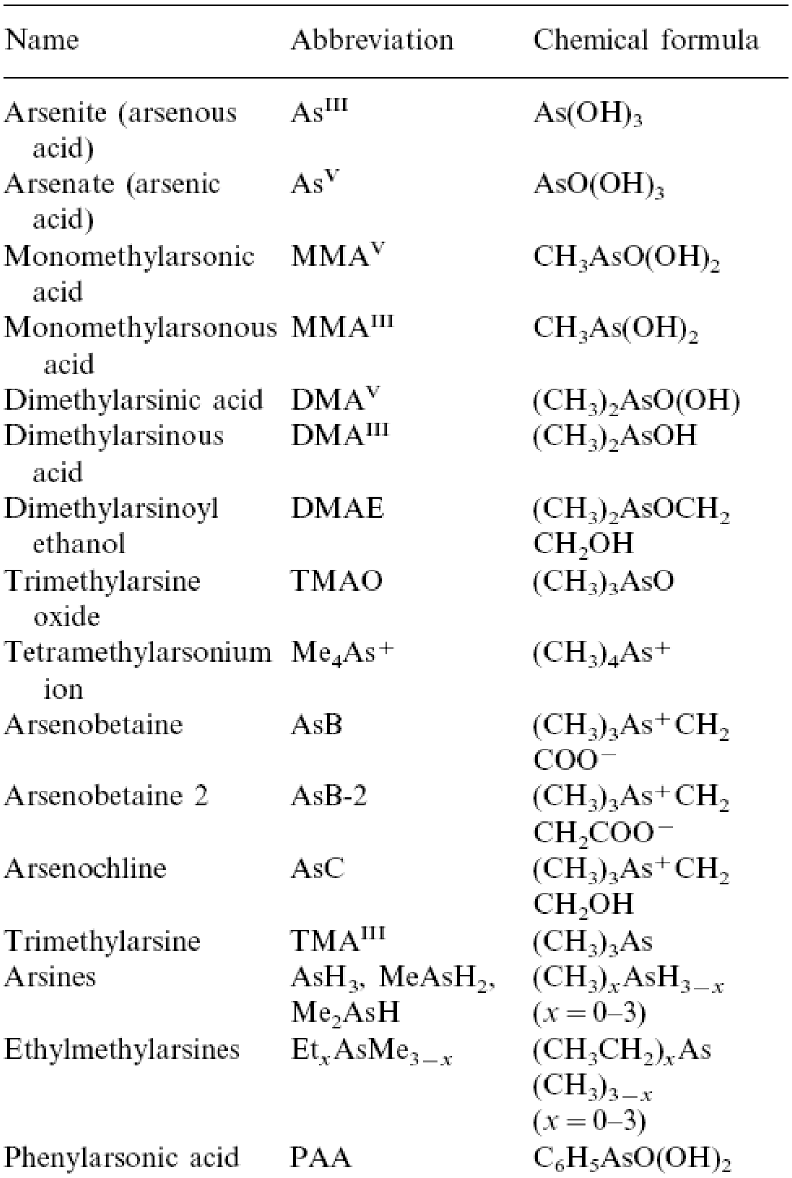
Water is essential for living beings and is the dominant arsenic exposure pathway. Dangerous arsenic concentrations in natural waters is now a worldwide problem and often referred to as a 20th–21st century calamity. High arsenic concentrations have been reported recently from the USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India. Among 21 countries in different parts of the world affected by groundwater arsenic contamination, the largest population at risk is in Bangladesh followed by West Bengal in India (Clara and Magalhães, 2002; Mohan and Pittman Jr., 2007) .

1.2 Arsenic

Arsenic is a ubiquitous element that ranks 20th in abundance in the earth’s crust, 14th in the seawater, and 12th in the human body. Arsenic has the symbol As with an atomic number of 33, atomic weight 74.9, specific gravity 5.73, melting point 817 $^{\circ}$C (at 28 atm), boiling point 613 $^{\circ}$C and vapor pressure 1mm Hg at 372 $^{\circ}$C.

Arsenic is steel grey, very brittle, crystalline in nature and oxidizes on rapid heating to arsenous oxide with odor of garlic. Arsenic exists as inorganic or organic compounds in the environmental and in biological systems (Table 1.1). In the environment, it combines with oxygen, chlorine and sulfur to form inorganic arsenic compounds. Arsenic combines with carbon and hydrogen to form organo-arsenic compounds in animals and plants. Inorganic arsenic compounds are mainly used to preserve wood and organic arsenic compounds are used as pesticides, primarily for cotton crop. Therefore, arsenic can be released into the environment from sources such as pesticides applications, wood preservatives, mining activities and petroleum refining. It is found exclusively as arsenite (Arsenic-III) or arsenate (Arsenic-V), with a minor amount of methyl and dimethyl arsenic compounds in groundwater (Hung et al.,2004). Arsenite can be converted to arsenate under oxidizing conditions (e.g. well-aerated surface water). Likewise, arsenate can become arsenite under reducing conditions (e.g. anaerobic groundwater) (Tahir et al., 2008; Mohan et al., 2007). Depending on the physico-chemical condition of the environment, some arsenic compounds can be highly soluble (metal arsenites are much more soluble than the corresponding metal arsenates), resulting in a high level of bioavailability. The presence of these compounds has therefore been declared as a major risk to human health in variousparts of the world (Lièvremont et al., 2009; Clara and Magalhães, 2002).

Table 1.1. Arsenic species commonly detected in the environmental and biological systems (Gong et al. 2002).



Name	Abbreviation	Chemical formula
Arsenite (arsenous acid)	As^{III}	$As(OH)_3$
Arsenate (arsenic acid)	As^{V}	$AsO(OH)_3$
Monomethylarsonic acid	MMA^{V}	$CH_3AsO(OH)_2$
Monomethylarsonous acid	MMA^{III}	$CH_3As(OH)_2$
Dimethylarsinic acid	DMA^{V}	$(CH_3)_2AsO(OH)$
Dimethylarsinous acid	DMA^{III}	$(CH_3)_2AsOH$
Dimethylarsinoyl ethanol	DMAE	$(CH_3)_2AsOCH_2CH_2OH$
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$
Tetramethylarsonium ion	Me_4As^+	$(CH_3)_4As^+$
Arsenobetaine	AsB	$(CH_3)_3As^+CH_2COO^-$
Arsenobetaine 2	AsB-2	$(CH_3)_3As^+CH_2CH_2COO^-$
Arsenochline	AsC	$(CH_3)_3As^+CH_2CH_2OH$
Trimethylarsine	TMA^{III}	$(CH_3)_3As$
Arsines	AsH_3, $MeAsH_2$, Me_2AsH	$(CH_3)_xAsH_{3-x}$ $(x = 0–3)$
Ethylmethylarsines	Et_xAsMe_{3-x}	$(CH_3CH_2)_xAs(CH_3)_{3-x}$ $(x = 0–3)$
Phenylarsonic acid	PAA	$C_6H_5AsO(OH)_2$

Naturally occurring arsenic is composed of one stable isotope, ^{75}As. As of 2003, at least 33 radioisotopes have also been synthesized, ranging in atomic mass from 60 to 92. The most stable of these is ^{73}As with a half-life of 80.3 days. Isotopes that are lighter than the stable ^{75}As tend to decay by β^+ decay, and those that are heavier tend to decay by β^- decay, with some exceptions.

Arsenic has three allotropes. These are metallic grey, yellow and black arsenic. The most common allotrope of arsenic is grey arsenic. Yellow arsenic (As_4) is soft and waxy, This form of arsenic is the least stable, most reactive, most volatile, least dense, and most toxic of all the allotropes. Yellow arsenic is produced by rapid cooling of arsenic vapour with liquid nitrogen. It is rapidly transformed into the grey arsenic by light. The yellow form has a density of 1.97 g/cm^3.

1.3 Applications of Arsenic

Only about 5% of arsenic consumption is of the metallic element. Most of this is used to alloy (mix) arsenic with lead, copper, or other metals for specific uses. As a metalloid, arsenic is a semiconductor, like silicon. This means it conducts some electricity like a metal, but not all the electricity a true conductor like copper would conduct. Consequently, about 1/10 % of arsenic is consumed in the manufacture of gallium arsenide semiconductors for use in electronics. In particular gallium arsenide (GaAs) is used in diodes, transistors and lasers. Indium arsenide (InAs) is used in infrared detectors and Hall effect applications.

Arsenic is used as an additive for metallurgical purposes due to its semi-metallic properties. Examples include: adding 2% to lead to produce lead shot where the addition increases sphericity; a 3% addition to lead alloys increases mechanical properties and high temperature properties; and 0.15-0.50% addition to copper for high temperature applications. Some arsenic is also used in glass-making.

Lead hydrogen arsenate is used as a herbicide and pesticide. Similarly chromated copper arsenate or Tanalith is used to treat timber and wood products.

The majority of U.S. consumption is in the form of chromated copper arsenate (CCA), a chemical used as a wood preservative for telephone poles, fence posts, pilings, and foundation timbers. The CCA significantly reduces rot and eliminates wood destruction by termites, ants and other insects. However, the use of CCA is being phased out in the U.S., and a major decrease in the arsenic market is expected as a result.

Formerly the most important use of arsenic compounds, was as an insecticide sprayed in fields and orchards. This use has entirely disappeared in most countries, due to the poisonous nature of arsenic compounds. Arsenic contamination is a problem in some well-water and may be associated with mine drainage.

1.4 Chemical and Physical Properties of Arsenic Compounds

In natural water systems, arsenic predominately exists in the inorganic form as oxyanions of trivalent arsenite, As(III), or pentavalent arsenate, As(V). Oxidizing conditions favor the formation of arsenate species (H_3AsO_4, $H_2AsO_4^-$ and $HAsO_4^{2-}$), whereas reducing conditions favor arsenite species (H_3AsO_3 and $H_2AsO_3^-$). The species $H_2AsO_4^-$, $HAsO_4^{2-}$ and H_3AsO_3 prevail under environmental conditions, where the pH spans 4 to 9

Elementary arsenic is fairly insoluble, whereas arsenic compounds may readily dissolve. Arsenic is mainly present in watery solutions as $HAsO_4^{2-}$(aq) and $H_2AsO_4^-$ (aq), and most likely partially as H_3AsO_4 (aq), AsO_4^{3-}(aq) or $H_2AsO_3^-$ (aq). Examples of solubility of arsenic compounds: arsenic(III)hydride 700 mg/L, arsenic(III)oxide 20 g/L, arsenic acid ($H_3AsO_4 \cdot 1/2\ H_2O$) 170 g/L, and arsenic(III)sulfide 0.5 mg/L.

Of the several forms of arsenic, As(III), As(V), MMA^V, and DMA^V undergo acid–base equilibria, thus different major and minor species will be present depending on the pH. H_3AsO_3 dissociates sequentially in water according to Eqs. (1)–(3)

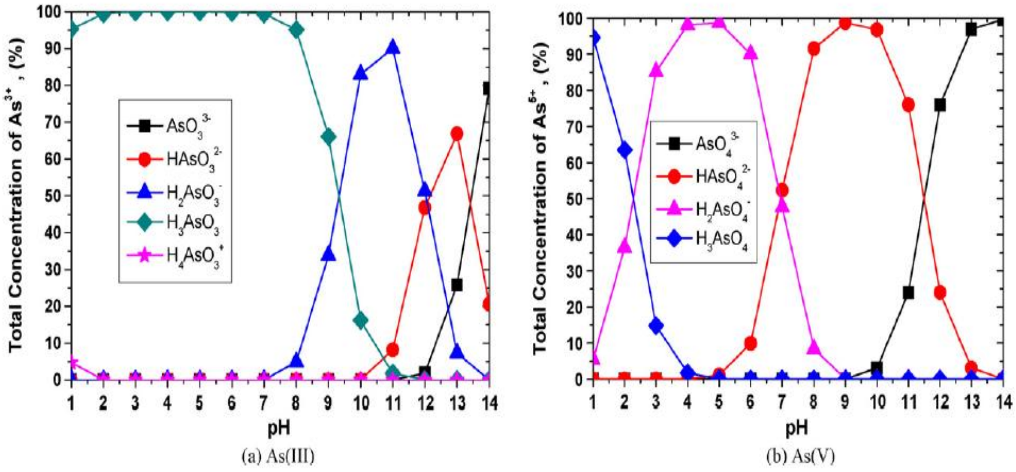
$$H_3AsO_3 \leftrightarrow H_2AsO_3^- + H^+ \qquad pK_{a1} = 9.2 \qquad (1)$$
$$H_2AsO_3^- \leftrightarrow HAsO_3^{2-} + H^+ \qquad pK_{a2} = 12.1 \qquad (2)$$
$$HAsO_3^{2-} \leftrightarrow AsO_3^{3-} + H^+ \qquad pK_{a3} = 13.4 \qquad (3)$$

Fig. 1.1 shows that at neutral pH, H_3AsO_3 is the dominant species while $H_2AsO_3^-$ represents a small fraction (<1.0%) and the contribution of $HAsO_3^{2-}$ and AsO_3^{3-} is insignificant.

As(V) is a triprotic acid (Eqs. (4)–(6)).

$$H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+ \qquad pK_{a1} = 2.3 \qquad (4)$$
$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+ \qquad pK_{a2} = 6.8 \qquad (5)$$
$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+ \qquad pK_{a3} = 11.6 \qquad (6)$$

At pH 7, almost equal concentrations of $H_2AsO_4{}^{-}$ and $HAsO_4{}^{2-}$ will be present (Fig. 1.1).



(a) As(III)

(b) As(V)

Figure 1.1. Distribution of arsenic(III) and arsenic (V) species as a function of pH of solution (input parameter – As concentration: 2.7×10−5 mol/L) (Dodbiba et al., 2009).

Both redox potential (E_h) and pH impose important controls on arsenic speciation in the natural environment. Fig. 1.2 shows the E_h – pH diagram for inorganic As compounds in the natural environment. Under oxidizing conditions (high E_h values), inorganic arsenic occurs primarily as H_3AsO_4 (iAs^{V}) at $pH<2$, and both $H_2AsO_4{}^{-}$ and $HAsO_4{}^{2-}$ species exist in the pH range from 2–11. At low E_h values, H_3AsO_3 is the predominant inorganic arsenic species (iAs^{III}) under reducing conditions (Fig. 1.2). If Eh values below −250 mV exist in the environment, arsenic compounds such as As_2S_3 in the presence of sulfur or hydrogen sulfide can be formed (Fig. 1.2) but these conditions are not environmentally relevant. The solubility of these compounds is very limited under neutral and acidic conditions. Under very strong reducing conditions, arsine and elemental arsenic are formed (Fig. 1.2) but again, only rarely, if ever in the natural environment (Sharma and Sohn, 2009).

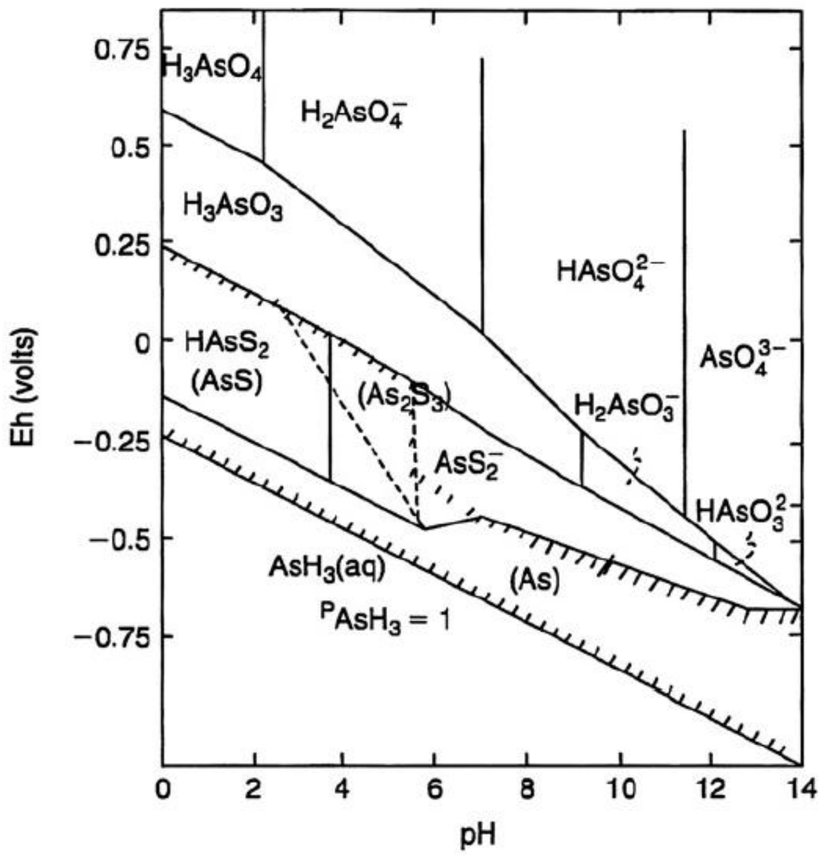


Figure 1.2. The E_h–pH diagram for arsenic at 25 °C and 1 atmosphere with total arsenic 10^{-5} mol L^{-1} and total sulfur 10^{-3} mol L^{-1}. Solid species are enclosed in parentheses in the cross-hatched area, which indicates a solubility in parentheses in the cross-hatched area, which indicates a solubility of less than $10^{-5.3}$ mol L^{-1} (Sharma and Sohn, 2009).

1.5 Occurence

The terrestrial abundance of arsenic is around 1.5–3 mg kg−1. Source of arsenic in the environment includes natural and anthropogenic.

1.5.1 Natural Sources

Long before man's activities had any effect on the balance of nature, arsenic was distributed ubiquitously throughout earth crusts, soil, sediments, water, air and living organisms.

Arsenic is a rare crystal element comprising about 0.00005% of the earth's crust and the average concentration of arsenic in igneous and sedimentary rocks is 2 mg kg^{-1}. In most rocks it ranges from 0.5 to 2.5 mg kg^{-1}, though higher concentrations were found in finergrained argillaceous sediments and phosphorites.

Arsenic rarely occurs in free state, it is largely found in combination with sulphur, oxygen and iron. Arsenic naturally occurs in over 200 different mineral forms, of which approximately 60% are arsenates, 20% sulfides and sulfosalts (such as arsenopyrite, orpiment, realgar, lollingite, tennantite) and the remaining 20% includes arsenides, arsenites, oxides, silicates and elemental arsenic (As). Major arsenic-containing minerals are arsenopyrite (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3) (Mandal and Suzuki, 2002).

Arsenic occurs in the environment as a result of several inputs that contain this element as organic and inorganic forms. The presence of arsenic in natural water is related to the process of leaching from the arsenic containing source rocks and sediments. Influx of arsenic from various anthropogenically-induced sources may also contaminate both soils and ground water especially under anoxic conditions.

Concentrations of various types of igneous rocks range from < 1 to 15 mg As/kg, with a mean value of 2 mg As/kg. Similar concentrations (< 1–20 mg As/kg) are found in sandstone and limestone. Significantly higher concentrations of up to 900 mg As/kg are found in argillaceous sedimentary rocks including shales, mudstone and slates. Up to 200 mg As/kg can be present in phosphate rocks. Other important geological sources of arsenic are active volcanoes (e.g. Mexico, Italy, Japan) where volcanic activity can transport vast amounts of material from the Earth’s core into the biosphere in the form of magma and volcanic dust. Studies have shown arsenic concentations an order of magnitude higher in soils close to these active volcanoes compared with concentrations in reference soil samples (Fodor, 2001).

Arsenic occurs mainly as inorganic species but also can bind to organic materials in soils. Under oxidizing conditions, in aerobic environments, arsenates (iAsV) are the stable species and are strongly sorbed onto clays, iron and manganese oxides/hydroxides and organic matters. Arsenic precipitates as ferric arsenate in soil horizons rich in iron. Under reducing conditions arsenites (iAsIII) are the predominant arsenic compounds. Inorganic arsenic compounds can be methylated by microorganisms, producing under oxidizing conditions, monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAsO).

The presence of arsenic in natural water is generally associated with the geochemical environments such as basin-fill deposits of alluvial-lacustrine origin, volcanic deposits, inputs from geothermal sources, mining wastes and landfills. Occurrence of arsenic in natural water depends on the local geology, hydrology and geochemical characteristics of the aquifer materials. Furthermore, the geochemical characteristics of the aquifer material and their interactions with the aqueous media also play an important role in controlling retention and/or mobility of arsenic within the subsurface environment. Uncontrolled anthropogenic activities such as smelting of metal ores, use of arsenical pesticides and wood preservatives agents may also release arsenic directly to the environment (Jain and Ali, 2000).

Arsenic is found at low concentration in natural water. In seawater, the concentration of arsenic is usually less than 2 μg L^{-1}. The levels of arsenic in unpolluted surface water and groundwater vary typically from 1–10 μg L^{-1}. In freshwater, the variation is in the range of 1-10 μg L^{-1} rising to 100–5000 g L^{-1} in areas of sulfide mineralization and mining. In thermal waters, concentrations of up to 8.5 mg L^{-1} and 1.8–6.4 mg L^{-1} have been reported in New Zealand and Japan, respectively (Sharma and Sohn, 2009). Turkish geothermal waters had more than 1000 μg/L of arsenic in total and Na_2HAsO_4 was found to be the dominant form in these samples (Fodor, 2001).

In air, arsenic exists predominantly absorbed on particulate matters, and is usually present as a mixture of arsenite and arsenate, with the organic species being of negligible importance except in areas of arsenic pesticide application or biotic activity. The human exposure of arsenic through air is generally very low and normally arsenic concentrations in air ranges from 0.4 to 30 ng m^{-3}. According to USEPA the estimated average national exposure in the U.S. is at 6 ng As m^{-3}.

1.5.2 Anthropogenic Sources

Anthropogenic sources exceed natural sources in the environment by 3:1 (Mandal and Suzuki, 2002). Mining, metal smelting and burning of fossil fuels are the major industrial processes that contribute to arsenic contamination of air, water and soil. The use of arsenic-containing pesticides in the past has left large areas of agricultural land contaminated. The use of arsenic in the preservation of timber has also led to contamination of the environment.

Arsenic is one of the components of a large number of compounds generated by human activities (precious metals mining, pharmaceutical manufacturing, wood processing, glassmaking industry, electronics industry, chemical weapons etc.). Arsenic has been widely used in agriculture: sodium arsenite, which is the only known fungicide available for protecting grape vines from excoriosis, was indeed used until 2001. The main anthropogenic sources of atmospheric arsenic contamination are As-rich fossil fuels producing arsenic oxide (As_2O_3), which is highly toxic. It has been calculated that arsenic is retained in the atmosphere for less than 10 days before being released in the formof dust or precipitated by rainfall. The atmospheric As levels have been found to be highest near industrial sites: higher levels therefore occur in the northern hemisphere, where there are many industrial sites, compared to the southern hemisphere. Mine wastewaters are the fluids with the highest arsenic contents. Sulphurous mineral outcrops are naturally subject to oxidation, since they come in contact with both air and water, leading to the gradual development of sulphuric acid and the solubilisation of the metals present. Acid mine drainage (AMD) waters result from water percolating through excavated ores containing sulphites and/or collecting in galleries as a result of seepage or underground water movements. These effluents, which often contain extremely high levels of toxic metals, constitute one of the main environmental problems with which the world’s mining industries are faced . The production of AMD is favoured and amplified by both chemical and biological catalytic reactions. Acidic waters affect the structure of the communities of micro-organisms they harbour, and although some forms of life (mainly consisting of bacteria and archaea) are able to survive under these conditions, the number of species present (i.e., the biodiversity) usually decreases. In addition, the low pH levels generally existing in these environments inhibit the growth of many bacteria contributing to the decomposition of the organic matter present in the water, and thus reduce the amount of nutrients available for other species. In extreme cases, the higher organisms inhabiting running waters receiving AMD effluents disappear completely over long stretches (Liévremont, 2009).

1.6 Toxicity of Arsenic

The occurrence of arsenic in natural waters has received much attention during recent years, because of its potential toxicity on human health. In natural waters, arsenic may occur as arsenite As(III), arsenate As(V), monomethylarsonic acid (MMAA), and dimethylarsenic acid (DMAA). In groundwater, it exists predominantly in the form of As(III) and As(V). Methylated arsenic species have rarely been reported to be present in groundwaters at levels above 1 mg L^{-1}. Among these forms, inorganic arsenic is far more toxic than the organic forms. The levels of toxicity for As(III) and As(V) are so different (i.e. As(III)>As(V)) (Kumar and Riyazuddin, 2008).

Arsenic is toxic to both plants and animals and inorganic arsenicals are proven carcinogens in humans. The toxicity of arsenic to human health ranges from skin lesions to cancer of the brain, liver, kidney, and stomach. A wide range of arsenic toxicity has been determined that depends on arsenic speciation. Generally inorganic arsenic species are more toxic than organic forms to living organisms, including humans and other animals.

Exposure to arsenic trioxide by ingestion of 70–80 mg has been reported to be fatal for humans. Arsenite (iAs^{III}) is usually more toxic than arsenate (iAs^{V}). Recent studies found that MMA^{III} and DMA^{III} are more acutely toxic and more genotoxic than their parent compounds.

The toxicity of different arsenic species varies in the order: arsenite > arsenate > monomethylarsonate (MMA) > dimethylarsinate (DMA)

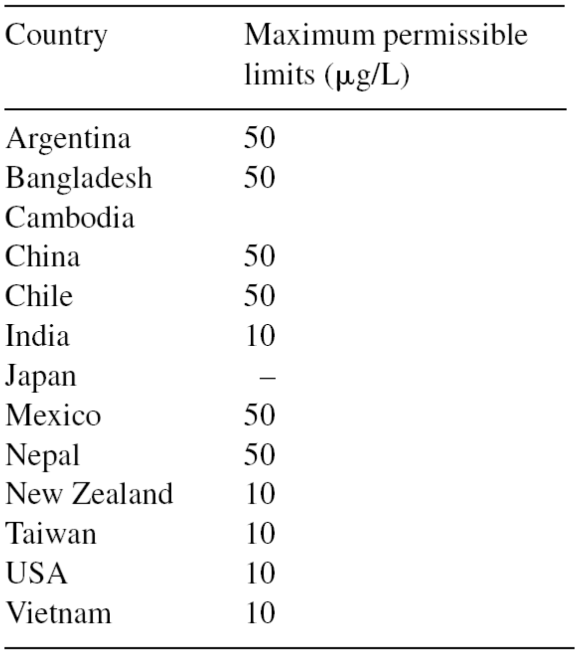
The toxicity of trivalent arsenic is related to its high affinity for the sulfhydryl groups of biomolecules such as glutathione (GSH) and lipoic acid and the cysteinyl residues of many enzymes. The formation of As(III)–sulfur bonds results in various harmful effects by inhibiting the activities of enzymes (Sharma and Sohn, 2009). The three most commonly employed biomarkers used to identify or quantify arsenic exposure are total arsenic in hair or nails, blood arsenic, and total or speciated metabolites of arsenic in urine. Because arsenic (as the trivalent form) accumulated in keratin-rich tissues such as skin, hair and nails), arsenic levels in hair and nails are used as indicators of past arsenic exposure. Normally inorganic arsenic is very quickly cleared from human blood. For this reason blood arsenic is used only as an indicator of very recent and/or relatively high level exposure, for example, in poisoning cases or in cases of chronic stable exposure (i.e. from drinking water). Studies show that in general blood arsenic does not correlate well with arsenic exposure in drinking water, particularly at low levels (Mandal and Suzuki, 2002).

The World Health Organization (WHO) and The U.S. Environmental Protection Agency (USEPA) promulgated stringent arsenic regulations to minimize these risks. The maximum contaminant level (MLC) for arsenic was set as 10 µg/L in February 2002, and the compliance deadline was scheduled for January 2006. In the prevailed TS 266 of Turkey (revised on 29th of April 2005); the arsenic limit of water standard for the purpose of humanitarian consumption was reduced to 10 µg/L from 50 µg/L. The arsenic limit of the water standard had been determined as 10 µg/L on 17th of February 2005 when Regulation on Water Intended for Humanitarian Consumption was published and entered into force (Tekbaş et al, 2008).

Table 1.2. Arsenic standards set by various organizations.

	World Health Organisation (WHO-1958)	World Health Organisation (WHO-1963)	World Health Organisation (WHO-1999)	Environmental Protection Agency (USEPA-1975)	Environmental Protection Agency (USEPA-2001)	European Community (EC-1998)	Turkey (TSE 266-1997)	Turkey (17th of February 2005 when Regulation on Water Intended for Humanitarian Consumption)
Arsenic (µg/L)	200	50	10	50	10	10	50	10

Table 1.3 Countries affected by arsenic contamination and maximum with permissible limits for drinking water (Mohan and Pittman Jr., 2007).



Country	Maximum permissible limits (μg/L)
Argentina	50
Bangladesh	50
Cambodia	
China	50
Chile	50
India	10
Japan	–
Mexico	50
Nepal	50
New Zealand	10
Taiwan	10
USA	10
Vietnam	10

1.7 Analytical Methods for Arsenic

Historically, colorimetric methods, base on the reaction of arsine gas with silver diethyldithiocarbamate or reduction of arsenomolibdate with tin(II), have been used for the determination of arsenic. However, colorimetric methods are appropriate for the determination of arsenic at mg/L level (Burguera and Burguera, 1997).

The numerous arsenic forms present in the environment and living organisms show large differences in their metabolism and toxicity. Therefore, speciation studies are of critical importance. Also the arsenic species occur at very low concentrations so that reliable results are achieved only by means of very sensitive methods of analysis.

Arsenic (III) and (V) are the most often determined species in environmental waters, soils and sediments, while organic arsenic species are common constituents of biological tissues and fluids. Usually the concentration of these species is at low ranges and necessitates a preconcentration step because most of the available detectors still lack the sensitivity for direct determination. Moreover, these detectors are also deficient in selectivity, thus a separation step is required prior to determination. The most popular analytical methods used for arsenic speciation are based on a combination of a powerful separation process with an adequate element-specific detector. The methods frequently used for separation and preconcentration are solvent extraction, precipitation and coprecipitation, ion-exchange chromatography (IEC), gas chromatography (GC) and high performance liquid chromatography (HPLC).

Numerous instrumental methods have been developed either for the determination of total arsenic or its methylated and inorganic forms in soils and sediments, water, air and biological fluids and tissues. Among them, the most commonly used include ultraviolet spectrometry, electrochemical methods (EQ), atomic absorption spectrometry (AAS) mainly coupled to hydride generation (HG-AAS), in continuous flows or flow injection systems (FI), atomic emission spectrometry (AES), generally with inductively coupled plasma (ICP-AES), ICP-mass spectrometry (ICP-MS), electrothermal-AAS in graphite furnace (ETAAS), X-ray spectrometry, neutron activation analysis (NAA), atomic fluorescence spectrometry (AFS), capillary electrophoresis, voltametry techniques, etc. On-line combinations of some separation techniques (e.g., HPLC or IEC) with the most sensitive detection methods (AAS or ICPAES) seem to be highly successful and lower detection limits are obtained, specially if HG is performed before detection (Burguera and Burguera, 1997).

1.8 Hydride Generation – Atomic Absorption Spectrometry

Hydride generation atomic absorption spectrometry (HG-AAS) is currently the most popular technique for routine determination of arsenic at μg/L level exploit the reduction of some arsenic compounds to gaseous arsines. The gas is then thermally decomposed to give elemental arsenic for atomic detectors like AAS. Early methods for arsine generation involved the dissolution of metals (Zn, Mg, Al) in mineral acids to form nascent hydrogen which reacts with As(III) to form AsH_3. Other hydride ion precursors that have found use in generating hydrides are TiCl, SnCl, in concentrated HCl or Al in basic medium known as Fleitmann reaction. The effective reaction with $NaBH_4$, gained acceptance and is now almost universally used for the generation of hydrides ever since its introduced into analytical chemistry (Figure 1.3).

$$As(OH)_3 + 3BH_4^- + 3H^+ \longrightarrow AsH_3 + 3BH_3 + 3H_2O$$

$$BH_3 + 3H_2O \longrightarrow H_3BO_3 + 3H_2$$

Figure 1.3. Hydride generation reaction (Hung et al., 2004)

It is well known that trivalent and pentavalent arsenic show different behavior in the generation process, although it was claimed that some procedures only measure the total content of As in the sample. However, it was demonstrated that even at high concentrations of borohydride and at optimized acid concentrations, the response obtained from As(V) is lower than that of As(III). (Anthemidis et al., 2005; Coelho et al., 2002).

The process of formation of arsine from As(V) suggests that there are two steps in the reaction: the reduction of As(V) to As(III) and the subsequent formation of AsH_3 some procedures, As(V) is reduced to As(III) prior to HG by the use of reducing reagents like: KI, thiosulphate, or mixtures of KI-ascorbic acid and L-Cysteine to achieve pre-reduction for the determination of total arsenic (Burguera and Burguera, 1997).

As an efficient sample introduction method, HG enhances sensitivity normally by 10–100-fold over the more commonly used liquid sample nebulization procedures. Also, the target arsenic species can be separated from almost all other accompanying materials in the sample through the HG process. Only gaseous hydrides are introduced to the detector, and the sample matrix is left in the liquidwaste. Thus, spectral and chemical interferences encountered in the detection systems are essentially eliminated (Gong et al., 2002).

There are two basic modes of hydride generation (Figure 1.4). In the direct transfer mode, hydride released from a sample solution is directly transported to an atomizer. Three direct transfer methods are currently employed; continuous flow (CF), flow injection (FI) and batch.

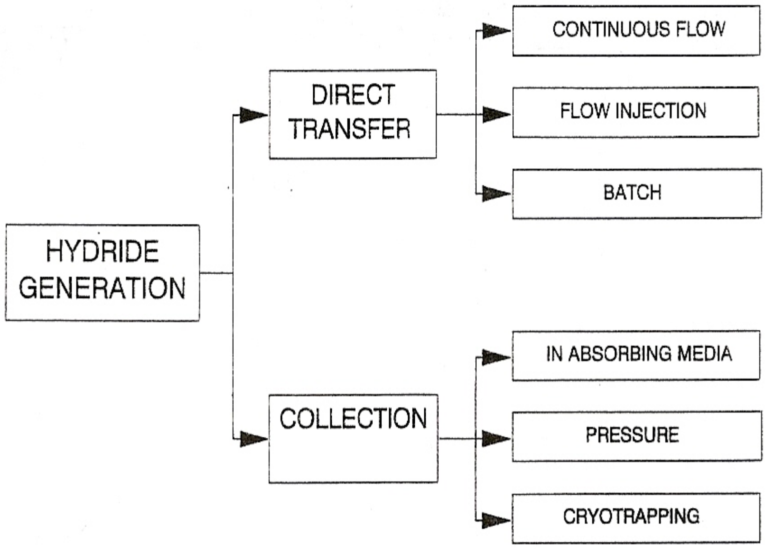


Figure 1.4 Methods of hydride generation.

In the collection mode, the hydride is trapped in a collection device, considered as a part of the generator, until the evolution is completed and is then transported to an atomizer all at once. Collection methods were employed much more frequently in the early years of the application of hydride generation since the metal/acid system used then was relatively slow so that it could take several minutes for the reaction to reach completion. Obviously, it was advantageous to collect the released hydride and then to sweep it to the atomizer in the shortest possible time. It should be stressed that when using the BH_4^-/acid system as the reducing agent the need to collect released hydride is much less pressing so that the simpler direct transfer methods are more often utilized presently.

Continuous Flow

The sample and reagents are first mixed by means of an automatic sampler and multi-channel proportioning pump system, then passed to a gas/liquid separator or stripping column where the hydrides are removed from the liquid prior to transfer to the atomizer.

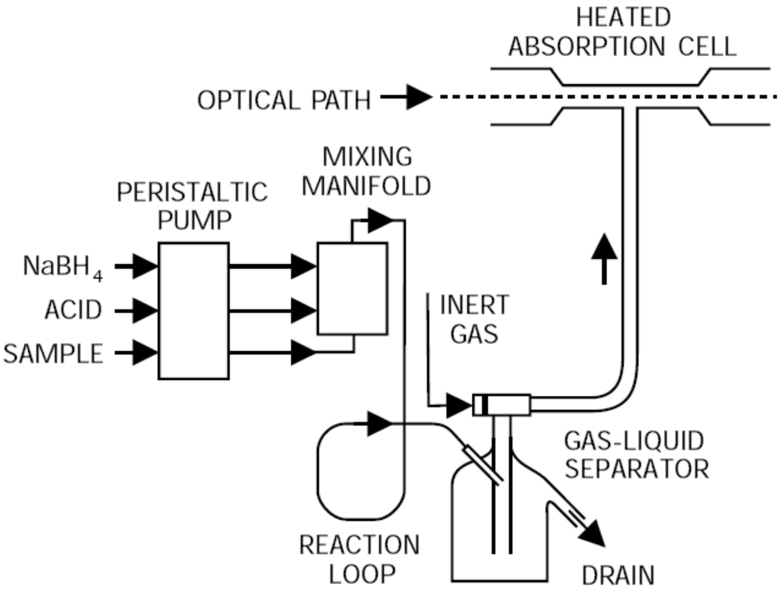


Figure 1.5 Schema of continuous flow.

Batch mode

A batch generator is a vessel made of glass or plastic serving both as the reactor as well as the gas-liquid separator. Figure 1.6 shows an example of the batch generator. A batch of acidified sample solution is placed inside and then the reducing agent, most conveniently tetrahydroborate solution, is introduced either using a pump or manually employing a syringe. Released hydride is thus supported by the purge gas flow to the atomizer together with the hydrogen formed from reducing agent decomposition. After finishing the hydride evolution the reacted mixture has to be disposed to waste, generator is rinsed and a new batch of simple is added.

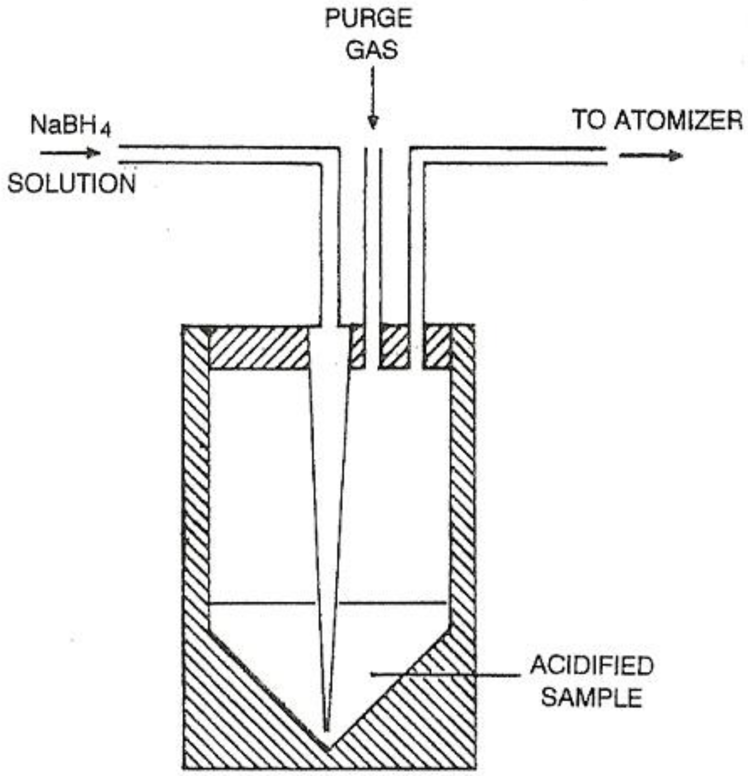


Figure 1.6. Schematic presentation of the batch generator.

1.9 Preconcentration Techniques

Since the toxicities and the behaviour of inorganic species are different and toxic, speciation of arsenic at trace level is of great importance. Preconcentration techniques are usually required in order to determine such low levels of arsenic.

Pre-concentration techniques of trace metals, like sorption of the analyte on solid materials, modified or not with organic reagents have frequently been used. The metal or the metal-complex is eluted from the solid material by a suitable solvent and afterwards the determination of the metal is performed (Bortoleto and Cadore, 2005). In column adsorption, the sorption of As(V) is more favorable compared to As(III), due to the faster kinetics of As(V) compared to As(III) (Choong et al., 2007). Strong acids and bases seem to be the best desorbing agents to produce arsenic concentrates (Mohana and Pittman Jr., 2007).

The usual reactions for As pre-concentration make use of organic reagents which are able to separate As(III) from As(V), such as dithiocarbamate and dithiophosphate compounds sorbed on solid materials.

Some inorganic materials, such as ion-exchange resins, zeolites, and alumina, goethite, clay, kaolinites, activated carbon, chitosan beads, coconut husk, coal, fly ash, ferrous iron, zirconium oxide, red mud, petroleum residues,rice husk, human hair, sawdust, manganese greensand, orange juice residues, akaganéitenanocrystal and chome waste have also been used as sorbent materials for ions from aqueous solutions (Bortoleto and Cadore, 2005; Choong et al., 2007). As it is easy to remove the adsorbent from aqueous media after treatment, sorption technique is generally considered to be a promising method and has been studied for arsenic removal as well (Xu et al., 2002). Sorption is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical forces. So far, various adsorbents for arsenic removal have been developed which include metal-loaded coral limestone, hematite and feldspar, sandy soils, activated carbon, activated alumina, lanthanum-loaded silica gel, and hydrous zirconium oxide, etc. Iron or iron coated materials are the most commonly adopted adsorbents for arsenic removal from the contaminated water. Several studies have been conducted to adsorb arsenic on various iron coated materials such as iron oxide-loaded slag, iron oxide-coated sand, iron impregnated sand, and iron hydroxide-coated alumina (Haque et al., 2008).

The use of carbon extends far back into history. Its origin is impossible to document. Charcoal was used for drinking water filtration by ancient Hindus in India, and carbonized wood was a medical adsorbent and purifying agent in Egypt by 1500 B.C. Modern activated carbon industrial production was established in 1900–1901 to replace bone-char in sugar refining. Powdered activated carbon was first produced commercially from wood in Europe in the early 19th century and was widely used in the sugar industry. Activated carbon was first reported for water treatment in the United States in 1930. Activated carbon is a crude form of graphite with a random or amorphous highly porpus structure with a broad range of pore sizes, from visible cracks and crevices, to crevices of molecular dimensions. Active carbons have been prepared from coconut shells, wood char, lignin, petroleum coke, bone-char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste, waste rubber tire, etc (Mohan and Pittman Jr., 2007). Activated carbon is also commonly used as the material in arsenic treatment. Eguez and Cho (1987) measured the sorption of As (III) and As (V) using activated carbon at various pH values. From the effect of temperature on sorption, they could determine the isoteric heat of adsorption., Other researchers (Huang and Fu, 1984; Gimbel and R. Hobby, 2000; Eguez and E.H. Cho, 1987) impregnated carbon with various metal ions such as iron oxide in order to improve arsenic adsorption. The iron oxide impregnated activated carbon has shown higher As(III) and As(V) removals compared with the non-impregnated carbon. Rajakovic (1992) found that carbon pretreated with Ag^+ or Cu^{2+} ions improved As(III) adsorption but reduced As(V) adsorption. Evdokimov et al. (1973) reported that arsenic adsorption can be improved by impregnating carbon with ferric hydroxide or tartaric acid. Rajakovic and Mitrovic (1992) showed that chemically treated activated carbon exhibits high adsorption capacity for arsenic. Peraniemi et al. (1994) used zirconium-loaded activated carbon and successfully removed arsenic, selenium, and mercury.

Manju et al. (1998) prepared a coconut husk carbon (CHC) by carbonizing one part of coconut husk with 1.8 parts by weight of sulfuric acid (18 M) at 150 °C for 24 h. The carbonized material (CHC) was water washed to remove acid and dried at 105 °C. The CHC (10 g) was mixed with 100mL of 100 mmol/L copper solution (initial pH 8.5). The mixture was shaken for 24 h at 30 °C and filtered. The filtrate’s pH was 6.5. The resulting copper-impregnated coconut husk carbon (CuCHC) was water washed until the filtrate was copper free. Optimum As(III) adsorption conditions on this copper-impregnated activated carbon were established. Maximum adsorption capacity occurred at pH 12.0. Capacity increased going from 30 to 60 °C. Spent adsorbent was regenerated using 30% H_2O_2 in 0.5M HNO_3 (Mohan and Pittman Jr., 2007).

Red mud is a waste material formed during the production of alumina when bauxite ore is subjected to caustic leaching. A typical Bayer process plant generates a 1–2 tonnes of red mud per ton of alumina produced. Red mud has been explored as an alternate adsorbent for arsenic. An alkaline aqueous medium (pH 9.5) favored As(III) removal, whereas the acidic pH range (1.1–3.2) was effective for As(V) removal. Heat and acid treatments on red mud increased its adsorptive capacity. Authors suggested that it is advantageous to use awaste material of red mud liquid phase in the treatment of arsenical wastewater, possibly conjunction with red mud solids as adsorbent. Brunori et al. (2005) also utilized red mud for treating contaminatedwaters and soils with particular attention to the Italian regulatory system. Experiments studied the metal trapping ability of treated red mud and the subsequent release of these trapped metals at low pH conditions. The treated red mud exhibited a high metal trapping capacity and metal release at low pH was generally low. The removal capability of treated red mud was increased using more mud in contact with the solution. After 48 h, only 35% of

As (corresponding to an absolute value of 230 µg/L) was removed with 2 g/L, but the percentage significantly increased up to 70% (corresponding to an absolute value of 400 µg/L) with 10 g/L (Mohan and Pittman Jr., 2007).

Iron oxides also have been widely used as sorbents to remove contaminants from wastewater and liquid hazardous wastes compared to activated carbon. Removal has been attributed to ion exchange, specific adsorption to surface hydroxyl groups or coprecipitation. Hydrous ferric oxide (HFO) is an important sorbent in wastewater treatment especially for hazardous chemical. Olivier et al. (2005) removed arsenic groundwater by filtering the water through sand and zero-valent iron. As(V) sorbed on the forming hydrous ferric oxides (HFO) resulted from the oxidation of iron (Choong et al., 2007). Different similar sorbent materials have been also used, including amorphous iron hydroxide and ferric hydroxide. Other types of ferric products, such as ferrihydrite, silica that containing iron (III) oxide, iron-oxide impregnated activated carbon, Ce(IV)-doped iron oxide, iron oxide-coated sand, iron(III)-Poly(hydroxamic acid) complex, ferric chloride, Fe(III)-doped alginate gels, nanocomposite adsorbent based on silica and iron(III) oxide, and iron oxide-coated polymeric materials are also used in arsenic treatment. Other reported works on the metal oxide based adsorbents include manganese oxide, zirconium oxide and alumina.

All the aforementioned methods clearly demonstrate that iron coated materials are an efficient adsorbent for arsenic. Different types of sands, alumina, etc. have been coated with iron salts because Fe(III) has a strong affinity toward inorganic arsenic species and creates favorable adsorption sites for arsenic throughout the various adsorption mechanisms such as mono and bidentate surface complex formation, ligand exchange, and electrostatic attraction. One such adsorbent, light expanded clay aggregates (LECA), has been proposed as a new material by Haque et al. (2008). In addition, FeO and Al_2O_3 have been found in the chemical composition of this adsorbent that clearly facilitates arsenic adsorption according to Gupta et al. and Hlavay and Polyak.

Sperling et al. (1992) determined Cr(III) and Cr(VI) in water using FI-FAAS, after pre-concentration on activated alumina. In 1994, Ebdon et al. used activated alumina in the acid form to pre-concentrate As, Cr, Se, and V before their determination by ICP-MS, with good pre-concentration factors. Recently, Lin and Wu evaluated the use of activated alumina as a sorbent for arsenite and arsenate ions in a procedure for the decontamination of water. An efficient on-line system for arsenic pre-concentration using activated acid alumina as the sorbent material coupled to HG-AAS was developed and was shown to be fast and of low cost. The analyte in the pentavalent oxidation state is reduced to its trivalent form with l-cysteine and the total inorganic arsenic is sorbed onto activated alumina in the acid form in a mini-column coupled to a FI-HG AAS system (Bortoleto and Cadore, 2005).

Narcise et al. (2005) developed a flow injection-column preconcentration-hydride generation atomic absorption spectrophotometric (FI-column-HGAAS) method for determining μg/L levels of As(III) and As(V) in water samples, with simultaneous preconcentration and speciation using anion exchange microcolumn and pH control of sample based on pKa prior to hydride generation and detection by AAS.

3-(2-Aminoethylamino) propyltrimethoxysilane (AAPTS) is a kind of silylating and coupling reagent which was used to modify the surface of inorganic materials and organic polymer. AAPTS modified ordered mesoporous silica was synthesized and used as SPE material for preconcentration/ separation of As(III) and As(V) by Chen et al. (2009).

An octadecyl immobilized silica mini-column is used for selective retention of the complex between As(III) and APDC, while the sorption of As(V) is readily accomplished by a 717 anion exchange resin mini-column by Chen M. et al. (2009). The retained As(III)–PDC complex and As(V) are effectively eluted with a 3.0 mol/ L hydrochloric acid solution as stripping reagent.

Aluminum-loaded Shirasu-zeolite P1 (Al-SZP1), was prepared and employed for the adsorption and removal of arsenic(V) (As(V)) ion from aqueous system. Al-SZP1 was found with a high As(V) adsorption ability, equivalent to that of activated alumina, and seems to be especially suitable for removal of As(V) in low concentration. Al-SZP1 was prepared by treating a P1 type Shirasu-zeolite (SZP1) with aluminum sulfate solution. Shirasu is of volcanic origin and is located in southern Kyushu area of Japan in large quantities, and SZP1 is easily synthesized by one-step reaction from Shirasu. Al-SZP1 was found effective to the adsorption of not only As(V), but also phosphate and fluoride ions (Xu et al., 2002).

Biosorption is one of the important preconcentration-separation procedures for organic and inorganic substances including metal ions at trace levels (Bingol et al., 2009; Naiya et al., 2009; Akar et al., 2009; Vaghetti et al., 2009; Caner et al., 2009; Yang et al., 2009). Biosorption is defined as the removal of substances from solution by biological material (Wang and Chen, 2009). Biosorption is a physico-chemical process and includes such mechanisms as absorption, adsorption, ion exchange, surface complexation and precipitation (Ghasemi et al., 2008; Wang and Chen, 2009). Various biological materials including microorganisms, bacteria, fungi, yeast, algae, etc. have been used on biosorption studies (Gadd, 2009; Arief et al., 2008). Biosorption process has been also used for the speciation of various metals such as selenium, antimony, chromium, etc. Alternaria solani coated Diaion HP-2MG column system is used for speciation of As(III) and As(V) at first time by Tuzen et al. (2010) . The proposed method has the following advantages: simple, rapid and low analysis cost. The method proposed here is rapid and has good reproducibility. The detection limits of analytes are superior to those of preconcentration techniques for analyses.

Recent studies have shown that nano-scaled adsorbents have a higher adsorption capacity for arsenic than larger particles. The use of CuO nanoparticles provides an adsorbent with a higher surface area and therefore, a higher adsorption capacity. Martinson and Reddy (2009) synthesized CuO nanoparticles and evaluated them as an adsorbent to remove As(III) and As(V) from groundwater. The CuO nanoparticles had a surface area of 85 m^2/g and were 12–18 nm in diameter. Adsorption occurred within minutes and CuO nanoparticles effectively removed As(III) and As(V) between pH 6 and 10. The maximum adsorption capacity was 26.9 mg/g for As(III) and 22.6 mg/g for As(V). The presence of sulfate and silicate in water did not inhibit adsorption of As(V) but only slightly inhibited adsorption of As(III). High concentrations of phosphate (>0.2 mM) reduced the adsorption of arsenic onto CuO nanoparticles. X-ray photoelectron spectroscopy (XPS) indicated that As(III) was oxidized and adsorbed in the form of As(V) on the surface of CuO. The CuO nanoparticles were also able to remove arsenic (to less than 3 lg/L) from groundwater samples. These results suggest that CuO nanoparticles are an effective material for arsenic adsorption and may be used to develop a simple and efficient arsenic removal method (Martinson and Reddy, 2009).

A nanocrystalline-based TiO_2 adsorbent has been developed for effective removal of As(V) and As(III) (Pena et al., 2005, 2006). The nanocrystalline TiO2 was prepared by hydrolysis of titanium sulfate solution (Meng et al., 2005). The TiO2 produced was in the anatase form with an average crystalline particle size of 6 nm. Adsorbed As(III) in the TiO_2 filterwas oxidized to As(V) in the presence of dissolved oxygen (Jing et al., 2009).

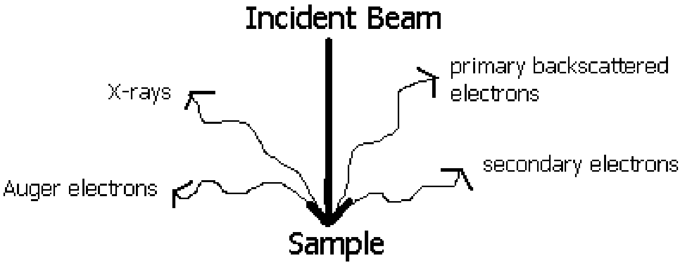
Solid phase extraction sorbent, nanometer titanium dioxide immobilized on silica gel (immobilized nanometer TiO_2), was prepared by sol–gel method, and the adsorptive potential of immobilized nanometer TiO_2 for inorganic arsenic species (As(III) and As(V))was assessed by Liang and Liu (2007). It was found that both As (III) and As(V) could be adsorbed quantitatively on immobilized TiO_2 within a pH range of 5.0–7.5, and only As(III) could be quantitatively retained on the sorbent within a pH range of 9.5–10.5 while As(V) was passed through the microcolumn without the retention. Based on this fact, a new speciation scheme for inorganic arsenic was established, which involved determining total As at pH 6.0 and As(III) at pH 10, with As(V) obtained by difference. The adsorption capacity of immobilized nanometer TiO_2 for As(III) was found to be 4.22 mg /g. Under the optimized conditions, the detection limits of this method for As(III) were 24 ng/ L with an enrichment factor of 50, and the relative standard deviation (R.S.D.%) was 4.8% (n = 11, c=5ng/mL). The proposed method has been applied to the speciation of inorganic arsenic in natural water samples with satisfactory results (Liang and Liu, 2007).

Nanosized nickel based adsorbent was used for the first time as an adsorbent for As(III) and As(V) by our group. The mechanism of adsorption is under study (Henden et al., 2010).

1.10 Sem-Edx

Scanning Electron Microscopy (SEM) allows for visual observation of an area of interest in a completely different way from that of the naked eye or even normal optical microscopy. SEM images show simple contrasts between organic-based and metallic-based materials and thus instantly provide a great deal of information about the area being inspected. At the same time, Energy Dispersive X-Ray Spectroscopy (EDS), sometimes referred to as EDAX or EDX, can be used to obtain semi-quantitative elemental results about very specific locations within the area of interest. Methodology:

Simply put, SEM allows an area of interest to be examined at extremely high magnifications. SEM produces images of high resolution and detailed depth of field unlike those attainable using normal optical microscopy. As examples, surface structures, general anomalies, and areas of contamination can be easily identified and then if needed, isolated for further analysis. A specimen containing the area(s) of interest is placed within the vacuum chamber located at the bottom of the SEM column. An electron source, located at the top of the column, produces electrons, which pass through the column and are incident upon the specimen. The electron beam is directed and focused by magnets and lens inside of the SEM column as it approaches the specimen. The beam“swings” across the sample causing some of the electrons to be reflected by the specimen and some to be absorbed. Specialized detectors receive these electrons and process the signal into a usable format. Typically, the three different detectors used are referred to as: Secondary Electron, Backscatter, and Xray.



Secondary Electron – The secondary electron detector is primarily used to observe surface structure(s) associated with the specimen. This detector converts the electrons reflected by the specimen surface into a signal that can be displayed as an image on a monitor. Subsequently these images can be captured as a photograph, if desired. SEM images, as well as any “captured” photographs, are grayscale in appearance as opposed to color because the electrons being detected are actually beyond the light spectrum. Backscatter – The backscatter detector operates similar to the secondary electron detector as it also “reads” electrons that are being reflected by the test specimen and displays them for observation and / or photography. For this detector type however, the grayscale observed in the images is a direct result of the element(s) present in the area being observed. X-Ray – The term X-ray detector is a general term for the type of detector used to perform Energy Dispersive X-Ray Spectroscopy (EDS). The X-ray detector, or more specifically, the EDS technique is used to qualitatively and most of the time “semi-quantitatively” determine the elemental composition of an area of interest which was visually identified and observed using the secondary electron and backscatter detectors mentioned above. As the electron beam from the SEM itself strikes the specimen surface, the electrons within the atoms of this area of interest are elevated to an excited state. When the electrons in these atoms then return to their ground state, a characteristic x-ray is emitted. These x-rays are then gathered by the X-ray detector and converted into “useful” information. An image can, as described above, be generated but more importantly, these x-rays emitted from the specimen give information as to the elemental composition of the area. As a result, the EDS technique can detect elements from carbon (C) to uranium (U) in quantities as low as 1.0 wt%. In combination with the SEM itself, the specific area of analysis for a given specimen of interest can be adjusted simply based on the magnification at which the specimen is being observed. Both SEM and EDS can be used for evaluating and/or analyzing samples whether it’s simply for screening purposes or for a failure related issue. Typically, SEM provides the visual “answer” while EDS provides the elemental “answer”. In both cases, areas of interest can be observed aerially or in cross section.

A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

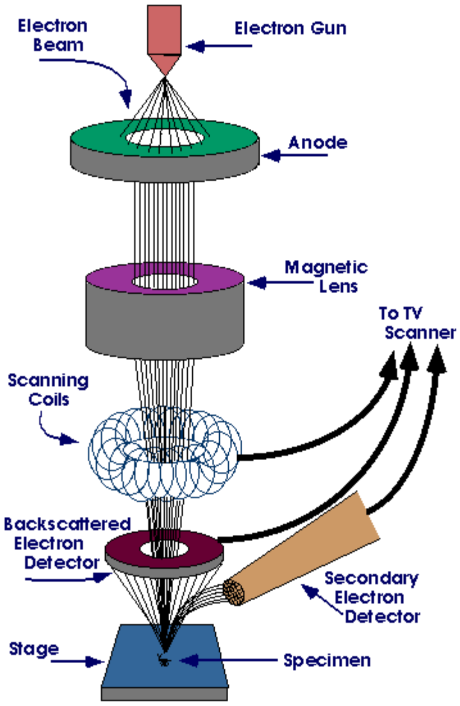


Figure 1.7. Schematic diagram of an SEM.

Figure 1.7 shows a schematic of the imaging system in a typical scanning electron microscope starting from the electron source. A stream of monochromatic electrons generated by an electron gun is condensed by the first condenser lens to both form the beam and limit the amount of current, as well as, in conjunction with the condenser aperture, to eliminate the high-angle electrons from the beam. The second condenser lens focuses the elctrons into a thin, tight, coherent beam and an objective aperture is used to further eliminate high-angle electrons from the beam. A set of coils is used to scan the beam in a grid fashion. The objective lens focuses the scanning beam onto the specimen desired, one point at a time. Interaction between the electron beam and the sample generates back scattered electrons (BSE), X-ray , secondary electrons (SE), and Auger electrons in a thick or bulk sample. These various electrons are detected and the signal detected contains information about the specimen under investigation. BSE is more sensitive to heavier elements than SE. The X-ray radiation can be detected in a technique called energy dispersive X-ray (EDX) spectroscopy that can be used to identify specific elements.

1.11 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used technique to investigate the chemical composition of surfaces.

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra high vacuum (UHV) conditions.

XPS is based on the principle that, when a surface is irradiated with X-rays, photoelectrons will be ejected. If X-ray lines of sufficiently narrow widths are used, the photoelectrons have characteristic energies related directly to the atomic levels from which they came; Xps commonly uses either the Al Kα (1486.6 eV) or the Mg Kα (1253.6 eV) lines. With such low-energy excitation, the photoelectrons must originate in the outer few monolayers only if they are to escape without energy loss. The resultant energetic electrons are then collected and counted, after dispersion, by an electrostatic analyzer. A photoelectron energy spectrum then consists of a plot of counts as a function of kinetic energy. Such spectra may be used for analytical purposes or to gain insight into the chemical bonding of the elements present. The technique is fully quantitative in so far as the area under a characteristic peak can be related directly to the concentration of the corresponding atomic species in the surface layer.

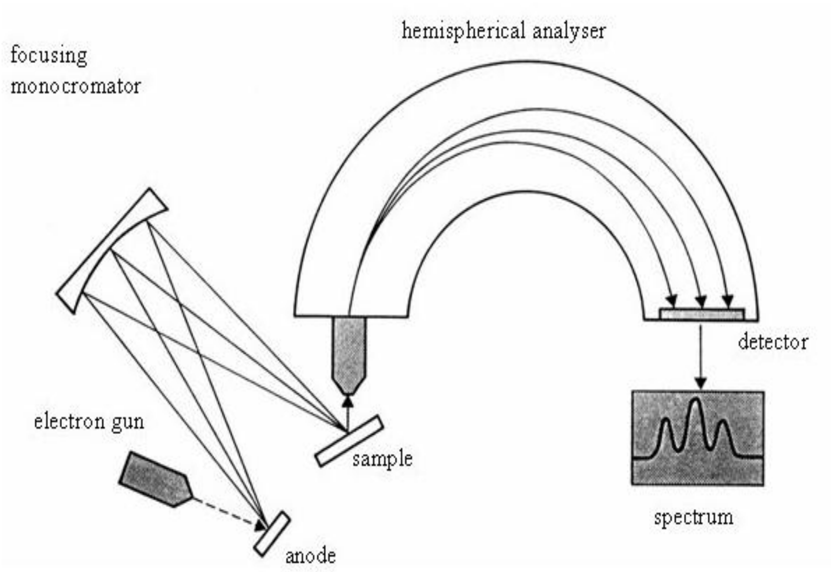


Figure 1.8 Schematic view of an X-ray photoelectron spectrometer with monochromator.

The sensitivity of XPS is of the order of 0.1.% for most elements. Chemical information can be extracted from the spectrum by detailed considerations of the position (with a typical resolution of ±0.1 eV) and shape of peak envelopes. This information can be interpreted readily by comparison with spectra of standard compounds, recorded in the same experiment, or by consulting the voluminous and mature literature on Xps investigations of various compounds (Myhra et al., 1983).

1.12 Thermogravimetric Analysis

The main function of TGA is the monitoring of the thermal stability of a material by recording the change in mass of the sample with respect to temperature. Figure 1.9 shows a simple diagram of the inside of a typical TGA. Inside the TGA, there are two pans, a reference pan and a sample pan. The pan material can be either aluminium or platinum. The type of pan used depends on the maximum temperature of a given run. As platinum melts at 1760 ^{0}C and alumium melts at 660 ^{o}C, platinum pans are chosen when the maximum temperature exceeds 660 ^{0}C. Under each pan there is a thermocouple which reads the temperature of the pan. Before the start of each run, each pan is balanced on a balance arm. The balance arms should be calibrated to compensate for the differential thermal expansion between the arms. If the arms are not calibrated, the instrument will only record the temperature at which an event occurred and not the change in mass at a certain time. To calibrate the system, the empty pans are placed on the balance arms and the pans are weighed and zeroed.

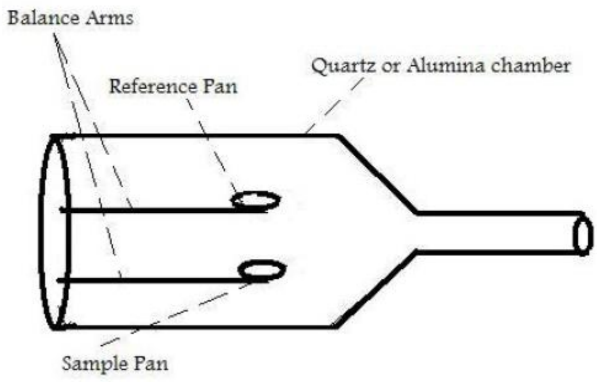


Figure 1.9. Schematic representation of a TGA apparatus.

As well as recording the change in mass, the heat flow into the sample pan (differential scanning calorimetry, DSC) can also be measured and the difference in temperature between the sample and reference pan (differential thermal analysis, DTA). DSC is quantitative and is a measure of the total energy of the system. This is used to monitor the energy released and absorbed during a chemical reaction for a changing temperature. The DTA shows if and how the sample phase changed. If the DTA is constant, this means that there was no phase change. Figure 1.10 shows a DTA with typical examples of an exotherm and an endotherm.

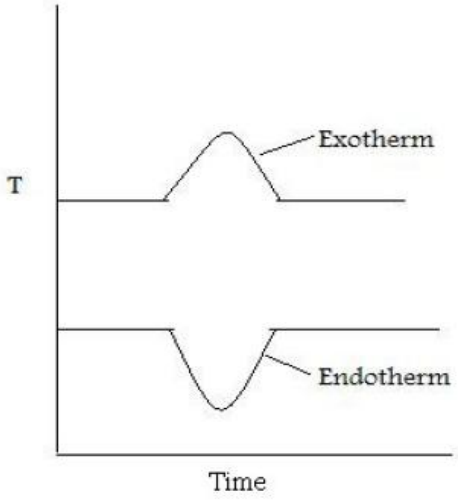


Figure 1.10 Simplified representation of the DTA for an exotherm and an endotherm.

When the sample melts, the DTA dips which signifies an endotherm. When the sample is melting it requires energy from the system. Therefore the temperature of the sample pan decreases compared with the temperature of the reference pan. When the sample has melted, the temperature of the sample pan increases as the sample is releasing energy. Finally the temperatures of the reference and sample pans equilibrate resulting in a constant DTA. When the sample evaporates, there is a peak in the DTA. This exotherm can be explained in the same way as the endotherm. Typically the sample mass range should be between 0.1 to 10 mg and the heating rate should be 3 to 5 ^{0}C/min. The thermal analysis can be performed in a controlled atmosphere, usually oxygen, nitrogen or helium, with adjustable flow rates (Barron, 2010)

1.13 X-Ray Diffraction (XRD)

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.

X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector.

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being Kα and Kβ. Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Kα1and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuKα radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation ($n\lambda=2d \sin \theta$), constructive interference occurs and a peak in intensity occurs. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

1.14 Nanoparticles

Over the past decade, nanomaterials have been the subject of enormous interest. These materials, notable for their extremely small feature size, have the potential for wide-ranging industrial, biomedical, and electronic applications. As a result of recent improvement in technologies to see and manipulate these materials, the nanomaterials field has seen a huge increase in funding from private enterprises and government, and academic researchers within the field have formed many partnerships.

Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. Their defining characteristic is a very small feature size in the range of 1-100 nanometers (nm). The unit of nanometer derives its prefix nano from a Greek word meaning dwarf or extremely small. One nanometer spans 3-5 atoms lined up in a row. By comparison, the diameter of a human hair is about 5 orders of magnitude larger than a nanoscale particle (Hickman, 2002).

The variety of nanomaterials is great, and their range of properties and possible applications appear to be enormous, from extraordinarily tiny electronic devices, including miniature batteries, to biomedical uses, and as packaging films, superabsorbants, components of armor, and parts of automobiles (Hickman, 2002).

Nanomaterials fall into three broad categories: metal oxides, nanoclays, and carbon nanotubes. Metal-oxide nanoparticles, include nanoscale zinc oxide, titanium oxide, iron oxide, cerium oxide and zirconium oxide, as well as mixed-metal compounds such as indium-tin oxide and zirconium and titanium, as well as mixed-metal compounds such as indium-tin oxide. This small matter has an impact on many disciplines, such as physics, chemistry and biology. In paint and coatings nanomaterials fulfill decorative needs (e.g. color and gloss), functional purposes (e.g. conductivity, microbial inactivation) and improve protection (e.g. scratch resistance, UV stability) of paints and coatings. In particular nano-size metal-oxides, such as TiO_2 and ZnO or Alumina, Ceria and Silica and nano-size pigments find application in new paint and coating formulations.

When matter is reduced in size it changes its characteristics, such as color and interaction with other matter such as chemical reactivity. The change in the characteristics is caused by the change of the electronic properties. By the particle size reduction, the surface area of the material is increased. Due to this, a higher percentage of the atoms can interact with other matter, e.g. with the matrix of resins. Surface activity is a key aspect of nanomaterials. Agglomeration and aggregation blocks surface area from contact with other matter. Only well dispersed or single-dispersed particles allow to utilize the full beneficial potential of the matter. It is well known that strong intermolecular forces, such as van derWaals attraction, p–p interaction, etc., contribute to the aggregation of nanoparticles. As for magnetic nanoparticles, magnetic dipole–dipole interaction makes this kind of attraction stronger. Thus it is a challenge to obtain monodisperse magnetic nanoparticles dispersion. Different ligands, such as polymer and surfactants, have been used to modify the surface of nanoparticles for stabilization and to control the particle growth (Hou et al., 2005). In particular for small matter from several nanometers to couple of microns, ultrasonic cavitation is very effective in breaking agglomerates, aggregates and even primaries. When ultrasound is being used for the milling of high concentration batches, the liquid jets streams resulting from ultrasonic cavitation, make the particles collide with each other at velocities of up to 1000km/h. This breaks van der Waals forces in agglomerates and even primary particles (Gedanken, 2004).

A number of methods such as photolytic reduction, radiolytic reduction, sonochemical method, solvent extraction reduction, microemulsion technique, polyol process, and alcohol reduction have been developed for the preparation of metal nanoparticles. For the synthesis of various kinds of metal nanoparticles, some metals such as nickel, copper, and iron are relatively difficult because they are easily oxidized (Wu et al., 2009; Wu and Chen, 2003).

Various methods in preparation metallic nanoparticles invoke different properties with desired purposes. The widely exploited methods are:

The sol–gel method: Silver nanoparticles, for example, is prepared by mixing the $AgNO_3$ solution with tetraethylorthosilicate ($Si(OC_2H_5)_4$, TEOS), ethanol and water then with a few drops of HNO_3 as a catalyst. The mixed solution was dispersed and dried. The dried gels were reduced at a temperature of 400 ^{0}C for 30 min in hydrogen gas. The Ag particles have a size of about 5~10 nm with a profile distribution in the form of lognormal distribution. The nanoparticles are embedded in silica glass in wellseparated and protected matrix. The preparation of iron nanoparticles embedded in glass can be prepared with the same method by substituting $FeCl_3$ for the silver salt. The sol–gel method has advantages of yielding high purity, isotropic, and low temperature annealing while with shortage of cracking after dried by heavy doping. The free water absorbed in the porous gel and the H−O· bonds desorbed on the porous surface or the chemical absorbed hydroxyl groups which affects the optical absorption within the wavelengths of 160~4500 nm can be removed by high temperature sintering.

Hydrosol/magnetic fluid method: The pure metallic suspension particles such as noble metals can be prepared by hydrosol method by using reducing agent to embed in protective gelatin (Marzke and W. S. Glaunsinger, 1983). The advantage of the hydrosol method is that relatively narrow size distribution with average diameter of 20 A^0 can be achieved. The magnetic fluid with Fe_3O_4 particles surrounded by oleic acid as surfactant for protection from their aggregation and dispersed in water can be prepared as described (Upadhyay et al., 2000; Sharma and F. Waldner, 1977).

Vacuum deposition method: The presence of inert gas in vacuum chamber and lowering down the substrate temperature to liquid nitrogen temperature during thermal evaporation can reduce the momentum of the evaporated metallic atoms or clusters by collision with gas to obviate their further aggregation on the substrate. The evaporated metal atoms condensed just at where they reached without migration to the potential minimum thereby lose van der attraction between particles. The resulting smokes can be collected from the substrate or walls of the evaporationchamber with the particle sizes can be easily controlled between 30~1000 Å depending on the gas pressure, the evaporation speed, the type of gas used, and the substrate temperature (Cavicchi and R. H. Silsbee, 1984; Frank et al., 1985). Direct (DC) or radio frequency (RF) sputtering with the structure of deposited films mostly to be amorphous without substrate heating can successfully deposit refractory metals and alloys. Ball milling method: Hard and brittle ceramic materials can be ball-milled into nanoparticles to produce nanocrytals, noncrystals, and pseudocrystals. Powders of 500 nm sizes can be milled into several nm by strong vibrations when mixed with tungsten-carbide (WC) spheres. The shortages of ball milling are the surface contamination of the products and nonuniformity of the structure but is a simple method. Sometimes an addition of 1~2% of methanol or phenol can prevent diffusion and solid reaction of the nanoparticles (Lue, 2007).

Nickel nanoparticles have important applications in catalysts and conducting and magnetic materials. Ball milling, electrodeposition, thermal plasma, polyol process, chemical vapor deposition (CVD), decomposition of organicmetallic precursors, chemical reduction in the liquid phase have been applied to obtain pure metallic nickel nanocrystal. Chemical reduction of cations from the solution of metal salts using strong reduction agents may be the best way to prepare nickel nanostructure materials (Wu et al., 2009). It has the following advantages: using equipment simple, technological process short and controlling easy (Duan and Li, 2004).

The polyol process using ethylene glycol as a solvent and a reducing agent with a reflux at 120–180 °C and 1 atm has been used to produce many metal and bimetallic nanoparticles. A suitable soluble polymer (e.g., polyvinylpyrrolidone (PVP)) usually was added as a protective agent. In the absence of soluble polymer, the resultant particles were in the micrometer or sub-micrometer size range except at a quite low precursor concentration (e.g., 0.3 mM). However, it was difficult to remove completely the soluble polymer on the particle surface by simple washing. Thus, it might be an interesting challenge to prepare nickel nanoparticles with a precursor concentration above 1.0 mM in ethylene glycol without soluble polymer (Wu and Chen, 2003). Typically, an appropriate amount of nickel chloride (2.5– 45 mM) was dissolved directly in ethylene glycol. Then, an appropriate amount of hydrazine (0.05–0.9M) and of 1.0 M NaOH solution (10–72 μl/ml) were added in sequence. At a temperature of 60 ◦C, nickel nanoparticles were formed after about 1 h in a capped bottle with stirring. The resultant particles have been characterized to be pure nickel /Wu and Chen, 2003).

Solution reduction method is a new technology for preparing nanoscale particles in recent years Duan and Li (2004) prepared a Nickel nanoparticles s follows: nickel chloride hydrate were used as precursors, they were dissolved in an alcohol–water hydrazine solution, pH value of the solution was adjusted from 8.0 to 12 using sodium hydroxide, the precursor concentration was typically 0.2

mol/ L. The solution was stirred and reaction can happen by spontaneous autocatalytic reduction in the solution at room temperature. After about 20 min the metal particles were quantitatively precipitate from the solution, the metal particles were recovered by centrifugation, washed with distilled water and ethanol, and dried in vacuum drying oven at 50 °C. The nickel nanoparticles with various grain sizes were obtained by adjusting the pH value of the mixed solution. the shape of the Ni particles is predominantly spherical, the particles possess a size distribution of about 30–40 nm and are linked together to form chains at room temperature.

The hydrazine reduction route has been successfully adapted to continuous flow synthesis of nickel nanoparticles in nearcritical water by Hald et al. (2008) . Thus, pure nickel nanoparticles can be continuously produced in seconds rather than hours, and the particle size can be controlled between 40 and 60nm by increasing the reaction temperature from 150 to 350 ^{0}C. nickel nanoparticles with average sizes from 40 to 60nm were demonstrated. The method therefore provides some size control and enables the production of nickel nanoparticles without the use of surfactants. The pure nickel nanoparticles can be easily isolated using a magnet.

Wu et al. (2009) synthesized pure metallic nickel nanoparticle, spherical in shape, successfully by the chemical reduction of nickel chloride with hydrazine at room temperature without any protective agent and inert gas protection. Preparation procedure is described as follows: a desired amount of nickel chloride hexahydrate was dissolved into absolute ethanol (solution a). Another mixture was obtained by mixing potassium hydroxide and hydrazine monohydrate together (mixture b). Then solution a was poured into mixture b immediately with vigorous continued magnetic stirring at room temperature. The overall reaction time was about 2 h. The resultant product was washed thoroughly with deionized water for removal of reaction residues followed by washing with acetone. Finally, the black particles were soaked in acetone in a closed bottle for further characterization. XRD spectrum shows that the resultant product is pure face-centered cubic (fcc) structure metallic nickel. The method is simple, easy to operate, relatively cheap, and environmentally friendly.

The nanonickel catalyst was prepared with 4.0 g $NiCl_2.6H_2O$ dissolved in 30.0 ml ethanol solution and 10.0 g 80 wt.% $N_2H_4.H_2O$ alkaline solution containing 10.0 g NaOH and 10.0 ml distilled water. The reaction, with stirring, lasted for several hours until there were no bubbles released any more at room temperature. The obtained black nano-nickel catalyst was washed with distilled water till pH = 7, then washed with absolute alcohol to remove water and kept in absolute alcohol (Zhao et al., 2008).

Synthesis of nickel nano-particles with a coating of a hydrophilic surfactant has been carried out by use of sodium borohydride and sodium formaldehyde sulfoxylate (SFS) in aqueous medium. It is observed that an ideal temperature range for formation of nickel nanoparticles is between 50 and 100 °C. Nickel sulphate dihydrate (5 g/20 mL water) was taken in a beaker and dissolved completely. Sodium succinate (31.7 g/200 mL water) was added drop wise to nickel sulphate solution. The reaction mixture was allowed to stir for about 10 min at 60–70 °C by which time reddish colored solutionwas obtained. To this, sodium borohydridewas added or SFS in water and stirred for about 1–2 h. After cooling the reaction mixture to room temperature, it was filtered, washed with several portions of distilled water and finally with methanol. The black residuewas dried overnight in an oven to collect the free flowing black powder (Khanna et al., 2009).

The spray pyrolysis (SP) method is a very important method for the preparation of metal, metal oxide, non-oxide and composite powders (Messing, et al., 1993 ; Okuyama et al., 2003) because this method could produce submicron/nanoparticles with controlled composition and morphology, good crystallinity, and uniform size distribution, all of which can be readily obtained in only one step. In a typical SP process, a solution is atomized into an aerosol reactor where the droplets undergo solvent evaporation and solute precipitation within the droplet, and then undergo drying, followed by thermolysis of precipitate at a higher temperature, and finally sintering to form final particles (Messing, et al., 1993). Nagashima et al. (1990) first prepared nickel particles by a SP method of nickel precursors more than 10 years ago. They showed that nickel particles could be prepared from $Ni(NO_3)_2$ and $NiCl_2$ in a H_2–N_2 atmosphere with a residence time of several seconds, but porous and hollow nickel particles were obtained below its melting point, i.e., 1455 $^{\circ}$C. Since then, many researchers have reported on nickel particle formation by SP method. For example, similar results were obtained by Stopic et al. (1996; 1999) from $Ni(NO_3)_2$ precursor in H_2–N_2. Che et al. also produced nickel particles from $NiCl_2$ and $Ni(NO_3)_2$ in a H_2–N_2 atmosphere. They showed that nickel particles could be obtained at higher than 900 $^{\circ}$C with residence time of 5–20 s (Wang et al., 2004). All these investigations used H_2 as the reductive gas and no additives were employed. As a matter of fact, many reductants can be selected either gas or liquid. Che et al. and Xia et al. chose ammonia as the reducing agent. Nickel particles with a little NH_3 can be produced by this method. Formic acid is also selected as the reductive for nickel powder production by SP method in another paper of Xia et al. Kim et al. recently used a cosolvent, ethanol, as the reducing agent instead of the hazardous gas agent, viz. H_2. Nickel nanoparticles synthesized from nickel nitrate hexahydrate with hydrogen, formic acid, and ethanol as the reducing agents by using LPSP (low pressure spray pyrolysis) were investigated by Wang et al. (2004).

As the use of nanomaterials increases worldwide, concerns for worker and user safety are mounting. To address such concerns, the Swedish Karolinska Institute conducted a study in which various nanoparticles were introduced to human lung epithelial cells. The results, released in 2008, showed that iron oxide nanoparticles caused little DNA damage and were non-toxic. Zinc oxide nanoparticles were slightly worse. Titanium dioxide caused only DNA damage Carbon nanotubes caused DNA damage at low levels. Copper oxide was found to be the worst offender, and was the only nanomaterial identified by the researchers as a clear health risk (Wikipedia, 2010).

1.15 The Aim of Study

Arsenic contamination in water is a severe global problem. Since contamination of water due to arsenic compounds is a severe problem in regards to health hazards, trace arsenic determination is very important. This study aims to develop a novel preconcentration method for trace arsenic determination in waters by using Ni^0 / Ni_xB as a sorbent and HG-AAS as the measurement technique.

2.EXPERIMENTAL

2.1 Apparatus and Operating Conditions

A GBC 904 PBT model atomic absorption spectrometer was used. A quartz tube atomizer, a laboratory made batch type hydride generation system and the HG3000 automatic continuous flow hydride generator were employed.

Nüve water bath shaker equipped with a thermostat was used for sorption studies.

The pH measurements were performed by using a Orion 4 Star pH meter . pH meter was calibrated before every measurements.

For centrifugation, Nüve NF 800 was used at 3000 rpm.

TGA was performed using a Perkin Elmer Pyris Diamond TG/DTA instrument (Japan).

X-ray powder diffraction (XRD) pattern was obtained on a Philips X'Pert Pro X-Ray diffractometer with Cu Kα radiation (V= 45 KV, I= 40 mA).

SEM andEnergy Dispersive X-ray spectrometric (EDX) measurements were also made for the characterization of the sorbents using Philips XL-30S FEG Scanning Electron Microscop (Eindhoven , The Netherlands).

X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific K-alpha X-ray photoelectron spectrometer. Al Kα radiation was employed as the excitation source. Acquisition parameters :

Source type: Al K Alpha
Spot size: 400µm
Lens mode: Standard
Analyser mode. CAE: Pass energy 150 eV
Energy type size. 1.000 eV
No of energy steps: 1361
No. scans: 2
Total acq time: 2 mins 16,1 sec

In the manuel system, the hydride generation tube consists of a glass reaction vessel, 15 cm long and 1.5 cm in diameter, with a side arm. A silicone rubber bung was put into the side arm and the sample solution was injected into the reaction vessel through this bung using a plastic syringe. The top of the reaction vessel was closed with a rubber bung with two holes for carrier gas inlet and outlet. Both bungs were covered with Teflon tape. The laboratory-made hydride generation system is shown in Figure 2.1.

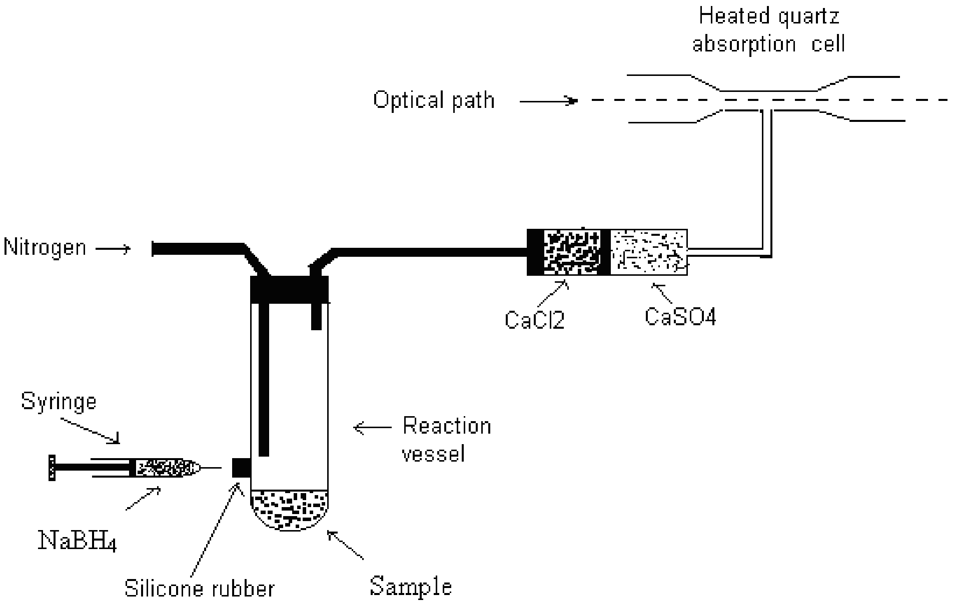


Figure 2.1. A laboratory-made hydride generation system.

In automated system, the acidified sample, blank, or standard, is continuously pumped and mixed with a pumped stream of sodium borohydride, to produce the gaseous hydrides. A flow of nitrogen is added to this mixture and the hydrides are stripped into the gas phase. A gas/liquid separator allows the gaseous, hydride containing phase, to enter the quartz tube atomizer in air-acetylene flame, and allows the remaining liquids to be pumped to waste.

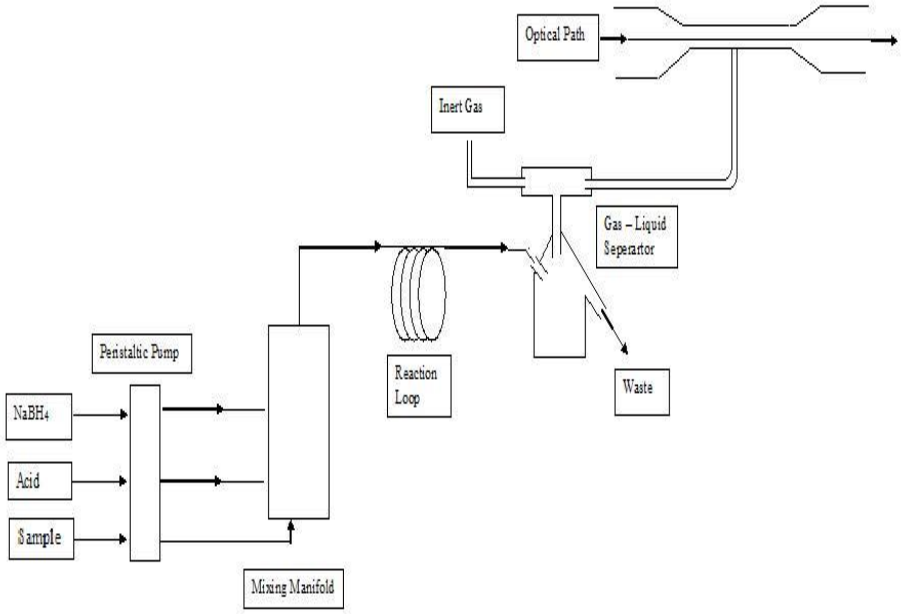


Figure 2.2. Automated hydride generation atomic absorption spectrometer.

The experimental conditions for batch type and automated hydride generation AAS system are listed in Table 2.1.

Table 2.1. Instrumental operating parameters for HG-AAS in arsenic determination.

Type	Batch Type	Automated
Element	As	As
Matrix	0.1 mol / L	1.7 mol / L
Lamp current (mA)	8.0	8.0
Wavelength (nm)	193.7	193.7
Slit width (nm)	1.0	1.0
Slit height	Normal	Normal
Instrument mode	Absorbans BC on	Absorbans BC on
Sampling mode	Manuel sampling	Pump system
Flame type	Air – Acetylene	Air – Acetylene
Acetylene flow	1.59	1.59
Air flow	10.6	10.6
Read time (s)	60	10
Measuring mode	Peak area	Peak area
Carrier gas	Nitrogen	Nitrogen

2.2 Reagents

All reagents and chemicals were analytical grade. Glassware was cleaned by soaking them in dilute nitric acid (10%) and rinsed with distilled water prior to use.

Arsenite [As(III)] Stock Standard Solution (1000.0 µg/mL): Prepared by dissolving 0.33 g As_2O_3 in concentrated HCl and diluting to 250 mL with distilled water. Stock solution contained 2 mol/L HCl.

Arsenate [As(V)] Stock Standard Solution (1000.0 µg/mL): Prepared by dissolving 1.04 g $Na_2HAsO_4.7H_2O$ in concentrated HCl and diluting to 250 mL with distilled water. Stock solution contained 2 mol/L HCl.

Standard Arsenite [As(III)] Solution (I) (10 µg/mL): Prepared by diluting 1 mL arsenite stock solution and making up 100 ml with distilled water.

Standard Arsenate [As(V)] Solution (I) (10 µg/mL): Prepared by diluting 1 mL arsenate stock solution and making up 100 ml with distilled water.

Standard Arsenite [As(III)] Solution (II) (0.5 µg/mL): Prepared by diluting 2.5 mL standard arsenite solution (I) and making up 100 ml with distilled water.

Standard Arsenate [As(V)] Solution (II) (0.5 µg/mL): Prepared by diluting 2.5 mL standard arsenate solution (I) and making up 100 ml with distilled water.

Working [As(III)] and [As(V)] Standards (2.5 / 5.0 / 10.0 / 20.0 µg/L): Standard arsenic solutions were prepared by appropriate dilution of the standard solutions I or II .

Ni(II) solution (25%): Prepared by dissolving 124 g $Ni(NO_3)_2.6H_2O$ in distilled water and adjusting the final acidity to 1 mol/L with HCl and completing the volume to 100 mL.

0.1%, 0.2%, 0.3%, 0.5% Ni(II) solutions were prepared by diluting apropriate volume of 25% Ni(II) solution with distilled water.

Automated system solutions:

Sodium tetrahydroborate(III) Solution (0.6% in 0.6% NaOH): 1.0 g sodium tetrahydroborate(III) (Merck) and 1.0 g sodium hydroxide (Merck) dissolved in 166 mL distilled water.

HCl for carrier solution (10.2 mol/L): Prepared by diluting appropriate volume of concentrated HCl (Merck).

2.3 Arsenic Determination Procedure

Since arsine formation efficiency from As(V) is low, for the determination of As(V), it was reduced to As(III) before reduction with THB. For reducing As(V) to As(III), 1 mL of concentrated HCl, 2 mL of 50 % KI and appropriate amount of ascorbic acid (to reduce I_2 formed)were added on to 9 mL of arsenic solution. Final KI concentration was 8.3%. Prereduction time used was 15 min.

Because of the possibility of As(III) in the solutions could be oxidized to As(V) during various treatments, for total arsenic determination pre–reduction with KI was always done before hydride generation with THB .

2.4 Preparation of Nickel Based Sorbent

In this study, nanonickel sorbent was prepared using two way. At the beginning of the study, sorbent was prepared daily piece by piece. In subsequent studies, sorbent was prepared in bulk at a time.

Sorbent 1:

25 % Ni(II) solution was prepared by dissolving 124 g $Ni(NO_3)_2.6H_2O$ in water and adjusting the final acidity to 1 mol/L with HCl. Then, 1 mL of this solution was diluted to 250 mL with distilled water. The Ni(II) concentration of the solution was 0.1 %. 10 mL 0.1 % Ni(II) solution was added into beaker and stirred on a magnetic stirrer. 2 mL of 4 % $NaBH_4$ was added using a pipette while still stirring on magnetic stirrer. Black precipitate immediately appeared after the first drop of sodium borohydride solution. Mixture was waited until gas bubbles disappeared. Afterwards, the mixture was put a plastic container and was shaked in a water bath for 30 minutes to obtain fine particules. To separate the black

nanoparticles from the liquid phase, it was centrifuged and supernatant was decantated. Then, particles were washed with distilled water and centrifuged at least three times. If the sorbent will be stored, it is washed with acetone at three times and it was stored in acetone.

Sorbent 2:

100 mL 2.5 % of Ni(II) solutions were divided into four parts. Each part of solution was added to beaker and stirred on a magnetic stirrer. Solution was reduced pouring 4% $NaBH_4$ in a burette. Black precipitate formation was observed. To separate the black nickel nanoparticles from the liquid phase, ultra centrifugation technique was used. Particles were washed and centrifuged at least three times first with 20 ml portions of water and then acetone to remove all of the water. Prepared nanoparticles were finally dried in water bath at 75 ^{o}C for two hours under Ar atmosphere.

2.5 Optimization Studies

2.5.1 Choice of Metal Ion for Sorbent

Solutions:

1. 500 μg/mL Cu (II) solution: Prepared by dissolving 0.0628 g $CuSO_4$ anhydride in distilled water and adjusting the final acidity to 0.05 mol/L with HCl and making up 50 ml with distilled water

2. 500 μg/mL Ni(II) solution : Prepared by dissolving 0.124 g $Ni(NO_3)_2.6H_2O$ in distilled water and adjusting the final acidity to 0.05 mol/L with HCl and making up 50 ml with distilled water.

3. 200 μg/mL Au(III) solution: Prepared by diluting 1 mL of 1000 μg/mL Au(III) to 5 mL.

Sorption Procedure:

Relevant nanometal particles were prepared as describe above.

10 mL 50 μg/mL pH~6 As(III) and As(V) solution was added on the sorbent

and was shaked in water bath at 25°C for two hours. After sorption, solutions were filtrated by black band filter paper. Filtrate was collected and prepared for arsenic determination.

Table 2.2. Arsenic sorption efficiency for Cu^0, Ni^0, Au^0 sorbent.

Arsenic Sorption %		
	As(III)	As(V)
Cu^0	15	21
Ni^0	>96	>98
Au^0	0	0

According to Table 2.2, the best arsenic sorption results were observed for nanonickel. Therefore nanonickel was chosen for further studies.

2.5.2 Optimization of Ni(II) Concentration for the Preparation of the Sorbent

In this study, the effect of various concentration of Ni(II) solutions on arsenic sorption was investigated. Thus, 10 mL of 0.05%, 0.1%, 0.2%, 0.3%, 0.5% Ni(II) solutions were taken. Nanonickel sorbents were prepared using this solutions according to the sorbent 1 as mentioned before.

For sorption 10 mL 100 ng/mL As(III) solution at pH~6 was added on to Ni^0 sorbent and was shaked for two hours.

Table 2.3 The effect of sorbent amount on arsenic sorption efficiency.

Arsenic Sorption %			
C_i (µg/mL) (10 mL)	Amount of Nickel in the Sorbent (mg)	As(III)	As(V)
500	5	94.9	-
1000	10	96.4	98.1
2000	20	96.4	-
3000	30	97.7	-
5000	50	96.3	-
C_i : Initial Ni(II) concentration			

By determination of arsenic remaining in the solution, it was seen that adsorption efficiency was almost 100%. Although the efficiency of Ni^0 which was prepared using 0.05% Ni(II) was 95%, sorbent prepared using 0.1% Ni(II) was choosen. Because sorbents were prepared from 0.05% Ni(II) solutions are difficult to centrifuge.

2.5.3 The Effect of Contact Time on Arsenic Sorption Efficiency

In order to choose the best contact time on arsenic sorption efficiency, 1, 5, 10, 30, 60 and 120 minutes were investigated at 25.0 ^oC. For sorption 25 mL of 50 ng/mL As(III) solutions at pH~6 and 10 mg of the sorbent was used. After filtration and then pre-reduction steps remained arsenic concentrations in solution were determined. The graph is shown in Figure 2.3.

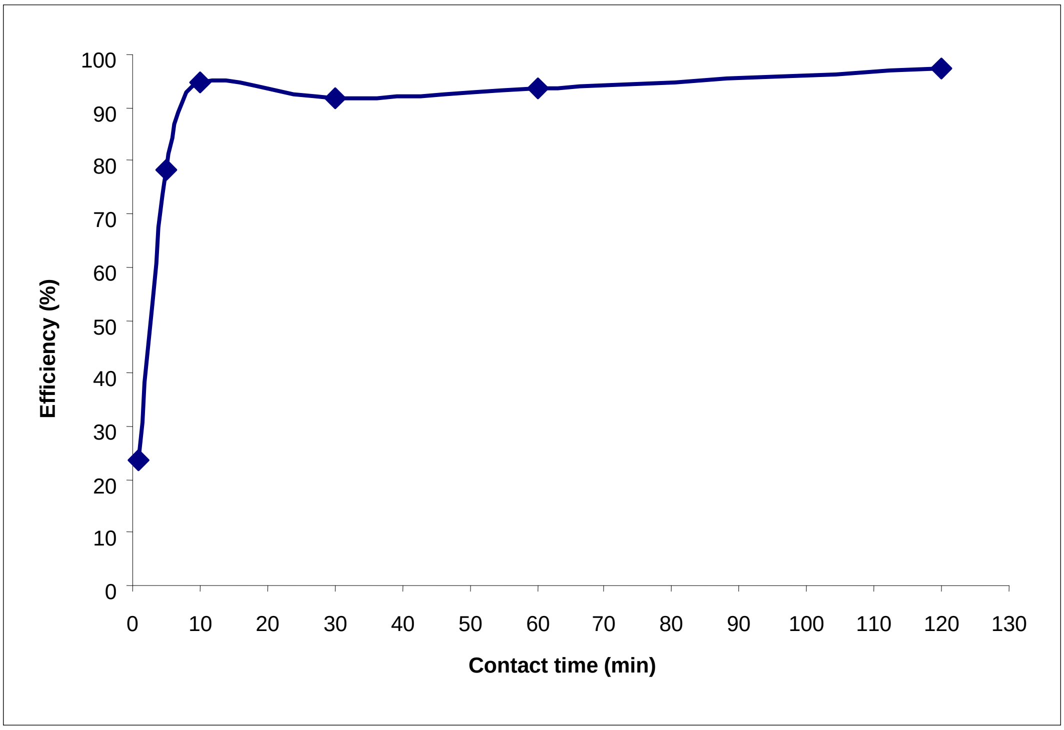


Figure 2.3 The effect of contact time on arsenic sorption.

Although sorption efficiency reached 95% in ten minutes with 10 mL sample volume, possibility of working with larger sample volumes were taken into consideration and contact time was chosen as one hour.

2.5.4 The Effect of Initial pH on Arsenic Sorption Efficiency

To determine the best initial pH of arsenic solution, the pH of 25 mL 100 ng/L portions of As(III) was adjusted to 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 using HCl or NaOH at various concentrations. 10 mg sorbent which was prepared by following the sorbent 1 was used. Contact time was chosen as one hour. After separation of liquid and solid phases, the solutions were analyzed. The graph is shown in Figure 2.4.

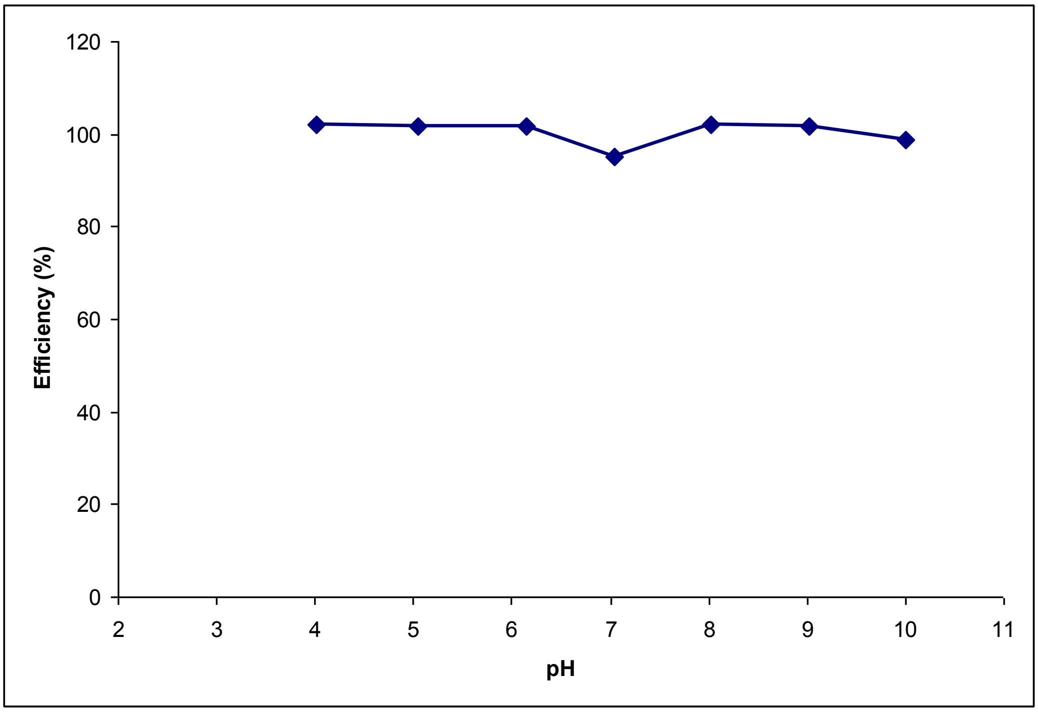


Figure 2.4. The effect of initial pH on arsenic sorption efficiency

According to Figure 2.4 at selected pH intervals, there was not a great change. So, pH 6 was chosen for further studies.

For separating liquid and solid phases filtration method and ultracentrifuge method were employed. Depending on the chosen separation method, final pH was found to vary. When sorbent was separated by filtration, final pH was found between 5.5 and 6.9. When sorbent was separated by ultra-centrifuge, final pH was found between 8.47 and 8.81. The differences in pH were attributed to the presence of paper.

2.5.5 The Effect of Reduction Time of Ni(II) with $NaBH_4$ on Arsenic Sorption Efficiency

In order to find out the time required for the reduction to be completed, the sorbents were shaken for 5, 10, 20, 40, 60, 120 and 180 minutes with $NaBH_4$ solution at 25 ^{0}C. 10 mg sorbents which were prepared according to the sorbent 1 were used. Arsenic in 20 mL of 1000 ng/mL As(III) solution at pH~6 was used for sorption. The graph is shown in Figure 2.5.

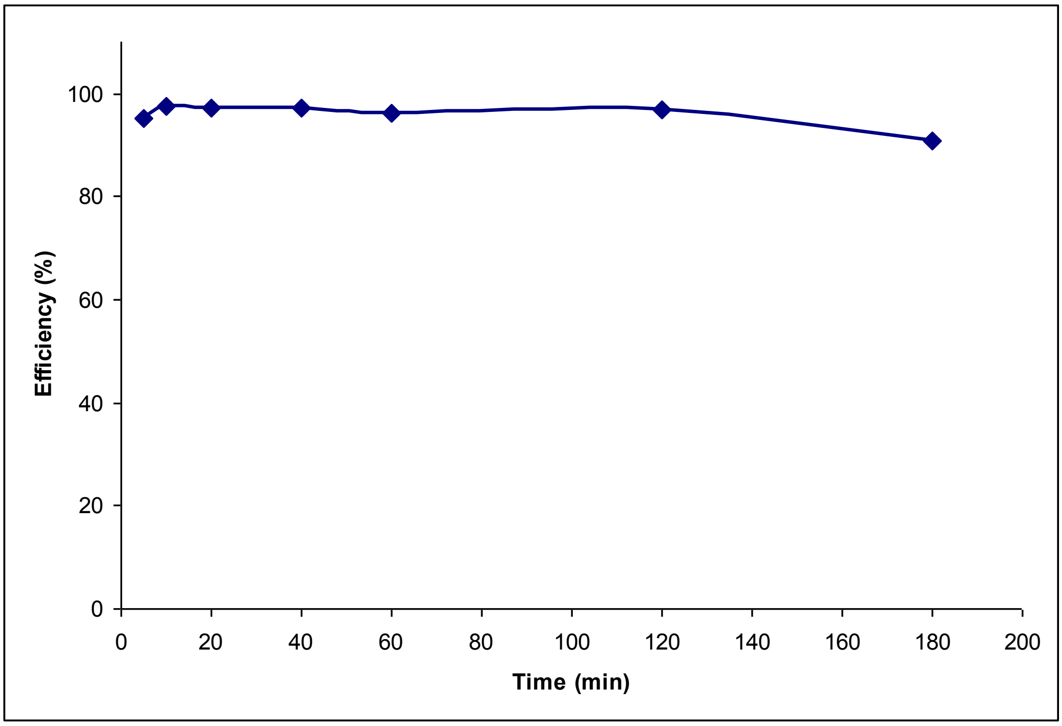


Figure 2.5. The effect of reduction time of Ni(II) with $NaBH_4$ on arsenic sorption efficiency

As seen from the Figure 2.5 the contact time of sorbent with $NaBH_4$ is not an significant parameter. However, shaking is necessary to avoid aggregation of the sorbent and obtain finer particles. So, the sorbent was prepared with the sorbent 1, it was shaken at 25 ^{0}C for 30 minutes.

2.5.6 Binary Vessel Studies

It is commonly known that the transition metals interfere in the determination of hydride-forming elements when the hydride generation (HG) technique is used. Different mechanisms have been suggested for the interference effects observed. According to the literature the predominant mechanism is probably due to the reaction of the interfering transition metal ions with the $NaBH_4$ reductant, and the precipitate which is formed is able to capture and catalytically decompose the evolved hydrides (Welz and Schubert-Jacobs, 1986). However, it was observed in our studies that black precipitate (nickel containing sorbent) adsorbs arsenate and arsenite ions, but not arsine.

2.5.6.1 The Investigation of Sorption of Arsine by The Pre-prepared Sorbent

To investigate whether sorbent adsorbs arsine gas, the nickel sorbent which was pre-prepared and stored in acetone was used.

For drawing the calibration graph, 1 mL of distilled water was put into the second reaction vessel. 1 mL of 4% $NaBH_4$ was added into the first reaction vessel containing arsenite standards (15-30-45-60 ng As/mL). The signals were measured and calibration graph was drawn (experiment a). Afterwards, Ni containing sorbent was put into the second reaction vessel and all the system was closed. Then, 1 mL 60 ng/mL As(III) was injected onto the 1 mL of 4% $NaBH_4$ solution in the first reaction vessel and the signal was measured.

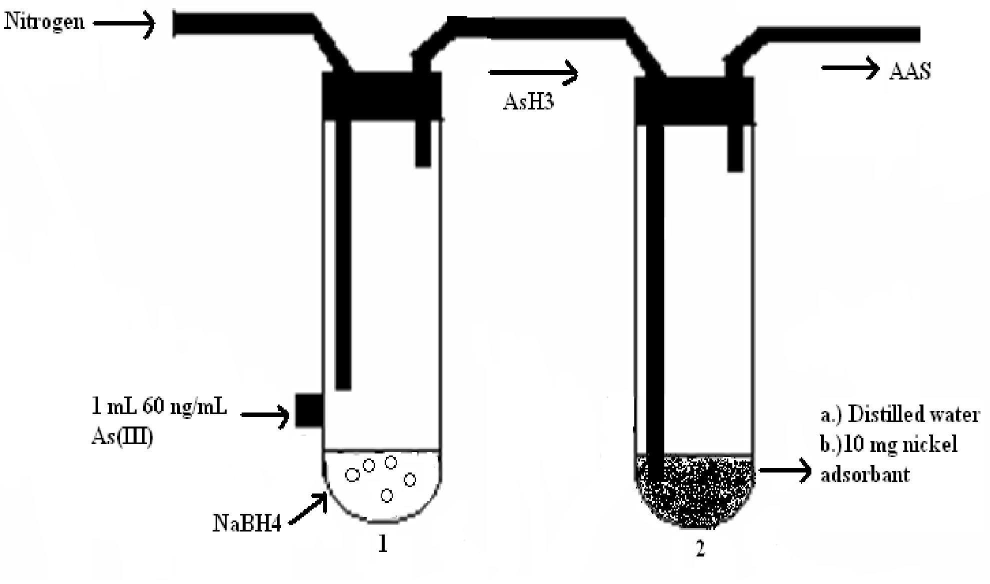


Figure 2.6. The investigation of sorption of arsine by the pre-prepared sorbent.

It was observed that the generated arsine gas was not adsorbed by the nickel sorbent.

2.5.6.2 Investigation of Analyte Sorption by the Sorbent

The difference of this study from previous one is the formation of sorbent in the reaction vessel during the experiment under hydride generation conditions.

Again, for drawing the calibration graph, 1 mL of distilled water was put into the second reaction vessel. 1 mL of 4% $NaBH_4$ was added into the first reaction vessel containing arsenite standards (15-30-45-60 ng As/mL). The signals were measured and calibration graph was drawn (experiment a). Afterwards, 1 mL of 0.05% (w/v) Ni(II) solution was put into the second reaction vessel and all the system was closed. After passing nitrogen gas through the system for about 15 seconds, Ni(II) was reduced by injecting 1 mL 4% $NaBH_4$. Then, 1 mL 4% $NaBH_4$ was injected onto the 1 mL of 45 ng/mL As(III) solution in the first reaction vessel and the signal was measured.

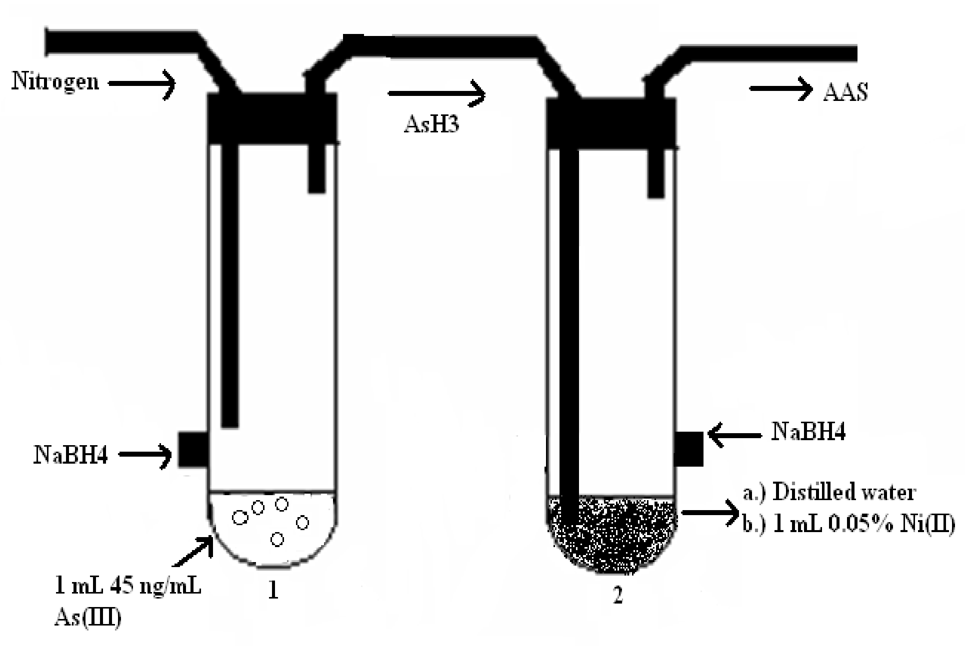


Figure 2.7. The investigation of sorption of arsine by the sorbent

It was observed that the generated arsine gas was not adsorbed by the sorbent in the second reaction vessel.

In the literature it was reported that in the presence of EDTA, no precipitation occured from solutions containing Ni(II) (Henden, 1982). In order to control the effect of EDTA on the arsenic signal suppression by nickel, 1 mL of a mixture containing 0.1% (w/v) Ni(II) and 20ng/mL As(III) and 0.033 mol/L

EDTA were added into the second vessel. Blue coloured nickel-EDTA complex was formed. Then, 1 mL 4% $NaBH_4$ was injected. There was no black precipitation and signal suppression of arsenic.

In the measurement without EDTA, 1 mL of a mixture containing 0.1 % (w/v) Ni(II) and 22.5 ng/mL As(III) was added into the second reaction vessel. Then, 1 mL of 4% $NaBH_4$ was injected. The black precipitate was formed and practically no arsenic signal was observed.

According to this studies, the nickel containing precipitate adsorbed arsenite ions, not arsine gas and also, under the exprimental conditions used in this study, the nickel signal suppression could be avoided by EDTA addition as reported earlier (Henden, 1982).

2.5.6.3 The Investigation of Sorption of Arsine by Ni(II) Solution

For calibration graph, 1 mL of distilled water was put into the second vessel (centrifuge tube). 1 mL of 4% $NaBH_4$ was added onto the As(III) solution in the first reaction vessel and the signals were recorded. Using As(III) standards calibration graph was drawn (experiment a). After drawing calibration graph, 1 mL of 0.05% (w/v) Ni(II) solution was put into the second vessel. 1 mL of 60 ng/mL As(III) solution was put into the first vessel and 1 mL 4% (w/v) $NaBH_4$ was then injected. The signal formed by 60 ng/mL As(III) was obtained. No significant sorption of arsine was observed by the Ni(II) solution in the second vessel.

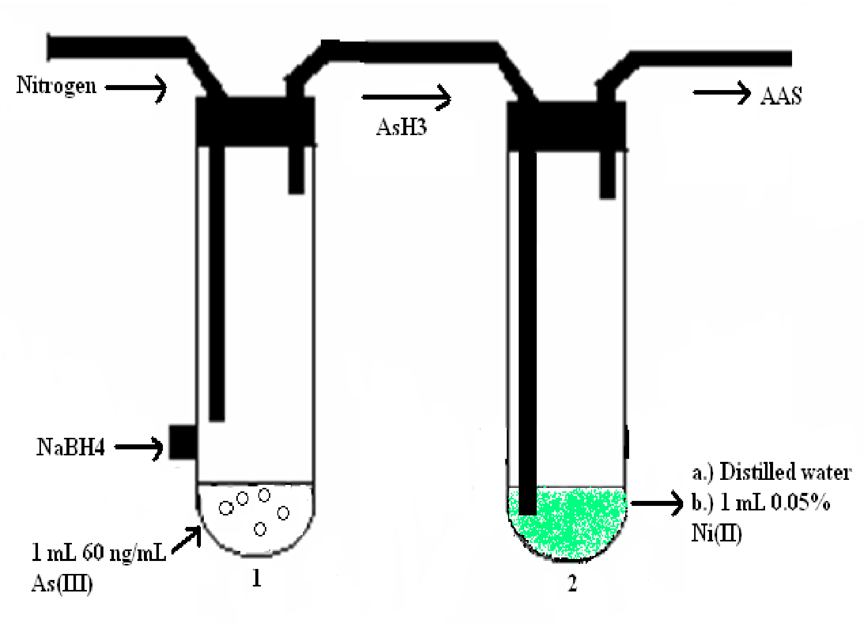


Figure 2.8. The investigation of sorption of arsine by Ni(II) solution.

2.5.7 As(III) sorption by $Ni(OH)_2$

It was observed that when the sorbent which was prepared according to the first method was exposed to air for some extended time before sorption, the colour of the sorbent turned to green that shows the formation of $Ni(OH)_2$.

In this study, we have investigated whether $Ni(OH)_2$ adsorbs As(III). For this, 30 mL of 100 ng/mL pH~6 As(III) solution was added onto previously prepared 10 mg $Ni(OH)_2$ and was shaken for an hour. By determination of arsenic remaining in the solution, it was seen that 19 % of the As(III) was adsorbed.

According to the literature (Pohl and Zyrnicki, 2002), the precipitation of Cd, Co, Cu and Ni hydroxides by adding NaOH was an efficient method of complete elimination of the transition metal interferences in the As and Se determination. The procedure was based on the removal of Ni(II) as $Ni(OH)_2$, while arsenic remaining in the solution. We have controlled the same procedure under our working conditions.

To precipitate hydroxides of Ni(II) with NaOH, to a calibrated flask (50 ml) containing about 20 ml of water, 50 µL of standard solutions of As(1000 µg/mL) and 5.0 ml of the bulk solution of the interferent Ni^{2+} (10 mg/mL) as $Ni(NO_3)_2.6H_2O$ or $NiCl_2.6H_2O$, 12 ml of 4.0 mol/L NaOH solution was added slowly while continuously swirling. Then, the solution with the precipitate was filled with water up to the volume of 50 ml and mixed thoroughly. The solution was filtered (the precipitate of the transition metal hydroxide was not washed) and the filtrate was collected. Next, a 20 mL of the aliquot of the filtrate was taken and placed in a 25 mL calibrated flask followed by the addition of 4.0 mL of concentrated HCl for neutralisation and the solution was diluted to 25 mL with water.

By determination of As(III) and As(V) concentration in the solution, it was found that $Ni(OH)_2$ did not adsorb As(III) significantly, but adsorbed As(V) with an efficiency of 41%.

2.5.8 Studies on the Recovery of Arsenic from the Sorbent

In this section batch tecnique was used for arsenic determination.

2.5.8.1 Arsenic Recovery with HNO_3

For arsenic sorption, 25 mL of 1000 ng/mL As(III) solution was added onto 10 mg sorbent and shaken for an hour. After sorption, liquid and solid phase were separated by filtration. The sorbent containing arsenic was dissolved by heating on hot plate for a few minutes after addition of 5 mL of 1 mol/L HNO_3. It was observed that sorbent could easily be dissolved by heating on a hot plate. However, the concentrations of arsenic measured in the solution after KI pre-reduction, were found to be much higher than the expected values. Therefore, NO_X interferences in the measurements were suspected and the study was repeated using 10% sulfamic acid solution.

2.5.8.2 Study with 1 mol/L HNO_3 + 10% Sulfamic Acid

1 mL of 10% Sulfamic acid was added onto the 10 mL arsenic solution in the above study and heated at 55 ^{0}C for 30 minutes. After determination of arsenic concentrations, the recovery was found as 92.2 ± 1.84 (n=5).

2.5.8.3 Arsenic Recovery with HCl

25 mL of 1000 ng/mL As(III) solution was added on 10 mg sorbent and was shaken for an hour for sorption. After sorption, liquid and solid phases were separated and solid phase was washed with distilled water several times. As(III) concentration was determined in supernatant solution, but no arsenic was detected.

The arsenic containing sorbent was dissolved by heating with 7 mL of 2 mol/L HCl on a hot plate. After pre-reduction with KI, arsenic in the solution was determined and the arsenic recovery was found as 97.3 ± 3.24 % (n=7).

To investigate the effect of KI pre-reduction step on the arsenic concentration found by dissolving the sorbent, 25 mL 1000 ng/mL As(III) solution and 10 mg sorbent was used. Arsenic containing sorbent was dissolved using 5 mL 2 mol/L HCl. It was seen that without pre-reduction step with KI, obtained As(III) signal was 55% lesser than expected values. This result is important and could prove that As(III) is oxidized to As(V) during sorption by the nickel containing sorbent.

The effect of pre-reduction step was also investigated after sorption of As(V). The sorbent containing arsenic was dissolved with HCl. It was found that without pre-reduction step, no arsenic could be detected. It means that As(V) is adsorbed without reduction to a lower oxidation state.

2.5.8.4 Studies with EDTA using Automated HG-AAS

For sorption, 25 mL 1000 ng/mL As (III) was added on 10 mg sorbent. After sorption, phases were separated and the sorbent was washed with distilled water several times. 5 mL 0.1 mol/L EDTA solution was added on sorbent and was heated. It was observed that blue coloured solution was formed and the minority of sorbent was not dissolved. The undissolved part of sorbent was left in centrifuge tube. This result may show that part of the sorbent is a nickel containing compound and at least some of the sorbent is elemental nickel or with a less probability a nickel compound that do not dissove in EDTA. By realizing KI pre-reduction, arsenic concentration was found as 92 % for As(III) and 90% for As(V) of the expected value, that is probably because of some of the arsenic was held by the undissolved sorbent. Without pre-reduction step, arsenic concentrations were found as 5.5 and 4.1 ng/mL while expected values were 10 ng/mL, for As(III) and As(V) sorption experiments, respectively. These relatively low results may be due to the lower signal efficiency of As(V).

2.5.9 The Effect of HCl Concentration on the Arsenic Recovery from the Sorbent

In this study, 25 mL 1000 ng/mL pH~6 As(III) solution was added onto 10 mg sorbent in falcon tubes and was shaken for an hour at 25 ^{0}C. After separating solid and liquid phases, 5 mL of acid solutions of different concentrations were added on the sorbents and falcon tubes were put in water bath. When sorbents were dissolved, apropriate dilutions were done. After pre-reduction of the solutions, absorbances were read.

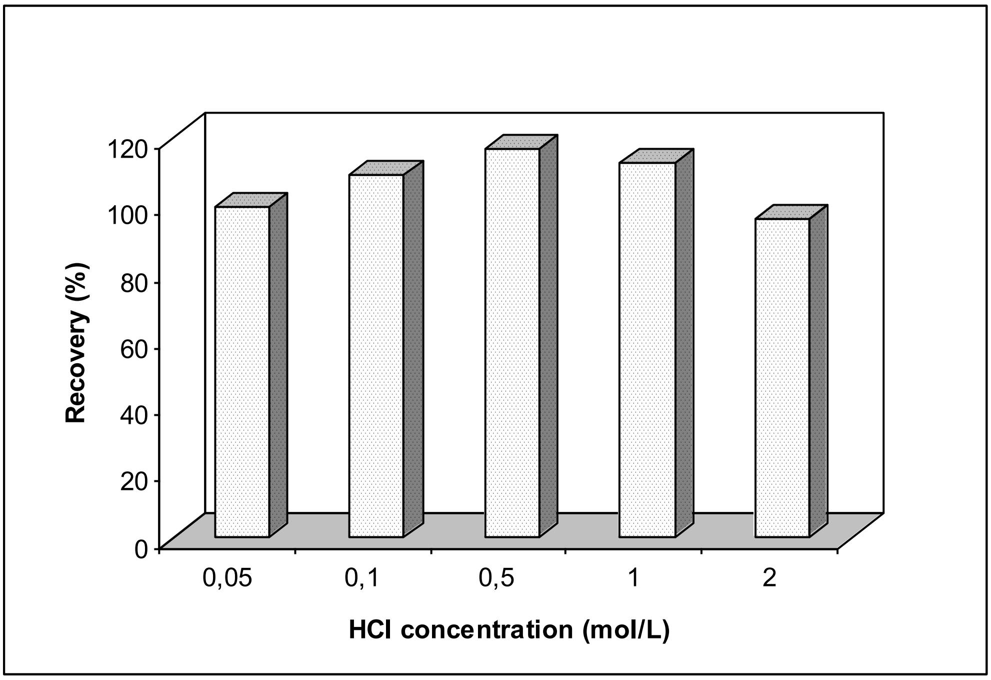


Figure 2.9. The effect of acid concentration on the arsenic recovery from the sorbent.

It was found that the recovery was 104.3± 6.18. The results were not affected by HCl concentrations significantly.

2.5.10 The Effect of Contact Time on pH

In order to investigate the effect of contact time on pH, As(III) solution at pH ~ 6 and distilled water were added on nickel sorbents. pH values of solutions were measured. The results are shown in Figure 2.10.

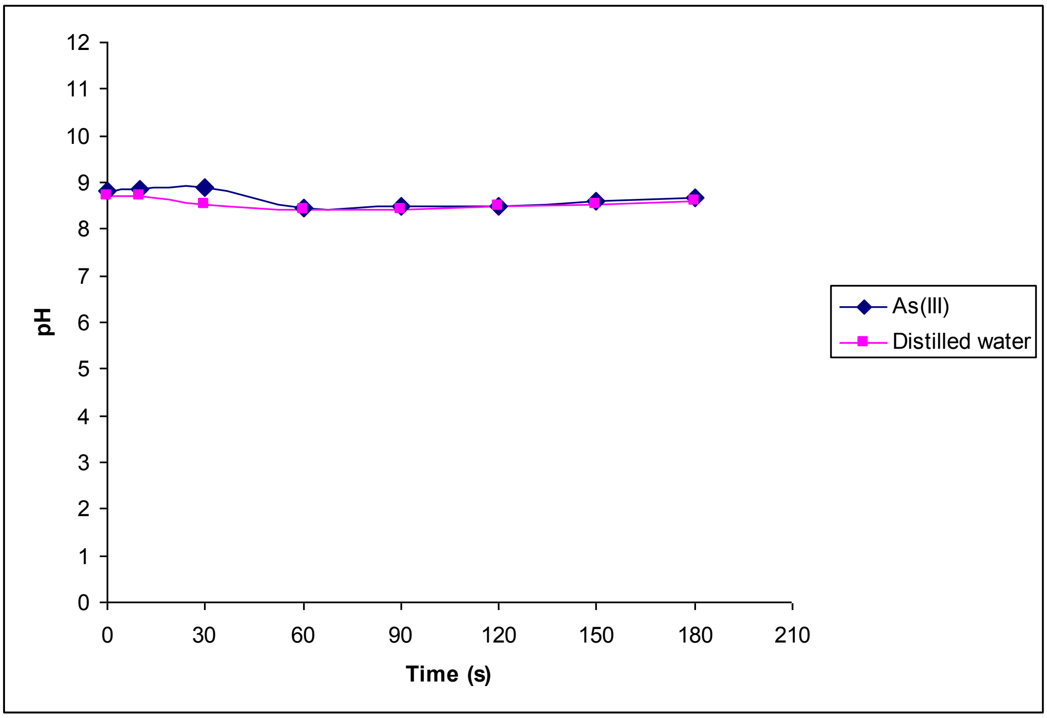


Figure 2.10**.** The effect of contact time on pH.

It was seen that pH values were reached to ~ 9. This value is in accordance with the pH value calculated from the Ksp of $Ni(OH)_2$. Thus, it may be concluded that $Ni(OH)_2$ exists on the surface of sorbent.

2.5.11 Calibration Graph Using Sorbent

50 mL of 2.5 - 10 ng/mL As (III) at pH ~ 6 was added on 10 mg Ni sorbents. The mixtures were shaken for 1 hour at 25 ^{0}C. Ni sorbent was separated from solution by centrifuge and then dissolved in 5 mL 2 M HCl and diluted to 25 mL. The calibration graph obtained in this range is shown in Figure 2.11.

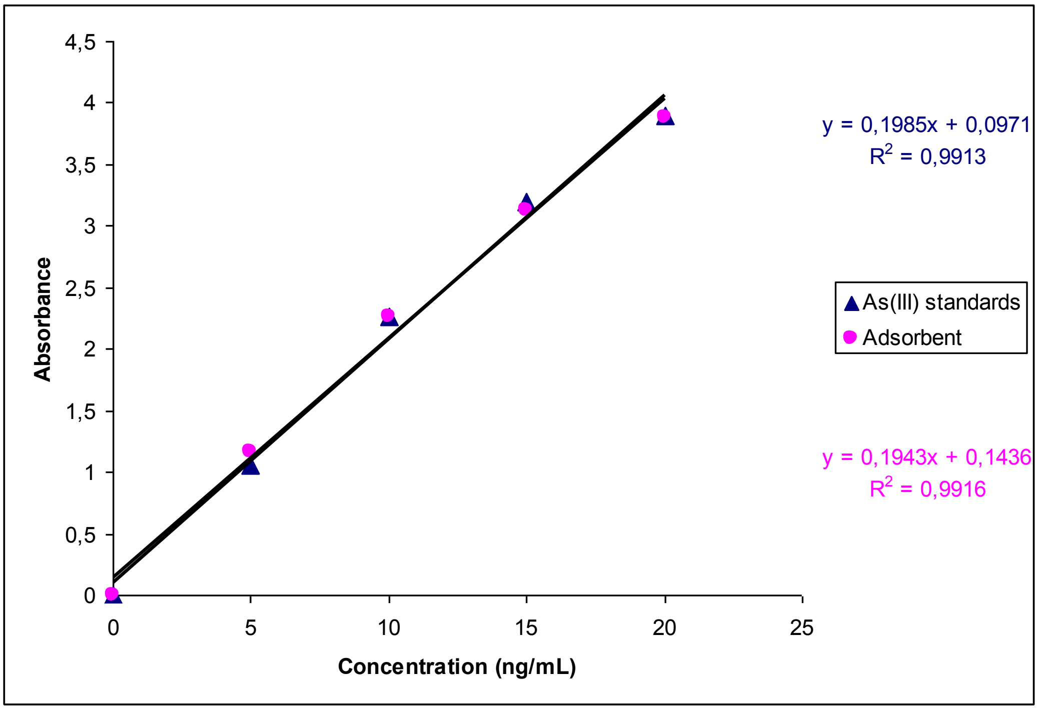


Figure 2.11. Calibration graph using sorbent.

2.5.12 Precision Study

50 mL of 5 ng/mL As(III) solutions at pH~6 was added on 10 mg Ni sorbent. The mixtures were shaken for an hour. After sorption, the sorbent was dissolved in 5 mL 2 mol/L HCl and the solution was diluted to 25 mL with water (If 100 % sorption:10.0 ng/mL As(III)).

Relative standard deviation for the determination of 5 ng/mL As (III) after concentrating twice as described above was found to be 3.35% (n=7).

2.5.13 Investigation of Sorbent Capacity

In this study, 50 mL 500 µg/mL pH~6 As(III) solutions were added on 10 mg Ni sorbent. The shaking time was 21 h. After sorption, Ni sorbents were dissolved in 2 mol/L HCL and final solution volumes were adjusted to 25 mL (in case of 100% sorption = 1000 µg/mL As(III)). The arsenic concentration was found as 877 µg / mL in 25 mL final solution,

877 µg / mL × 25 mL = 21925 µg   21.93 mg As/10.0 mg sorbent

2193 mg As (III)/1g sorbent = 2.19 g As(III)/ 1 g sorbent

The mechanism of the calculated unexpectedly high sorption capacity of the nano-nickel based sorbent is at present need explanation, but possibly some catalytic mechanism is involved.

2.5.14 The Effect of Sample Volume

The effect of the sample solution volume on the As(III) sorption was studied by using 25 – 250 mL sample volumes. 4 mL of 100 ng/mL As(III) solutions at pH~6 were added on 10 mg sorbents. The shaking time was an hour at 25 ^{0}C. After sorption the Ni-based sorbents were dissolved in 5 mL 2 mol/L HCl and final solution was diluted to 25 mL. The graph of results is shown in Figure 2.12.

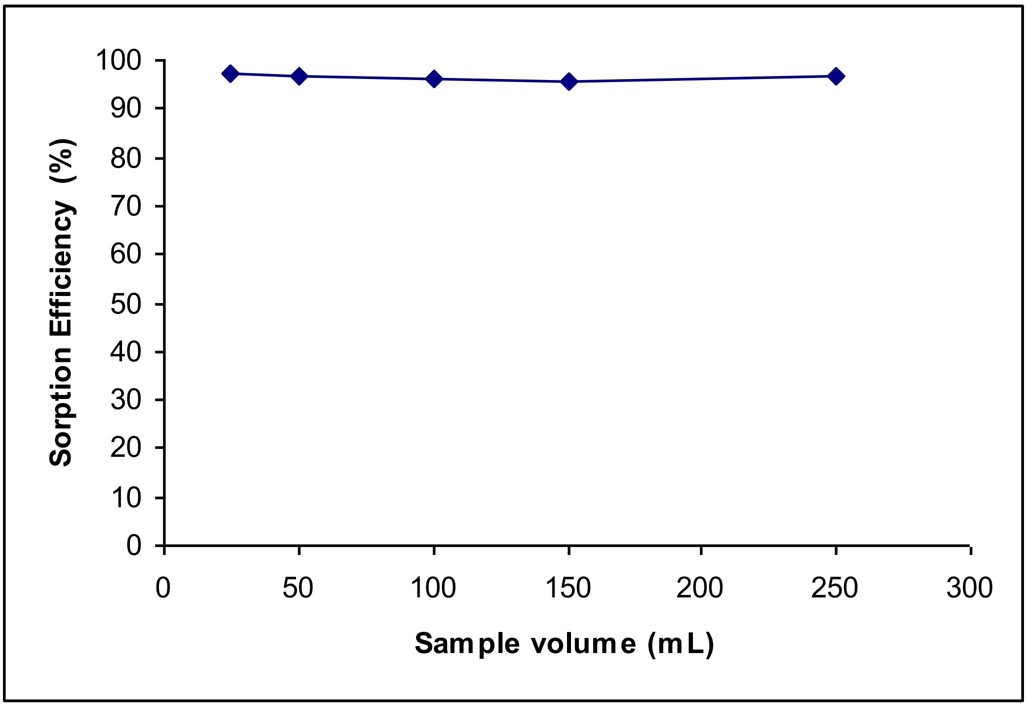


Figure 2.12. The effect of volume.on arsenic sorption efficiency.

It was observed that the sorption efficiency of the As(III) ions is not affected by sample volumes in this range.

2.5.15 Sorbent Preparation in Anaerobic Conditions

50 mL 2.5 % of Ni(II) solutions were put in a 100-mL polipropilen bottle. Three holes were made on the lid of the container. The first hole was for nitrogen gas inlet, second one was for $NaBH_4$ flow and the last one was for gas outlet.

While the Ni(II) solution was stirred on a magnetic stirrer, 4% $NaBH_4$ was introduced using a burette under N_2 atmosphere. Black precipitate formation was observed. To separate the black nickel containing nanoparticles from the liquid phase, ultra centrifugation technique was used. Particles formed were then washed and centrifuged at least three times first with 20 ml portions of water and then acetone to remove all of the water. Prepared nanoparticles were finally dried in water bath at 75 ^{o}C for an hour under nitrogen atmosphere.

2.5.15.1 Arsenic Sorption on the Sorbent Prepared Under Anaerobic Conditions

50 mL of 1000 ng/mL As(III) and As(V) solution was added on 10 mg sorbent. The mixture was shaken for an hour. After sorption, sorbent and liquid phase were separated by centrifugation. By determination of arsenic remaining in the solution, it was seen that sorption efficiency were 44 % for As(III) and 95% for As(V).

2.5.16 Arsenic Sorption on Metallic Nickel

10 mL of 100 ng/mL As(III) and As(V) solutions were added onto metallic nickel granules. The sorption time was an hour. By determining As(III) and As(V) concentrations, it was found that metallic nickel did not adsorb As(III) and As(V).

2.6 Characterization Studies

Characterizations of the sorbents were performed using techniques such as scanning electron microscopy and EDX, X-ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), thermogravimetric analysis and elemental analysis.

2.6.1 Scanning Electron Microscopy (SEM) and EDX

SEM images of synthesized nickel nanoparticles at 250x, 5000x, 25000x, 50000x and 100000x magnification are shown in Figure 2.13.

SEM analysis showed formation of spherical particles.

EDX results, that represent approximately 50 nm debth, showed that nickel, oxygen and boron are present at the surface of the sorbents. These results may show the presence of Ni, Ni_xB and $Ni(OH)_2$ on the surface of the adsorbents.

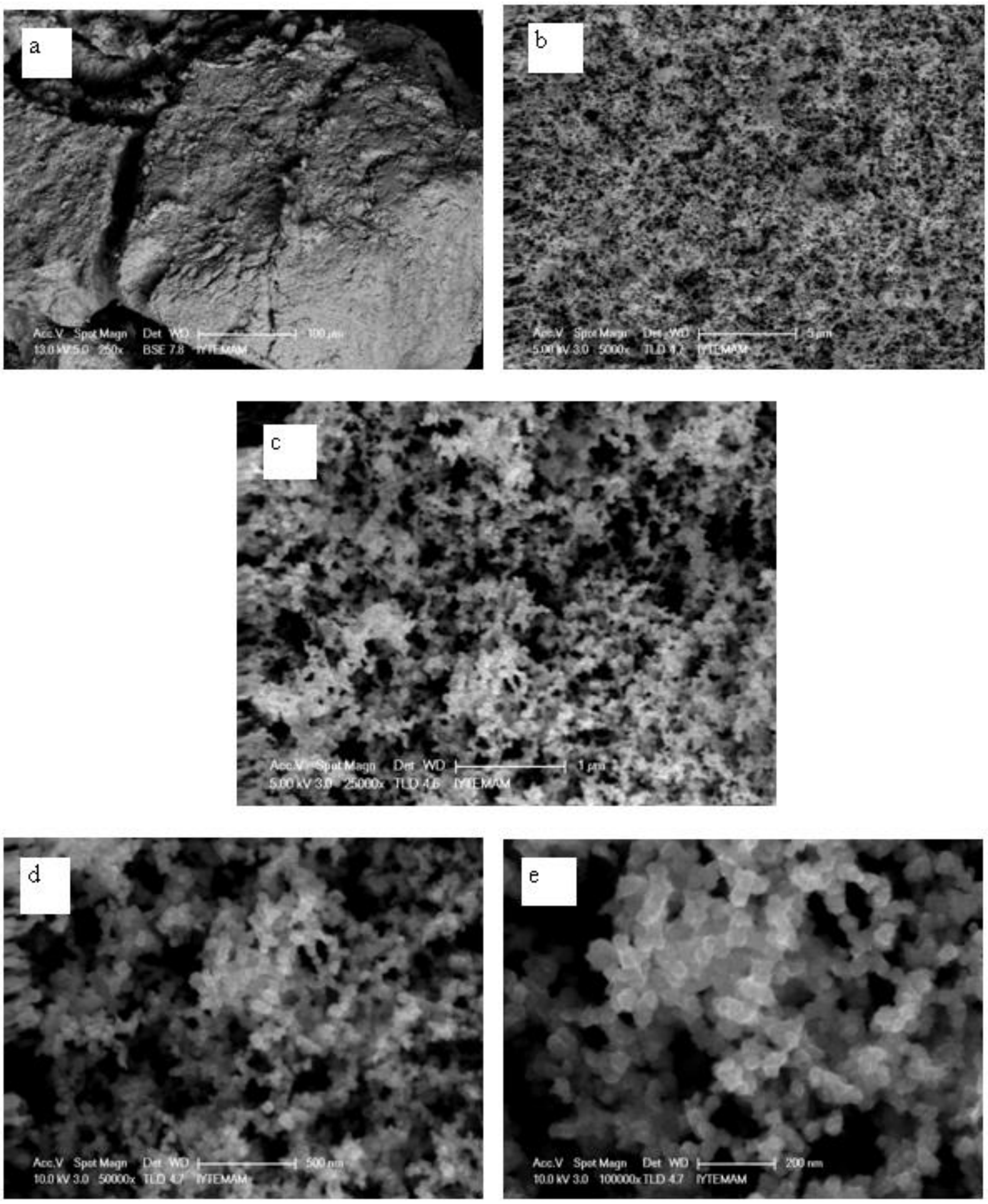


Figure 2.13. SEM analysis of sorbent a)250x, b)5000x, c)25000x, d) 50000x, e)100000x (Yayayürük and Henden, 2010)(unpublished work)

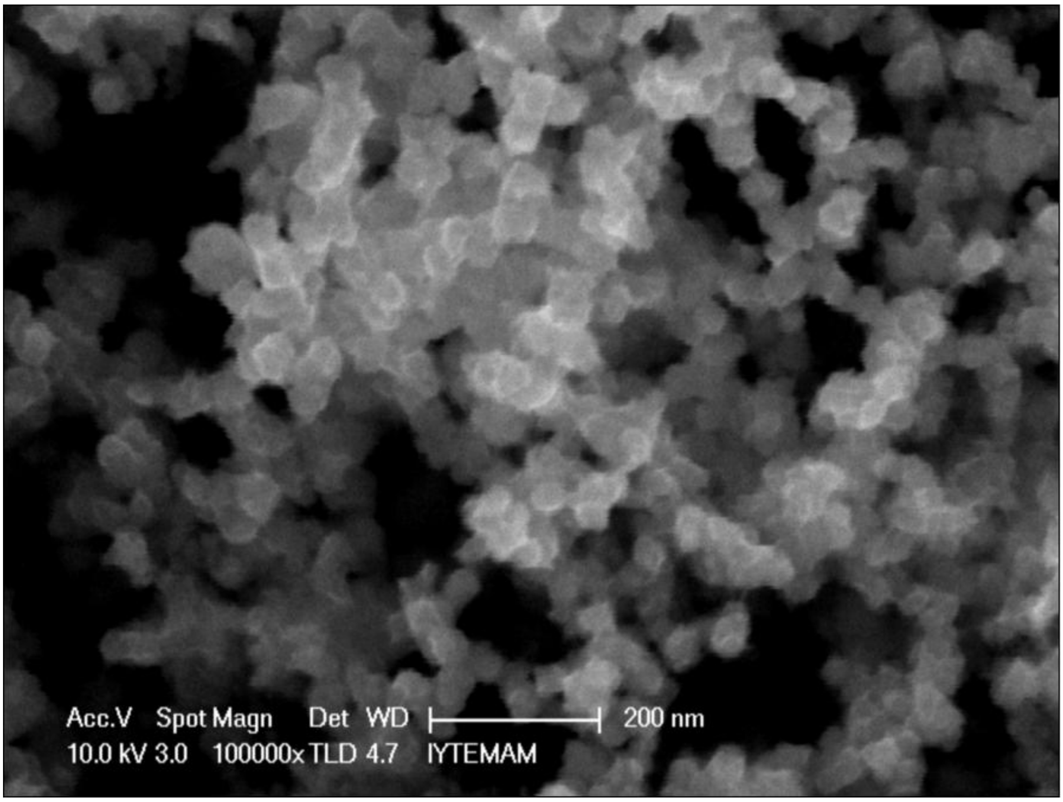
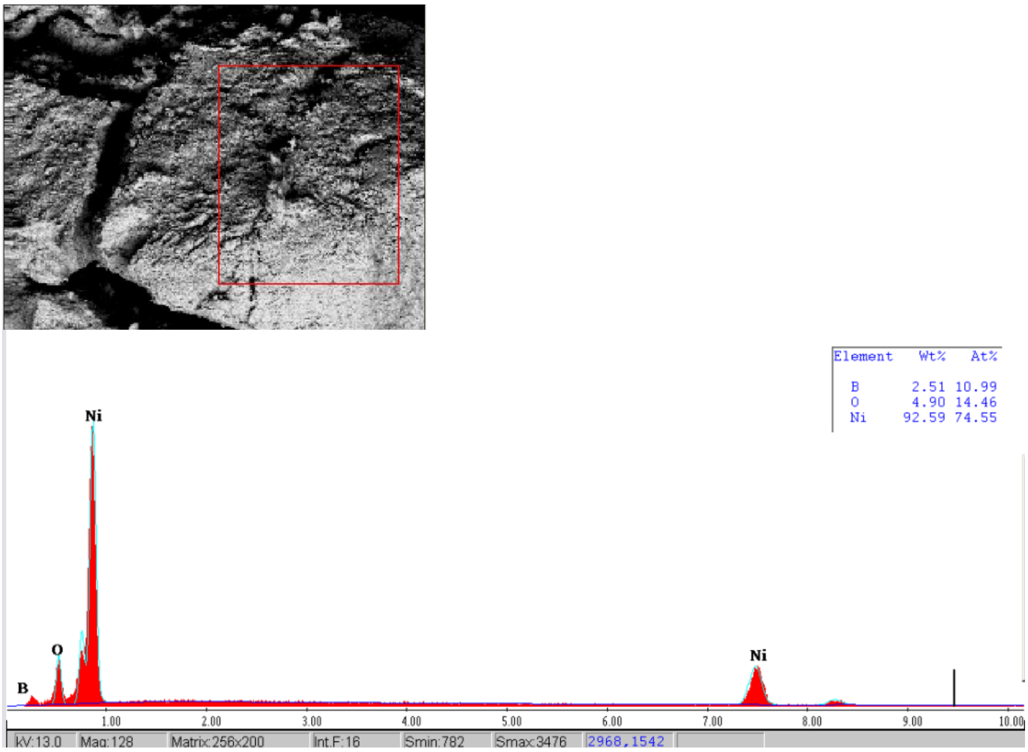
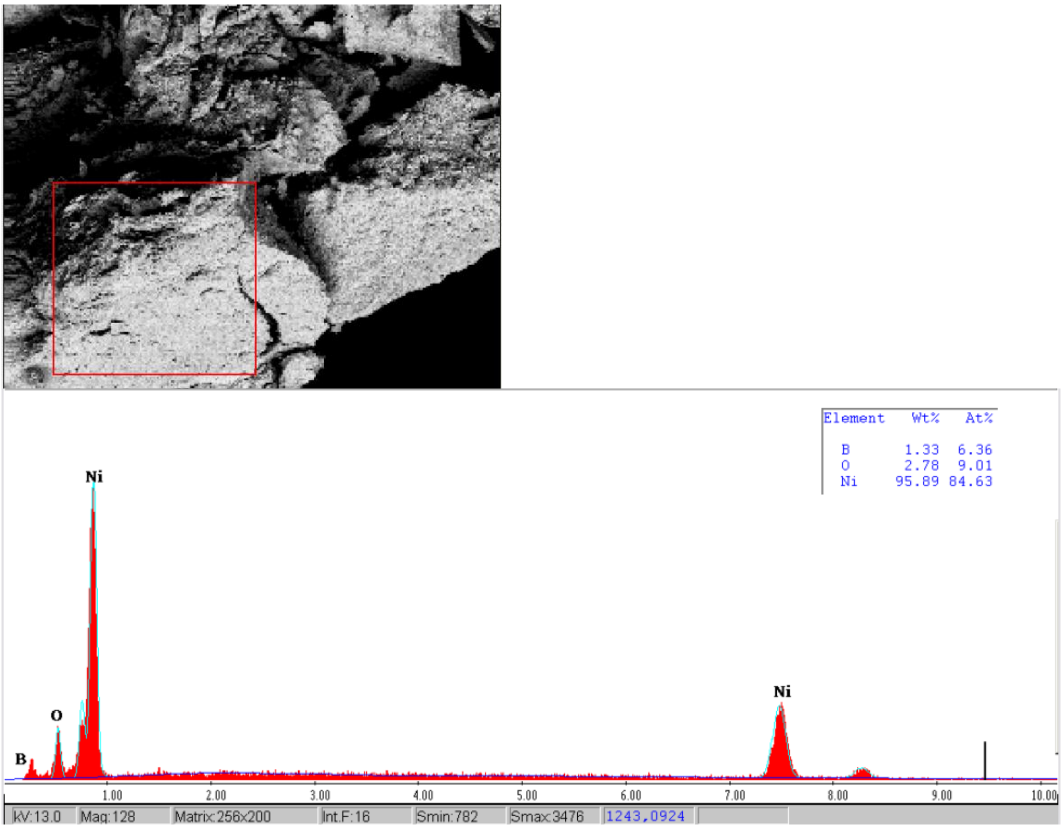


Figure 2.14. SEM analysis of sorbent (100000x)(Yayayürük and Henden, 2010)(unpublished work)



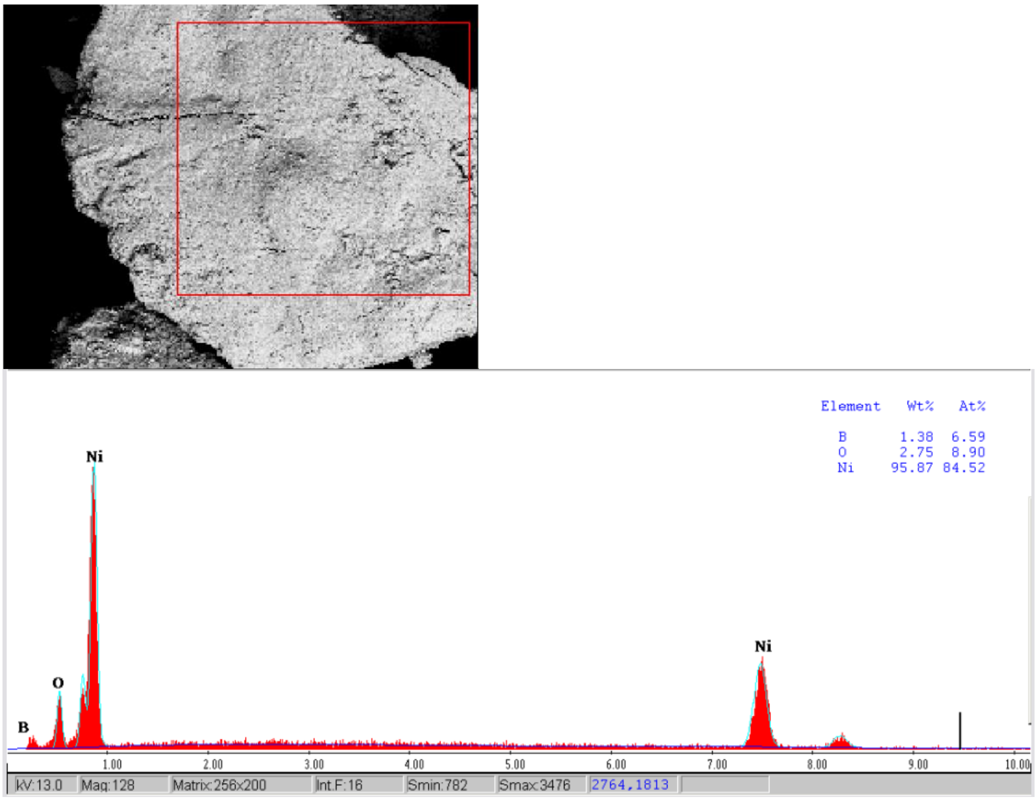
Element	Wt%	At%
B	2.51	10.99
O	4.90	14.46
Ni	92.59	74.55

Figure 2.15. EDX analysis of sorbent (Yayayürük and Henden, 2010)(unpublished work)



Element	Wt%	At%
B	1.33	6.36
O	2.78	9.01
Ni	95.89	84.63

Figure 2.16. EDX analysis of sorbent (Yayayürük and Henden, 2010)(unpublished work)



Element	Wt%	At%
B	1.38	6.59
O	2.75	8.90
Ni	95.87	84.52

Figure 2.17. EDX analysis of sorbent (Yayayürük and Henden, 2010)(unpublished work)

2.6.2 Thermogravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) is the measure of change in sample weight with increasing temperature. This measurement allows us to determine the degree of surface modification through comparison of the percent weight loss.

In figure 2.18 it was seen that water is lost in two steps (200–300°C and 320–420°C). In the first area bonded water is removed. The temperature profile shows a decomposition of $Ni(OH)_2$ range of 320–420°C.

$Ni(OH)_2$ is expected to undergo a single step decomposition as

$$Ni(OH)_2 \rightarrow NiO + H_2O$$

It was observed that nano nickel has a single step. It may be shown that nano nickel was not contain $Ni(OH)_2$.

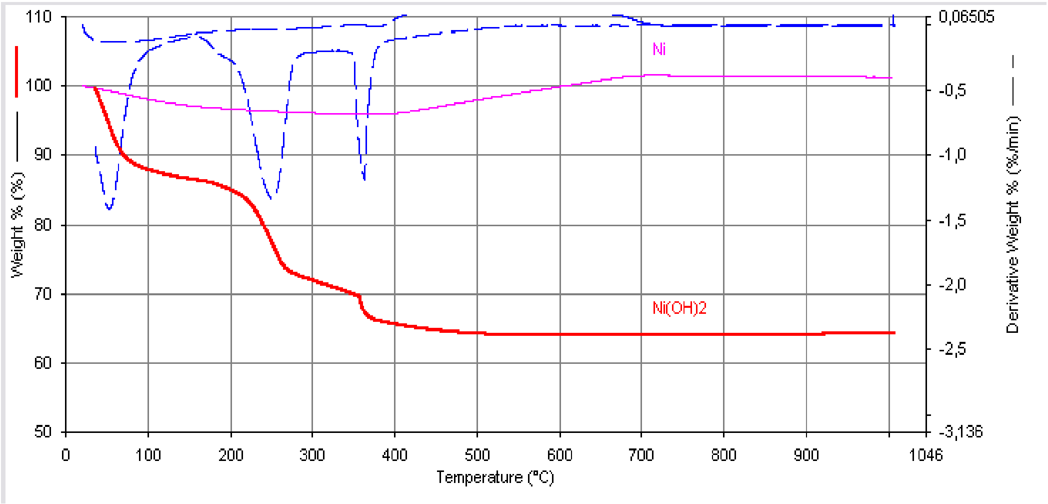


Figure 2.18. TGA graph of nickel based sorbent and $Ni(OH)_2$ (Yayayürük and Henden, 2010)(unpublished work)

2.6.3 X-ray Diffraction (XRD)

XRD graph of nickel based nanoparticles is shown in Figure 2.19.

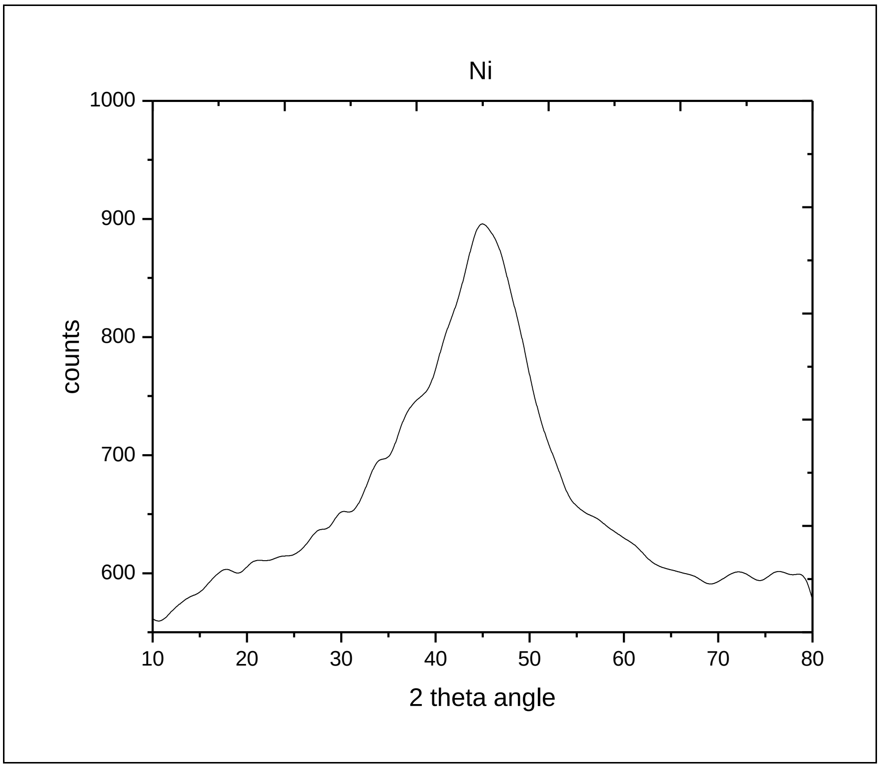


Figure 2.19. XRD of nickel based sorbent.(Yayaürük and Henden, 2010)(unpublished work)

The characteristic diffraction line at 45^o 2 theta degrees indicates the Ni-B as compared with the literature. Below the XRD spectra of Ni-B and Ni(OH)$_2$ in the literature (Krishnaveni et al., 2005) are shown in Figure 2.20 and Figure 2.21, respectively. The single broad peak shows the amorphous structure or nanostructure of the nickel boride (Krishnaveni et al.,2005).

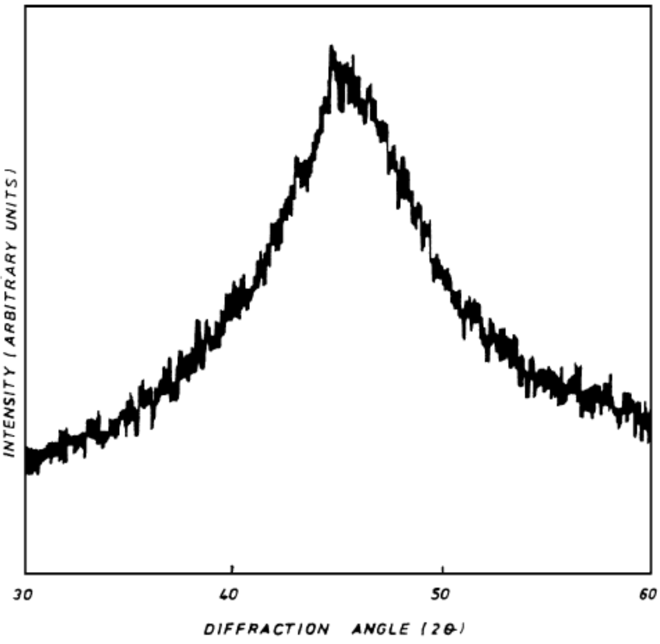


Figure 2.20. X-Ray diffraction pattern of electroless Ni –B deposit in as-plated condition (Krishnaveni et al., 2005).

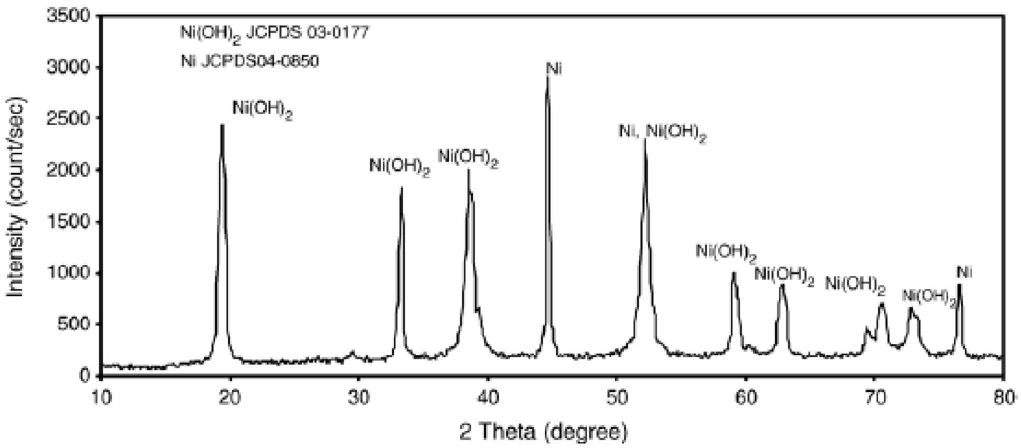


Figure 2.21. XRD analysis of the products mixture of $Ni(OH)_2$ and Ni Powder (Abdel-Aal et al,2007).

2.6.4 X-ray Photoelecton Spectrometry (XPS)

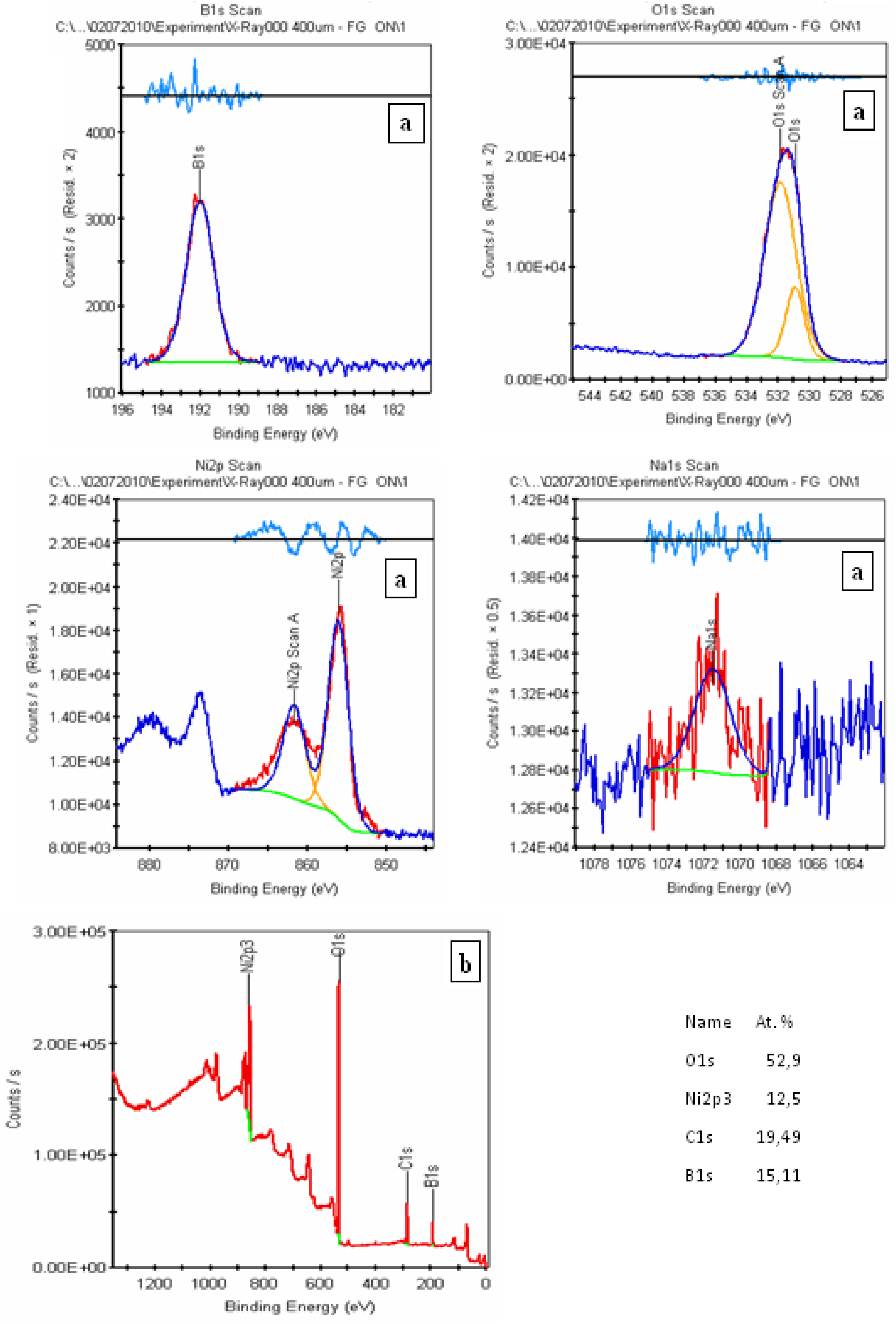
XPS was used to further determine the interaction of arsenate and arsenite on the surface of the sorbent. XPS wide scan spectra of the sorbents are shown in Fig. 2.22b - 2.27b, while the high-resolution spectra of As 3d, Ni 2p, B 1s, and O 1s regions are shown in Fig. 2.22a - 2.27a.

As shown in Fig. 2.22b - 2.27b, one major peak is clearly observed at binding energies of 531 eV for all of the sorbents, together with minor peaks. The major peak is assigned for O 1s. A small peak at binding energy of about 45 eV is observed after arsenic sorption. This peak indicates presence of arsenic in the sorbent after sorption (Zheng et al., 2009).

Generally, As(III) binding energies are about 1 eV lower than that of As(V). The single peak indicates the presence of a single species, and not a contribution of multiple species (Martinson and Reddy, 2009).

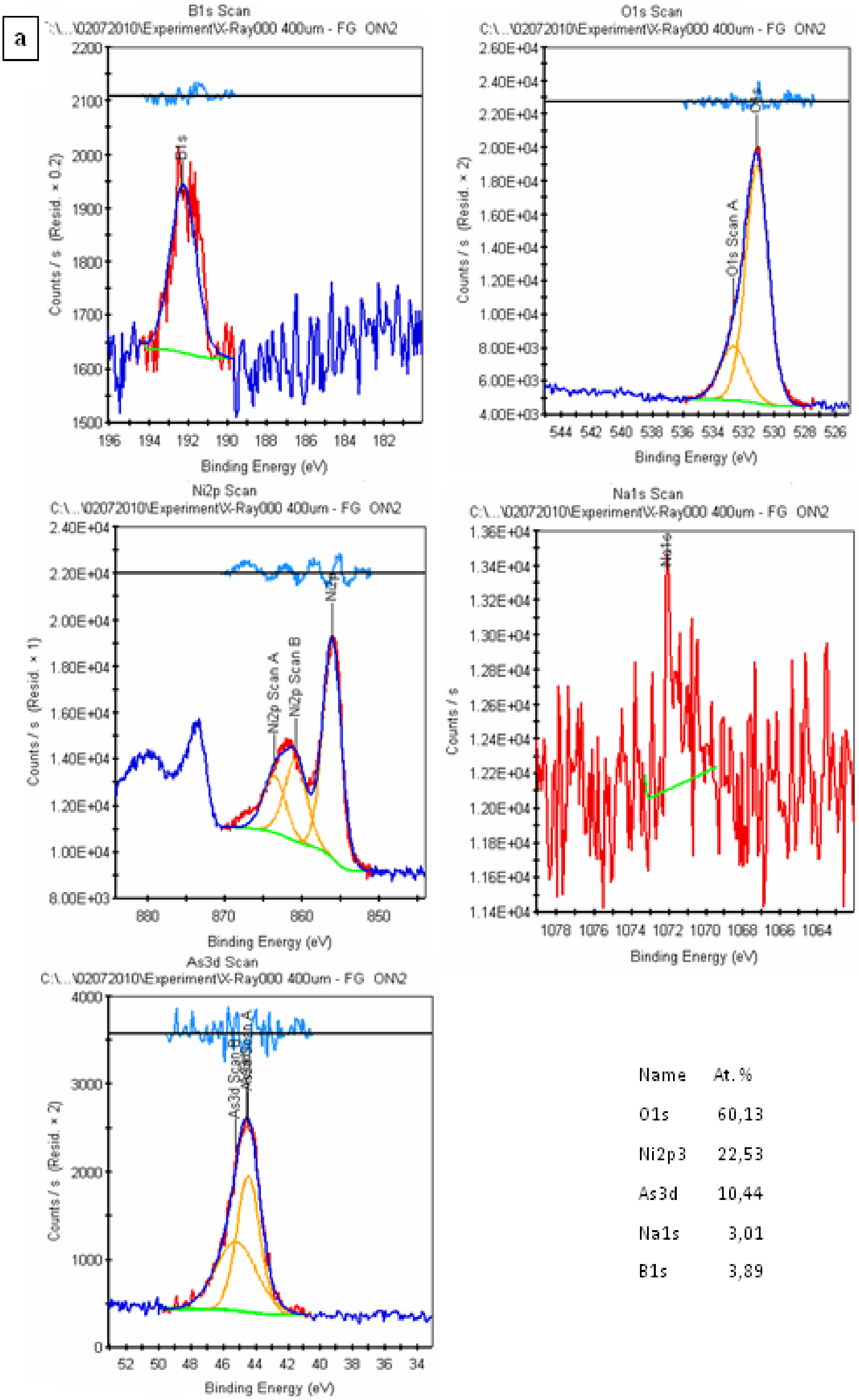
The high-resolution scans of As 3d are displayed in Fig 2.23a, 2.24a, 2.26a and 2.27a. In Fig. 2.23a, from the deconvolution of the curve, it can be clearly seen that the major peak at 45 eV consist of two peaks referring to As(III) and As(V) at binding energies of 44.44 and 45.19 eV, respectively, as reported by Lim et al. (2009). When As(III) is sorbed by the nickel/nickel boride sorbent, the As(III) peak reflects the binding of the adsorbate, without any oxidation on the sorbent, whereas the As(V) peak indicates the possible oxidation of As(III) to As(V) on the sorbent surface. When As(V) is sorbed by the nickel/nickel boride sorbent, it was confirmed that As(V) was sorbed as As(V), giving a single peak at binding energy of 45.06 eV, as shown in Fig 2.24a and 2.27a.

It can be observed in Fig.2.22a - 2.27a that the deconvoluation of the O 1s spectra of the samples produces metal oxide and hydroxide(-OH) peaks with the binding energies of 531.77.8 and 530.78 eV, as reported by Zheng et al.(2009).



Name	At.%
O1s	52,9
Ni2p3	12,5
C1s	19,49
B1s	15,11

Figure 2.22. XPS spectra of the nickel based sorbent prepared under aerobic conditions a) XPS spectra of Ni2p, B1s and O1s, b)XPS wide scan spectrum



Name	At. %
O1s	60,13
Ni2p3	22,53
As3d	10,44
Na1s	3,01
B1s	3,89

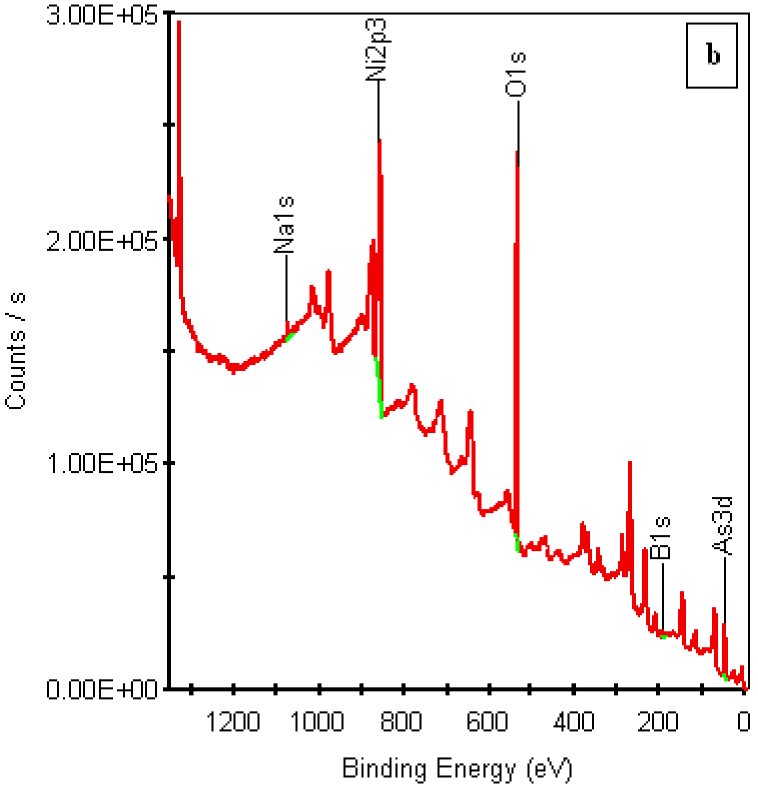
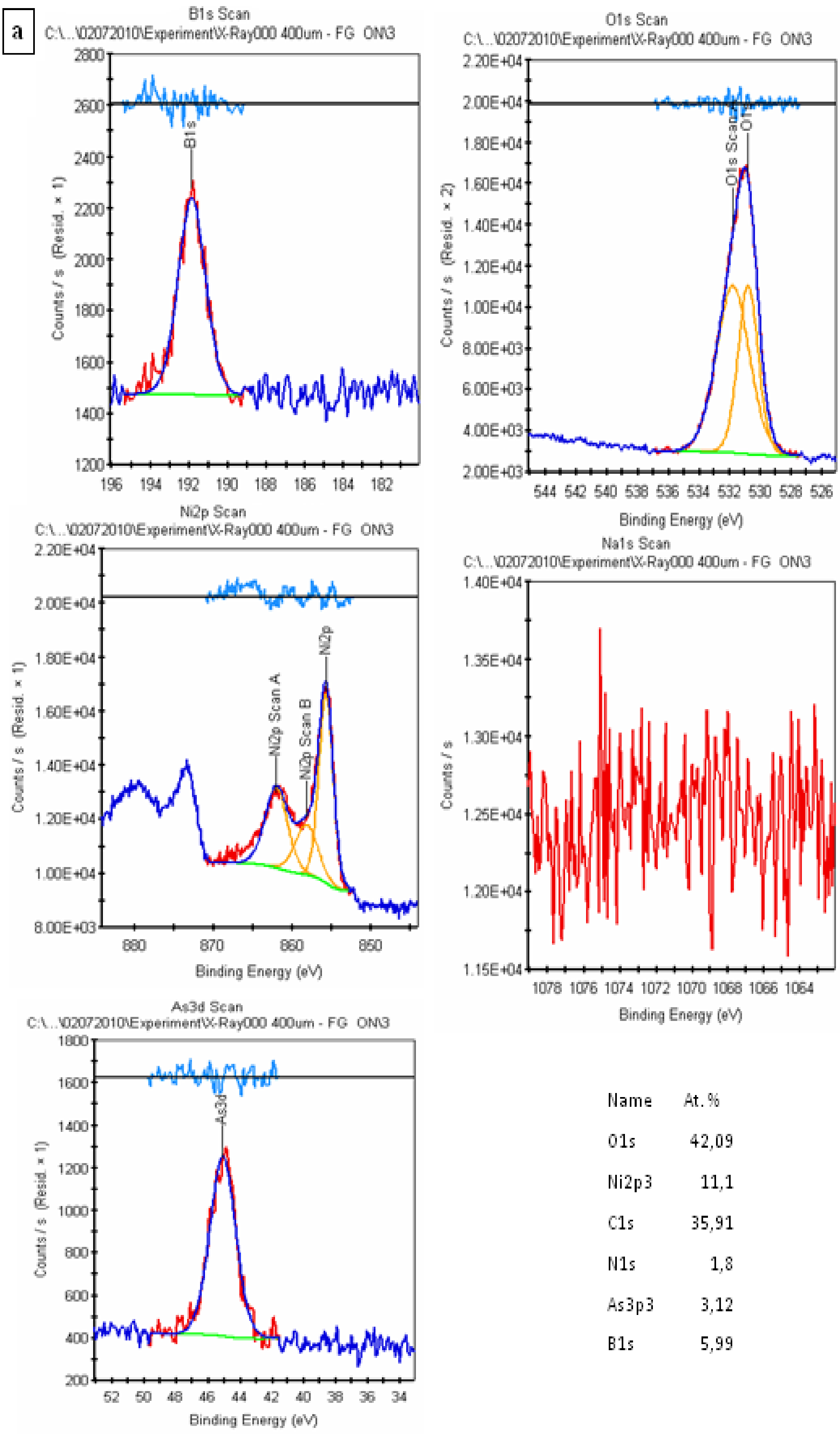


Figure 2.23 XPS spectra of As(III) loaded on the sorbent prepared under aerobic conditions, a) XPS spectra of Ni2p, B1s, O1s and As3d, b) XPS wide scan spectrum.



Name	At.%
O1s	42,09
Ni2p3	11,1
C1s	35,91
N1s	1,8
As3p3	3,12
B1s	5,99

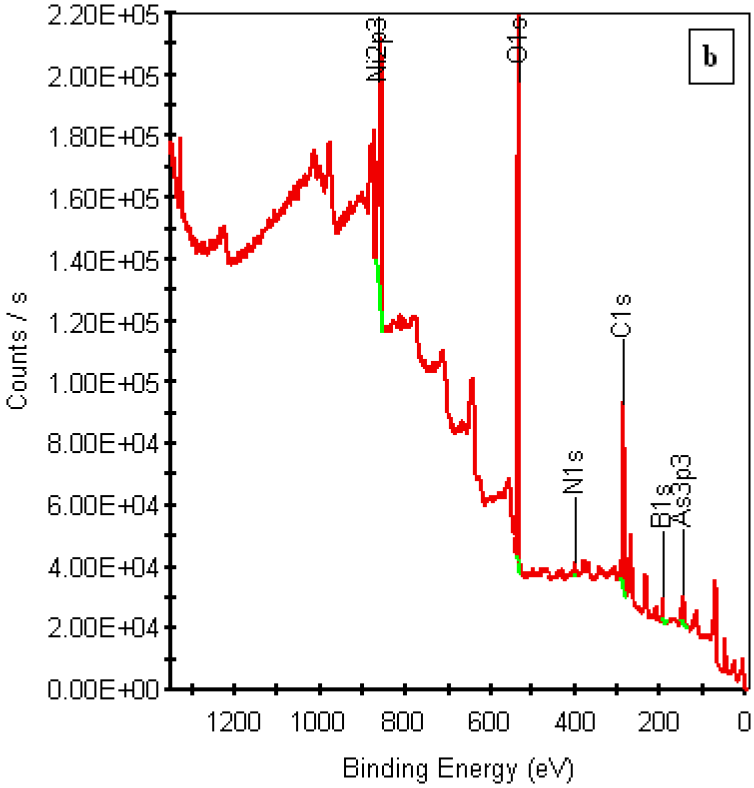
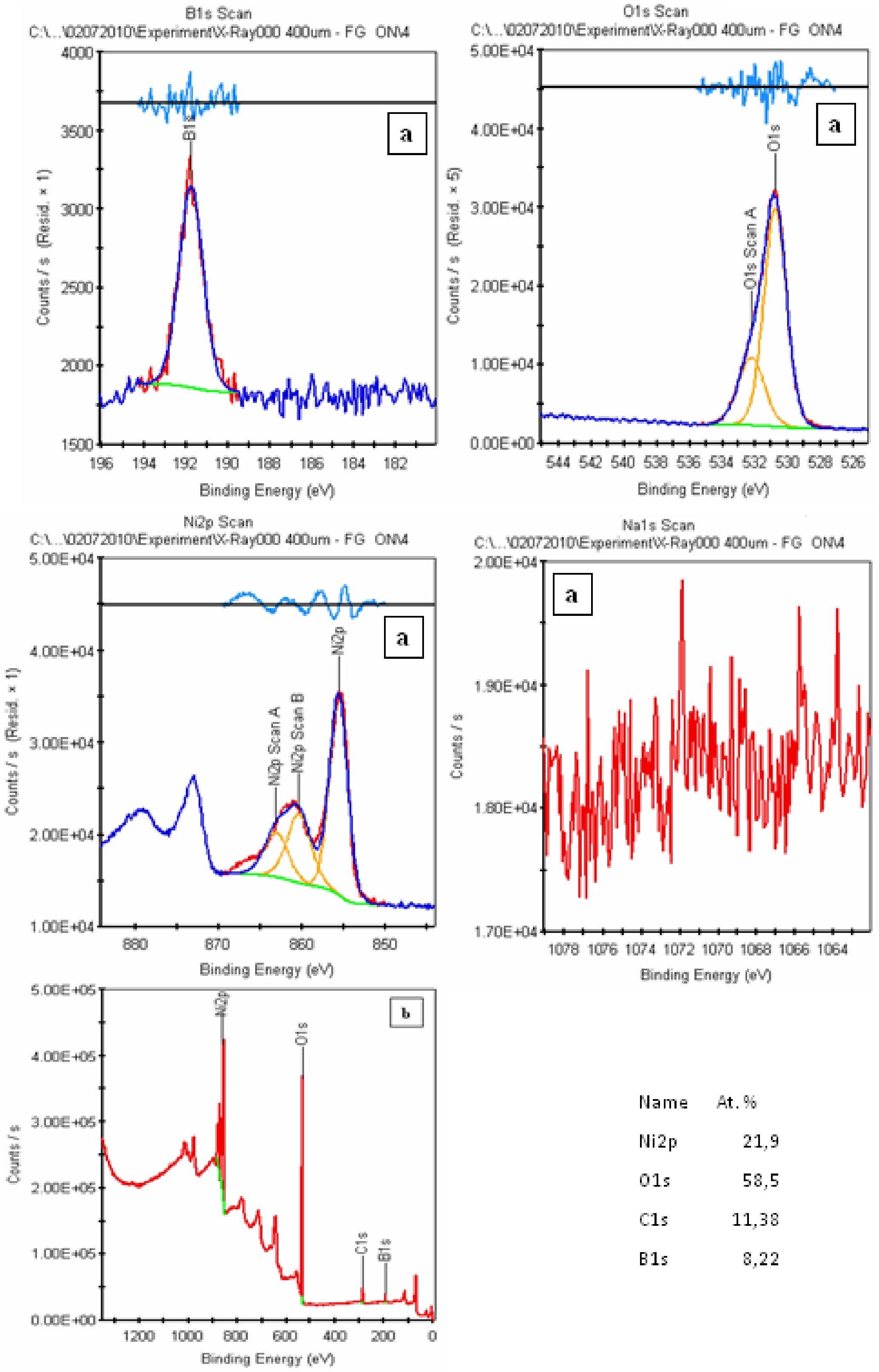


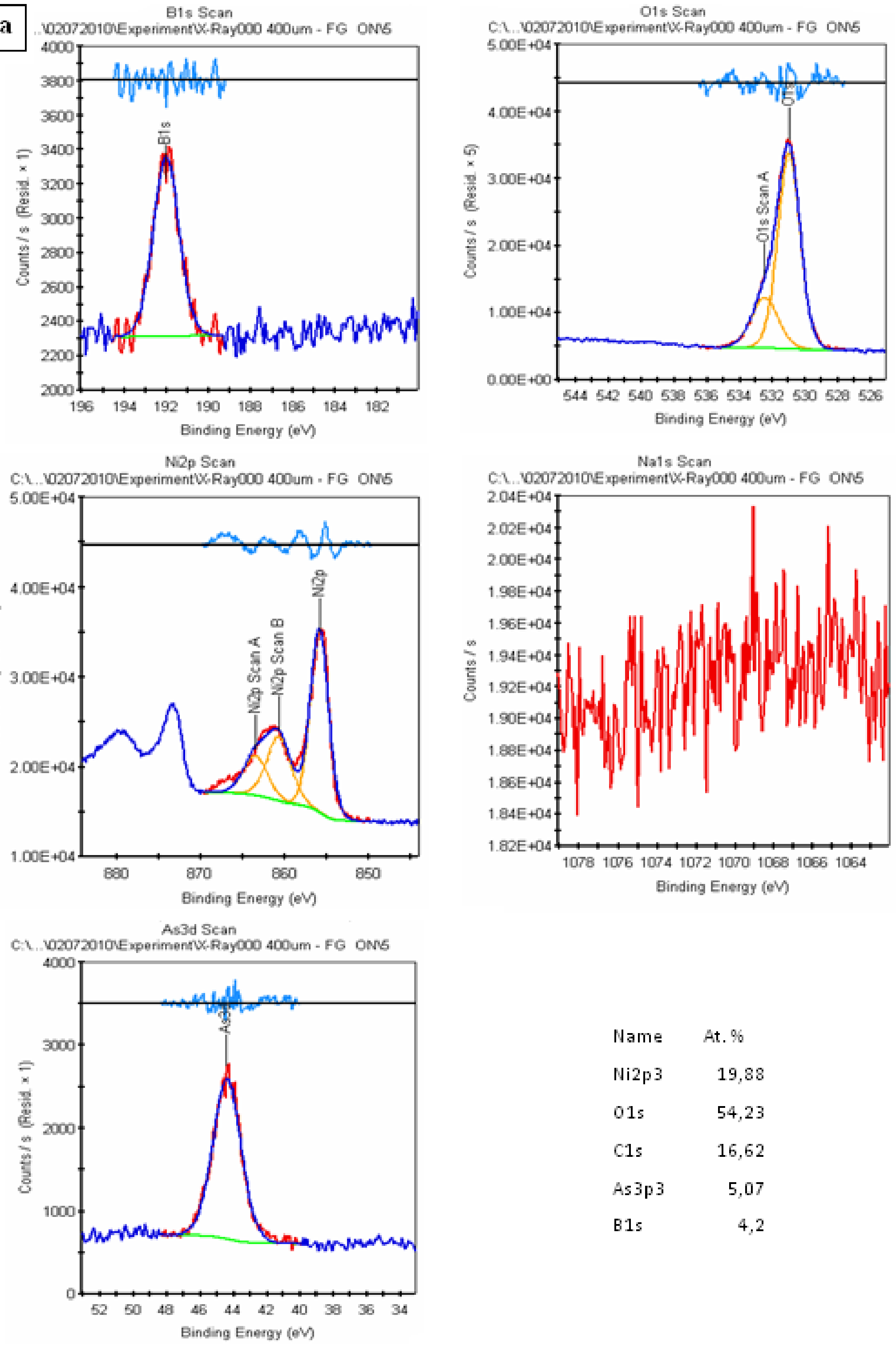
Figure 2.24 XPS spectra of As(V) loaded on the sorbent prepared under aerobic conditions, a) XPS spectra of Ni2p, B1s, O1s and As3d, b) XPS wide scan spectrum



Name	At. %
Ni2p	21,9
O1s	58,5
C1s	11,38
B1s	8,22

Figure 2.25 XPS spectra of the sorbent prepared under anaerobic conditions, a) XPS spectra of Ni2p, B1s and O1s, b)XPS wide scan spectrum

a



Name	At. %
Ni2p3	19,88
O1s	54,23
C1s	16,62
As3p3	5,07
B1s	4,2

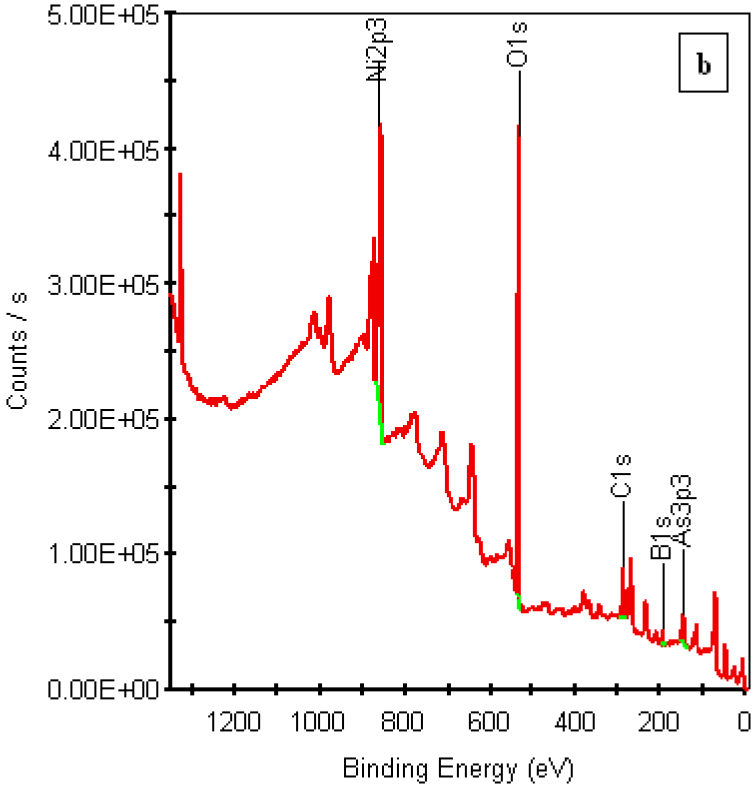
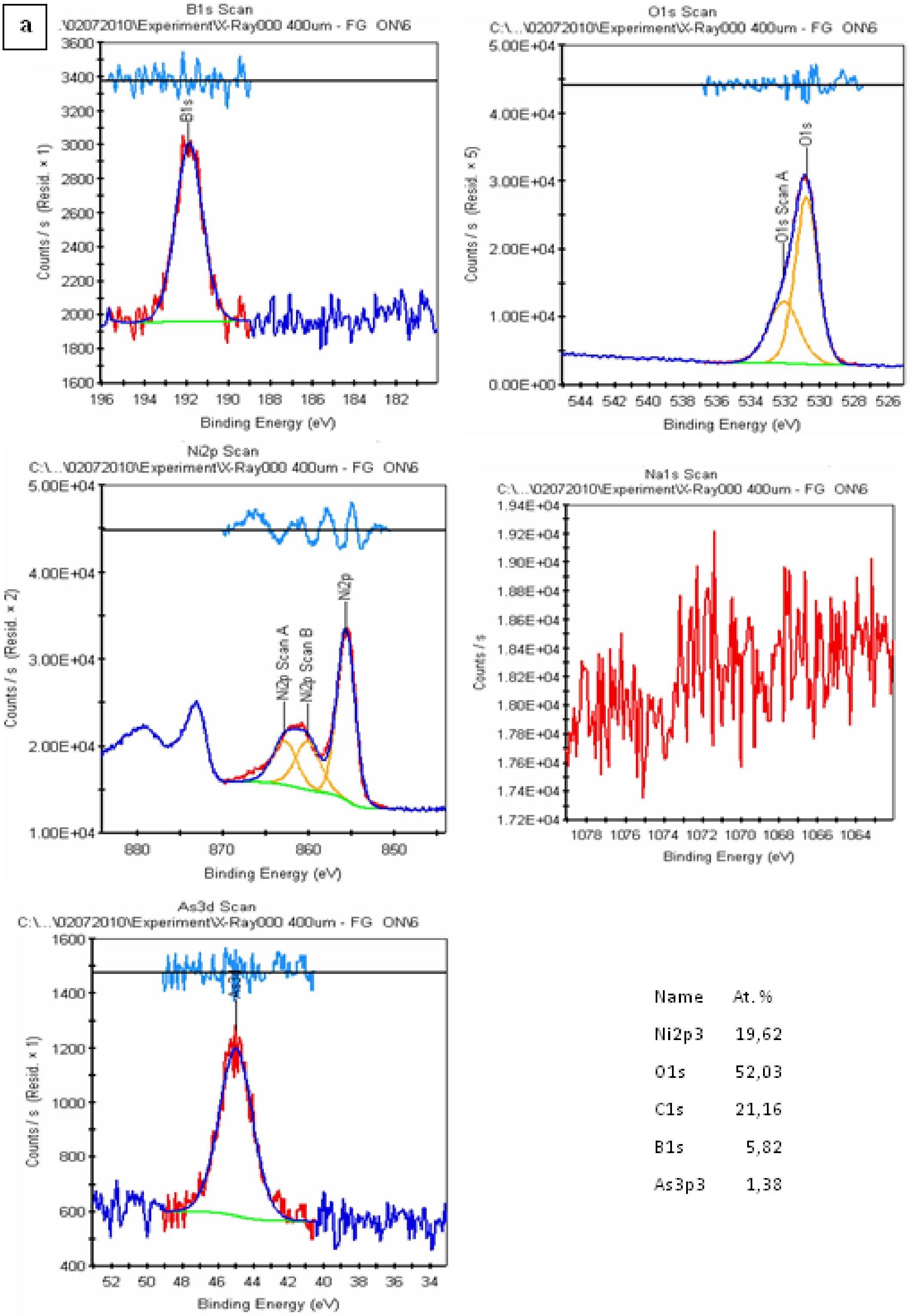


Figure 2.26 XPS spectra of As(III) loaded on the sorbent prepared under unaerobic conditions, a) XPS spectra of Ni2p, B1s, O1s and As3d, b)XPS wide scan spectrum

a



Name	At. %
Ni2p3	19,62
O1s	52,03
C1s	21,16
B1s	5,82
As3p3	1,38

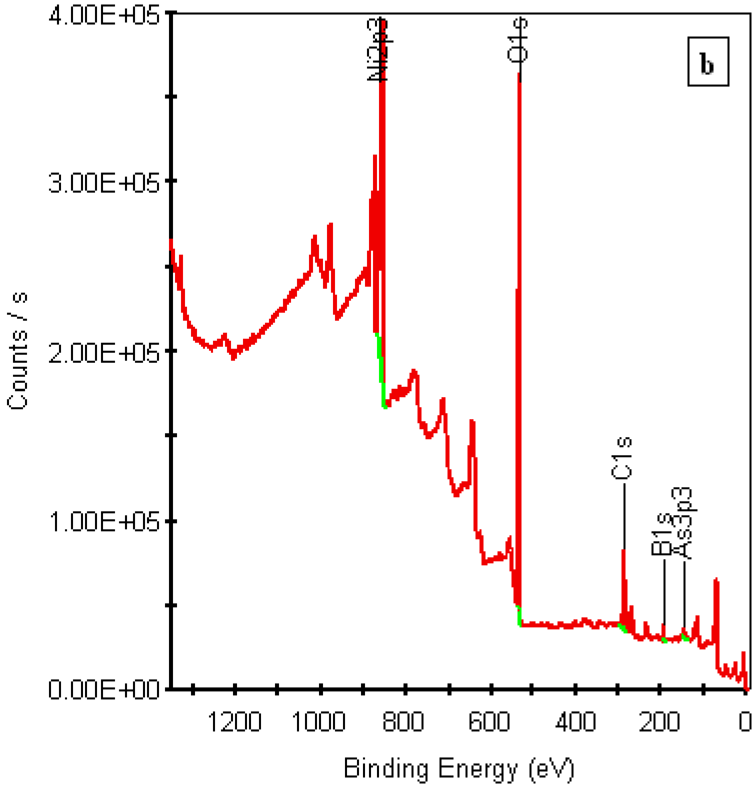
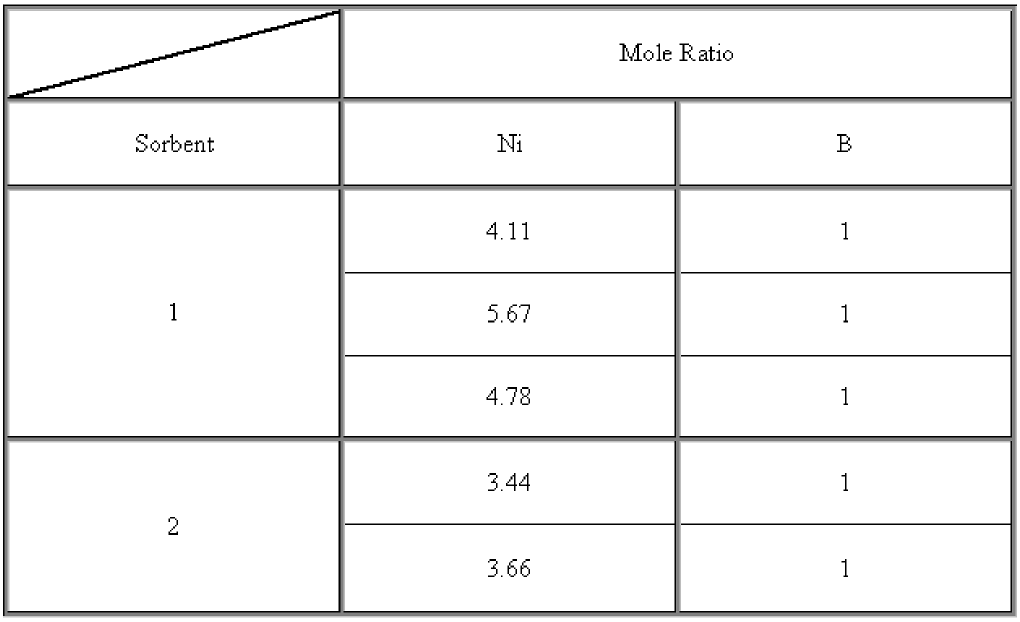


Figure 2.27 XPS spectra of As(V) loaded on the sorbent prepared under unaerobic conditions, a) XPS spectra of Ni2p, B1s, O1s and As3d, b)XPS wide scan spectrum

2.6.5 Determination of Ni and B in the Sorbent

Nickel sorbents were dissolved in 2 M HCl for the determination of total nickel and boron amount. After dilutions, Ni (II) concentration was determined by flame AAS and boron was complexed with azomethine-H (Zenki et al., 1989) then analyzed with a spectrophotometer. The results can be seen in Table 2.4.

Table 2.4. Determination of Ni and B in the sorbent



	Mole Ratio	
Sorbent	Ni	B
1	4.11	1
	5.67	1
	4.78	1
2	3.44	1
	3.66	1

1. Prepared under aerobic conditions
2. Prepared under anaerobic conditions

It is thought that under anaerobic conditions the structure of the sorbent is expected to be Ni_2B and some quantities of $H_4Ni_4BO_7$ (Glavee et al.,1992; Lugowska,1997).

According to literature, under anaerobic conditions the product is Ni_2B. The product after exposure to air turn to metallic $Ni+B_2O_3$

$$2Ni^{2+}(aq) + 4BH_4^-(aq) + 9H_2O \rightarrow Ni_2B + 12.5H_2 + 3B(OH)_3$$

$$\text{also } 4Ni_2B + 3O_2 \rightarrow 8Ni(s) + 2B_2O_3$$

$$B_2O_3 + 3H_2O \rightarrow 2B(OH)_3$$

Water can be used to convert the B_2O_3 to boric acid, which can be separated by water washing (Glavee et al.,1992 and 1994).

Under aerobic conditions the structure of the sorbent is possible a mixture of Ni_2B,Ni_3B, $H_4Ni_4BO_7$ and some quantities of metallic Ni. (Lugowska,1997).

3. CONCLUSION

A new nickel/nickel boride containing nanosorbent which provides high sorption efficiency and capacity for As(III) and As(V) was developed. The sorbent possesses fast sorption kinetic for both As(III) and As(V). Under the optimized conditions, the relative standard deviation for the determination of 5 ng/mL As(III) after two times concentration was found to be 3.35% (n=7).

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