University of Belgrade

Faculty of Technology and Metallurgy

Department of Analytical Chemistry and Quality Control

THE DEVELOPMENT AND APPLICATION OF HYBRID SORBENTS FOR DETERMINATION AND SELECTIVE REMOVAL OF ARSENIC(III) AND ARSENIC(V) FROM WATER

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RAZVOJ I PRIMENA HIBRIDNIH SORBENATA ZA ODREĐIVANJE I SELEKTIVNO UKLANJANJE ARSENA(III) i ARSENA(V) IZ VODE

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THE DEVELOPMENT AND APPLICATION OF HYBRID SORBENTS FOR DETERMINATION AND SELECTIVE REMOVAL OF ARSENIC(III) AND ARSENIC(V) FROM WATER

ABSTRACT

The aim of the thesis was the development and application of hybrid sorbents for determination of arsenic species in water and selective removal of arsenic from water. Water soluble arsenic species in natural water are inorganic (iAs) species, as arsenite, As(III) and arsenate, As(V).

It is important to note that in neutral conditions, As(V) species are completely in ionic forms ($H_2AsO_4^-$ and $HAsO_4^{2-}$), while As(III) is in molecular form (H_3AsO_3 or $HAsO_2$). This fact was the base for the application of anion exchange resin and selective hybrid resins for the separation, determenation and removal of iAs. As a result of anthropogenic pollution in water can be present organic (oAs) species as monomethylarsenic acid, MMAs(V) and dimethylarsenic acid, DMAs(V). Methods developed for iAs species should consider oAs species as interferences for the iAs determinations.

In the frame of these tasks, efficiency of three types of resins were investigated: a strong base anion exchange (SBAE) resin and two hybrid (HY) resins, HY-Fe which integrates sorption activity of hydrated iron oxides (HFO) with the anion exchange function and HY-AgCl which integrates effects of chemical reaction with the anion exchange function. Two systems were employed: a batch and a fixed bed flow system. The selective bonding of arsenic species on three types of resins makes possible the development of the procedure for measuring and calculation of all arsenic species in water. In order to determine capacity of resins, the preliminary investigations were performed in batch system and fixed bed flow system. Resin capacities were calculated according to breakthrough points in a fixed bed flow system which is the first step in designing of solid phase extraction (SPE) module for arsenic speciation separation and determination.

The investigations performed in the scope were focused on: I) separation of As(III) and As(V) species (in order to determine both arsenic species which are prevailing in natural waters), II) separation of organic arsenic species (in order to determine of DMAs(V) and MMAs(V) in natural waters) and III) collection, preconcentration and removal of all arsenic species.

The main achievement of thesis is that three methods for arsenic species determination were developed.

First method is a simple method for the separation and determination of iAs species in natural and drinking water which was the main task of the thesis. Procedures for sample preparation, separation of As(III) and As(V) species and preconcentration of the total iAs on fixed bed columns were defined. Two resins: SBAE and HY-Fe were utilized. The governing factors for the ion exchange/sorption of arsenic on resins in a batch and a fixed bed flow system were analyzed and compared. Acidity of the water, which plays an important role in the control of the ionic or molecular forms of arsenic species, was beneficial for the separation; by adjusting the pH values to less than 8.0, the SBAE resin separated As(V) from As(III) in water by retaining As(V) and allowing As(III) to pass through. The sorption activity of the hydrated iron oxides (HFO) particles integrated into the HY-Fe resin was beneficial for bonding of all iAs species over a wide range of pH values from 5.0 to 11.0. The resin capacities in flow system were calculated according to the breakthrough points and pH value of water 7.5. The SBAE resin bound 370 μg/g of As(V) while the HY-Fe resin bound 4150 μg/g of As(III) and 3500 μg/g of As(V). The high capacities and selectivity of the resins were considered as advantageous for the development and application of two procedures, one for the separation and determination of As(III) (with SBAE) and the other for the preconcentration and determination of the total arsenic (with HY-Fe resin).
The analytical properties of first method developed for the separation and determination of iAs: the limit of detection, LOD, was 0.24 μg/L, the limit of quantification, LOQ, was 0.80 μg/L and the relative standard deviations, RSD %, for samples with a content of arsenic from 10.0 to 300.0 μg/L ranged from 1.1 to 5.8 %.

Second method is a simple and efficient method for separation and determination of inorganic arsenic (iAs) and organic arsenic (oAs) in drinking, natural and wastewater. Three types of resins were used: SBAE, HY-Fe and HY-AgCl were investigated. The quantitative separation of molecular and ionic forms of iAs and oAs was achieved by SBAE and pH adjustment, the molecular form of As(III) that exists in the water at pH < 8.0 was not bonded with SBAE, which was convenient for direct determination of As(III) concentration in the effluent. The HY-Fe resin was convenient for the separation of DMAs(V) from all other arsenic species, which were retained on the HY-Fe resin that has a high sorption capacity for the arsenic species, 9000 μg/g. Efficiency of HY-Fe resin makes possible direct measurements of this

specie in the effluent. HY-AgCl resin retained all iAs which was convenient for direct determination of oAs species concentration in the effluent, the relative standard deviation (RSD) was between 1.3-5.6 %.

The third method is a simple and efficient method for separation and determination of dimethylarsenate DMAs(V). Two resins, SBAE and HY-Fe were tested. By simple adjusting pH value of water at 7.0, DMAs(V) passed through the HY-Fe column without any changes, while all other arsenic species (inorganic arsenic and monomethylarsenate, MMAs(V)) were quantitatively bonded on HY-Fe resin. The resin capacity was calculated according to the breakthrough points in a fixed bed flow system. At pH 7.0, the HY-Fe resins bonded more than 4150 μg/g of As(III), 3500 μg/g of As(V) and 1500 μg/g of MMAs(V). Arsenic adsorption behavior in the presence of impurities showed tolerance with the respect to potential interference of anions commonly found in natural water. DMAs(V) was determined in the effluent by inductively coupled plasma mass spectrometry (ICP-MS). The detection limit was 0.03 μg/L and relative standard deviation (RSD) was between 1.1-7.5 %.

For the determination of arsenic in all arsenic species in water two analytical methods were applied: the inductively coupled plasma mass spectrometry (ICP-MS) and hydride generation-atomic absorption spectroscopy (GH-AAS). Methods were established through basic analytical procedures (with external standards, certified reference materials and the standard addition method) and by the parallel analysis of some samples using the HG-AAS technique. Verification with certified reference materials proved that the experimental concentrations found for model solutions and real samples were in agreement with the certified values. ICP-MS detection limit was 0.2 μg/L and relative standard deviation (RSD) of all arsenic species investigated was between 3.5-5.1 %.
The interference effects of anions commonly found in water were found to be negligible. Both methods could be applied routinely for monitoring arsenic levels in various water samples (drinking water, ground water and wastewater).

Keywords: Arsenic; Speciation; Separation; Determination; Preconcentration; Ion exchange; Hybrid resin; Ion exchange resin, ICP-MS
Scientific field: Chemistry
Specific scientific field: Analytical chemistry

RAZVOJ I PRIMENA HIBRIDNIH SORBENATA ZA ODREĐIVANJE I SELEKTIVNO UKLANJANJE ARSENA(III) I ARSENA(V) IZ VODE

I Z V O D

Cilj izrade ove teze je razvoj i primena hibridnih smola kao sorbenata za određivanje i selektivno uklanjanje arsenovih vrsta u vodi. Arsenove vrste rastvorne i prisutne u prirodnoj vodi su neorganska jedinjenja arsena (iAs), arseniti As(III) i arsenati As(V). Bitno je naglasiti da se u neutralnim uslovima, As(V) nalazi u jonskom obliku ($H_2AsO_4^-$ and $HAsO_4^{2-}$), dok se As(III) nalazi u molekularnom obliku (H_3AsO_3 or $HAsO_2$). Ova činjenica je osnova za primenu anjonskih, jonoizmenjivačkih smola i selektivnih hibridnih smola za razdvajanje i uklanjanje iAs. Kao rezultat antropogenog zagađivanja u vodi mogu da budu prisutne i vrste organskog arsena (oAs) kao što je monometilarsenova, MMAs(V) i dimetilarsenova kiselina, DMAs(V). Svaka metoda koja je razvijena za određivanje iAs mora da razmatra i reši problem prisustva oAs kao smetnji za određivanje iAs vrsta.

U okviru postavljenih zadataka ispitana je efikasnost tri tipa smola: jako bazna anjonska smola (SBAE) i dve hibridne (HY), HY-Fe koja integriše sorpcionu aktivnost hidratisanog gvožđe oksida (HFO) sa anjonsko-izmenjivačkom funkcijom i HY-AgCl koja integriše efekte hemijske reakcije sa anjonsko-izmenjivačkom funkcijom. Ispitivanja su vršena u šaržnom i protočnom (s nepokretnim slojem) sistemu.

U sklopu istaknutih zadataka i ciljeva, ispitivanja u okviru teze su bila fokusirana na: I) razdvajanje As(III) i As(V) vrsta (u cilju određivanja obe ove vrste čije prisustvo preovlađuje u prirodnim vodama), II) razdvajanje organskog arsena vrsta (u cilju određivanja obe ove DMAs (V) i MMAs (V) u prirodnim vodama) i III) sakupljanje, pretkoncentrisanje i uklanjanje svih arsenovih vrsta u vodi.

Najvažniji doprinos ostvaren u izradi ove teze je razvoj tri metode za razdvajanje i određivanje arsenovih vrsta u vodi.

Prva metoda predstavlja jednostavnu metodu za razdvajanje i određivanje iAs vrsta u prirodnim vodama i vodi za piće, što je i bio glavni zadatak u tezi. Definisani su postupci za pripremu uzoraka, za razdvajanje As(III) i As(V) vrsta, i za pretkoncentrisanje ukupnog sadržaja neorganskog arsena, iAs u protočnom sistemu, u koloni s nepokretnim slojem sorbenta. Ispitane su dve vrste smole: SBAE i HY-Fe. Definisani su i analizirani svi parametri

šaržnog i protočnog sistema koji imaju najveći uticaj na jonsku izmenu i sorpciju arsena. Kiselost vode, koja igra vrlo važnu ulogu i u kontroli i prisustvu jonskih i molekulskih vrsta arsena u vodi, predstavlja važan faktor i za razdvajanju iAs arsena u vodi: podešavanjem pH vrednosti na vrednosti manje od 8,0, ostvaruje se mogućnost razdvajanja As(III) i As(V) vrsta: As(V) vrste se zadržavaju jer se nalaze u jonskom obliku, a As(III) vrste prolaze kroz kolonu bez zadržavanja jer se nalaze u molekulskom obliku. Sorpciona aktivnost čestica hidratisanog gvožđe-oksida (HFO) integrisanih u HY-Fe smolu bila je pogodna za vezivanje svih vrsta arsena u vodi, i to u širokom opsegu pH vrednosti od 5,0 do 11,0. Kapaciteti smola u protočnom sistemu računati su do tačke proboja i pri pH vrednosti od 7,50. Utvrđeno je da SBAE smola vezuje 370 µg/g As(V). HY-Fe smola vezuje 4150 µg/g As(III) i 3500 µg/g As(V). Ovi veliki kapaciteti smola predstavljaju prednost za razvoj i primenu dva postupka, jednog za razdvajanje i određivanje As(III) vrsta, sa SBAE smolom, drugog za koncentrisanje i određivanje ukupnog arsena u vodu (s HY-Fe smolom). Analitički parametri i karakteristike metode za razdvajanje i određivanje iAs vrsta u vodi su definisani: granica detekcije, LOD iznosi 0,24 µg/L, granica kvantifikacije, LOQ iznosi 0,80 µg/L, a relativna standardna devijacija, RSD %, za uzorke vode koji sadrže arsen od 10.0 do 300.0 µg/L ima vrednost u opsegu od 1,1 do 5,8 %.

Druga metoda predstavlja, takođe, jednostavnu i efikasnu metodu za razdvajanje i određivanje iAs i oAs vrsta u prirodnim vodama, vodi za piće i otpadnim vodama.
Ispitane su tri vrste smole: SBAE, HY-Fe i HY-AgCl. Kvantitativno razdvajanje molekulskih i jonskih vrsta iAs i oAs je ostvareno na SBAE podešavanjem pH vrednosti vode. Molekulski oblici As(III) koji su prisutni u vodi na pH vrednostima nižim od 8 ne vezuju se za SBAE smolu, što je iskorišćeno za direktno određivanje As(III) koncentracije u efluentu. HY-Fe smola je pogodna za razdvajanje DMAs(V) od svih drugih vrsta arsena. Sve arsenove vrste osim DMAs(V) zadržavaju se na smoli. Smola ima veliki kapacitet za arsenove vrste, 9000 µg/g. Selektivnost HY-Fe smole iskorišćena je za direktno određivanje DMAs(V) koncentracije u efluentu. HY-AgCl smola zadržava sve iAs vrste, a propušta oAs vrste što je pogodno za direktno određivanje koncentracije oAs u efluentu. Selektivno vezivanje arsenovih vrsta na tri tipa smola omogućilo je razvoj postupaka za merenje i proračun svih vrsta arsena u vodi, iAs i oAs. U cilju određivanja kapaciteta smola izvršena su preliminarna određivanja u šaržnom sistemu, a ti kapaciteti su provereni i potvrđeni u protočnom sistemu. Kapaciteti smola u protočnom sistemu su računati do tačke proboja, što je prvi korak u

projektovanju modula za ekstrakciju u čvrstoj fazi (SPE) koji se mogu koristiti za razdvajanje i određivanje arsenovih vrsta.

Treća metoda je jednostavna i efikasna metoda za razdvajanje i određivanje dimetilarsena, DMAs(V). Ispitane su dve smole: SBAE i HY-Fe. Jednostavnim podešavanjem pH vrednosti vode na pH 7,00, ostvareno je da DMAs(V) kvantitativno prolazi kroz kolonu sa HY-Fe bez ikakve promene u strukturi i koncentraciji. Druge arsenove vrste (neorganski arsen i monometilarsen, MMAs(V)) vezuju se kvantitativno za smolu. Kapacitet smole je veliki, smola vezuje 4150 μg/g As(III), 3500 μg/g As(V) i 1500 μg/g MMAs(V). Adsorpcija arsena neometana je od strane nečistoća ili od strane anjona koji se uobičajeno nalaze u vodi. DMAs(V) je određen u efluentu merenjem na ICP-MS-u. Detekcioni limit je bio 0,03 μg/L, a relativna standardna devijacija, RSD je bila u opsegu od 1,1 do 7,5 %.

Za određivanje arsena u svim arsenovim vrstama u vodi primenjene su dve analitičke metode: induktivno spregnuta plazma sa masenom spektrometrijom (ICP-MS) i atomska apsorpciona spektroskopija s generisanjem hidrida (GH-AAS). Metode su ustanovljene na osnovu standardnih analitičkih postupaka (pripremom standardnih rastvora, analizom sertifikovanih referentnih materijala i metodom standardnog dodatka), a izvršena je i provera paralelnim merenjem nekoliko uzoraka primenom HG-AAS tehnike. Verifikacija sa sertifikovanim referentnim materijalma potvrdila je da su eksperimentalno dobijene vrednosti za model rastvor i rastvore realnih uzoraka u saglasnosti. Merenja na ICP-MS-u imala su granicu detekcije 0,2 μg/L i relativnu standardnu devijaciju (RSD) za sve ispitivane arsenove vrste u opsegu od 3,5 do 5,1 %.

Analiza interferentnih, ometajućih anjona koji su karakteristični za prirodne vode je pokazala da se njihov uticaj na određivanje arsena predloženim metodama može zanemariti. Obe predložene metode mogu da se preporuče za rutinsko praćenje i analizu arsena u različitim uzorcima vode od vode za piće, podzemnih voda do zagađenih, otpadnih voda.

Ključne reči: arsen, specijacija, separacija-razdvajanje, određivanje, pretkoncentrisanje, jonska izmena, hibridne smole, jonoizmenjivačke smole, ICP-MS
Šira naučna oblast: Hemija
Uža naučna oblast: Analitička hemija

About the thesiss (important dates and structure)

This thessis is accomplished at the Department of Analytical Chemistry and Quality Control at the Faculty of Technology and Metallurgy, University of Belgrade during 2008-2012 under the supervision of prof. dr Ljubinka Rajaković.

Organization of the thesis

The thesis comprises of seven chapters: 1) the introduction, 2) the theoretical part, 3) the experimental part, 4) the results and the discussion of results, 5) the conclusion and 6) the references.

Each chapter explains and clarifies scientific work in standard manner for PhD thesis:

- In the introduction the main objects of thesis, the goals and the contributions of thesis are explained.
- Theoretical part comprehends the chemistry of arsenic, methods used for determination and separation of arsenic species from drinking water. Part of theoretical chapter is devoted to review of papers and research which present state-of-art in the field of arsenic investigations.
- Experimental part describes new methods and procedures for determination and selective separation of arsenic species from water. Established methods that include coupling of separation techniques such as IC, HPLC for the separation of arsenic species with a sensitive detection system such as ICP-MS, HG-AFS, and HG-AAS are discussed and the choice for routine determination of a large number of water samples was explained. As the most appropriate tool for arsenic determination, ICP-MS is applied in this work for real water samples containing As(III) and As(V) species. In the lack of coupled tools, a simple procedure for arsenic species separation on exchange resins was developed and proposed.
- Within the conclusion the final outcome of the thesis is written and explained.
- The references which are related to the topic are listed in sixth chapter. Criterions for the choice of references were contemporary approach for arsenic analysis, the influence of recent investigations to work within this thesis and also the published results.
- In order to have clear review of figures and tables, list of figures and tables is given.

Belgrade 2012.

Author

The main achievement and contribution of the thesis

The main achievement of thesis is that three methods for arsenic species determination were developed.

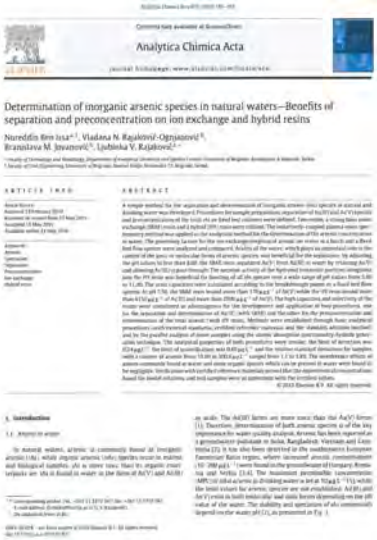
First method is a simple method for the separation and determination of iAs species in natural and drinking water which was the main task of the thesis.

Second method is a method for the separation and determination of iAs and oAs species in natural, drinking and waste water

Third method is a method for the separation and determination of dimethylarsenate in natural waters. For each method a scientific paper is published.

Papers published during thesis creating:

1. **N.B. Issa**, V.N. Rajaković-Ognjanović, B.M. Jovanović, Lj.V. Rajaković, Determination of Inorganic Arsenic Species in Natural Waters-Benefits of Separation and Preconcentration on Ion Exchange and Hybrid Resins, *Anal. Chim. Acta*, 673 (2010) 185-193
2. **N.B. Issa**, V.N. Rajaković-Ognjanović, A. Marinković, Lj.V. Rajaković, Separation and Determination of Arsenic Species in Water by Selective Exchange and Hybrid Resins, *Anal. Chim. Acta*, 706 (2011) 191-198
3. **N.B. Issa**, A.D. Marinković, Lj.V. Rajaković, Separation and determination of dimethylarsenate in natural waters, *J. Serb. Chem. Soc.*, 77 (6) (2012) 775–788



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ABBREVIATIONS

AAPTS	3-(2-aminoethylamino) propyltrimethoxysilane
AAS	atomic absorption spectrometry
AAS-GH	atomic absorption spectroscopy-hydride generation
AES	atomic emission spectrometry
AFS	atomic fluorescence spectrometry
AM	ammonium molybdate
amu	atomic mass unite
APDC	ammonium pyrrolidinedithiocarbamate
Ar	argon
As	arsenic
As(III)	arsenite
As(V)	arsenate
AsB	arsenobetaine
AsC	arsenocholine
ASV	anodic stripping voltammetry
^{o}C	degree Celsius
CNFs:	carbon nanofibers
CSV	cathodic stripping voltammetry
CTAB	cetyltrimethylammonium bromide
DDTC	diethyldithiocarbamete
DEAE-	diethylaminoethyl
DMAs(V)	dimethylarsenic acid
DMAs(III)	dimethylarsinous acid
DNPS	2,3-dimercaptopropane-1-sulfonate
DPCSV	differential pulse cathodic stripping voltammetry
EBV	empty bed volume
Eh	redox potential
FI	flow injection
GC	gas chromatography
GF-AAS	graphite furnace atomic absorption spectrometry
g	gram
hr	hour

H_3AsO_3	arsenic acid
$HAsO_2$	arsenous acid
HG-AFS	hydride generation atomic fluorescence spectrometry
HG-ICP-OES	hydride generation-inductively coupled plasma atomic emissiospectrometry
HMDE	hanging mercury drop electrode
HPLC-ICP-AES	high performance liquid chromatography linked to inductively coupled plasma atomic emission spectrometry
HPLC-ICP-MS	high performance liquid chromatography linked to inductively coupled plasma mass spectrometry
HR	high resolution
HS-SDME-ET-AAS	headspace single drop micro extraction coupled to electro therma atomic absorption spectrometry
HY	hybrid resins
HY-AgCl	silver chloride resin
HY-Fe (HFO)	hydrated iron oxides
iAs	inorganic arsenic species
ICP	inductive coupled plasma
ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
K	kelvin
L	liter
LC	liquid chromatography
LOD	limit of detection
LOQ	limit of quantification
m	mass
M	molar
mg	milligram
min	minute
mL	millilitre
mm	millimeter
MMAs(V)	monomethilarsenic acid
MMAs(III)	monomethylarsonous acid

mol	mole
MRT	polymeric organic materials-ion –selective
MS	mass spectra
m/z	mass to charge ratio
MΩ.cm	megaohm×centimeter
µg	micrograms
ng	nanogram
oAs	organic arsenic species
OES	optical emission spectrometry
PAS	phenylarsonic acid
PDC	pyrrolidine dithiocarbamate
pKa	dissociation Constant
ppm	parts per million
PTFE	polytetrafluoroethylene
P(V)	phosphate (V)
Q	flow rate
RC–GLS	reaction chamber/gas–liquid separator
RF	radio frequency
rmp	rotations per minute
RSD	relative standard deviations
SBAE	strong base anion exchange resin
SEC-ESI-MS	size exclusion chromatography coupled to electrospray ionization mass spectrometry
σ	standard deviation
SPE	solid phase extraction
SWCNTs	single-walled carbon nanotubes
TETRA	tetramethylarsonium ion
t	temperature
TMAO	trimethylarsine oxide
$TMAs^{+}$	tetramethylarsonium ion
TPAC	tetraphenylarsenium chloride
Triton-Cp	non ionic surfactants
TXRF	total Reflection X-Ray Fluorescence
τ	time

ULOQ	upper limit of quantification
V	volume
w/v	weight per volume

I INTRODUCTION

I INTRODUCTION

The object of the thesis was arsenic in water. Arsenic, As, is a metalloid. Arsenic's history in science, medicine and technology has been overshadowed by its feature as a poison. Arsenic is a synonym of toxicity. Arsenic exists in the –3, 0, +3 and +5 oxidation states [1]. These oxidation states cause arsenic to be very reactive and affect its physical and chemical behavior. The different chemical species or forms (speciation) of As exhibit different degrees of toxicity. The term speciation is also used to indicate the distribution of species in a particular sample or matrix. Arsenic is widely distributed throughout the environment. It is present in biota, the atmosphere, oceans, lakes, groundwater, sediments, and soils throughout the world. Arsenic is present in many minerals. Due to high mobilization of arsenic, both from natural and anthropogenic sources, it is reactive in aquatic environments and the atmosphere. Natural sources of arsenic mobilization include weathering of arsenic-bearing rocks, biological activity, and volcanic eruption. Anthropogenic sources include mining of metal ores, combustion of fossil fuels, pesticide, livestock feed additives, wood preservatives, and pigment production. In most cases of groundwater contamination, however, a combination of natural and anthropogenic actions leads to arsenic release [2]. Water soluble arsenic species existing in natural water are inorganic arsenic (iAs) species as arsenite, As(III) and arsenate, As(V) and organic arsenic (oAs) species as monomethilarsonic acid, MMAs(V) and dimethylarsinic acid, DMAs(V) [3]. In aquatic systems, inorganic arsenic, iAs, are the most prevalent forms, although oAs as methylated arsenic species is generated by aquatic biota in trace concentrations [3]. For the selective separation of arsenic species in these thesis three types of resins were investigated: a strong base anion exchange (SBAE) resin and two hybrid (HY) resins based on activity of hydrated iron oxides, HY-Fe, and silver chloride, HY-AgCl. Two systems were employed: a batch and a fixed bed flow system.

The aim of the thesis was to develop methods for the determination and selective separation of arsenic species from water. Speciation analysis is defined as the determination of the various chemical (oxidation/valence states) forms of the element which together make up the total concentration of that element on a sample. Speciation analysis is aiming to define and quantify the distribution of an element between the different species in which it occurs [1,4]. These structural levels are important in different areas, for instance, valence state and inorganic and organic speciation are of great importance in determining the availability and

toxicity of metals or metalloids, thus being very important in food, and also in clinical and biological fields. Concerning arsenic, the different chemical species or forms of As completely depends on the pH value.

Applying this concept to the arsenic species in water, one of the tasks in the thesis was to establish procedure for the separation and determination of iAs and oAs species in water. The investigations were focused on As(III) (in water it exists as: H_3AsO_3, $HAsO_3^{2-}$ and AsO_3^{3-}), As(V) (in water it exists as: H_3AsO_4, $H_2AsO_4^{2-}$ and AsO_4^{3-}), MMAs(V) and DMAs(V) as typical and prevailing arsenic species in water.

The use of hyphenated analytical techniques for on-line separation and determination of species are highly recommended, but in the lack of these highly sophisticated techniques an individual, intelligent strategy can be developed for selective and sensitive determination of species.

In order to separate arsenic species before analytical determination a non-chromatographic speciation method was applied, sorption on multifunctional ion-exchange and sorption materials. Three types of solid have been used: a strong base anion exchage (SBAE) resin and hybrid (HY) resins: HY-Fe and Hy-AgCl.

The investigations performed in the experimental work were focused on: I) separation of iAs (As (III) and As(V)) in order to determine both arsenic species which are prevailing in natural water and compare with total arsenic content in water sample), II) separation of iAs and oAs (in order to determine all inorganic and organic arsenic species which can be present in water and wastewater due to antrophogenic influence) and III) collection, preconcentration and removal of all arsenic species from water.

As the most appropriate tool for arsenic determination, ICP-MS was applied in the work for real water samples containing iAs and oAs species at low µg/L.

The contribution of the thesis is the development and application of methods for determination of arsenic speciec in natural and drinking water and their removal. Methods are based on coventional ion-exchange resins and new hybrid, HY, resins which integrate the anion exchange function with sorption and chemisorption on hydrated iron oxides, HY-Fe and silver chloride, HY-AgCl. Proposed methods could be applied routinely for monitoring arsenic levels in various water samples (drinking water, ground water and wastewater) and they are the base for the development of procedures for arsenic removal from water sources for drinking water.

The separation and preconcentration procedures were well coordinated with the ICP-MS technique for a sensitive determination of the total As concentration and iAs and oAs species at low µg/L. Measurements with certified reference materials proved that the measurements of arsenic species concentrations in model solutions and real samples were in agreement with the certified values. Both methods could be applied routinely for monitoring of arsenic levels in various water samples (drinking water, ground water and wastewater).

Available commercial arsenic removal technologies include adsorption, precipitation, membrane and hybrid membrane processes. Among them, sorption is considered to be relatively simple, efficient and low cost removal technique, especially convenient for application in rural areas. Wide range of sorbent materials for aqueous arsenic removal is available nowadays: biological materials, mineral oxides, different soils, activated carbons and polymer resins. Nevertheless, finding cheap and effective arsenic sorbent is still highly desired. Sorption by materials containing iron oxide is an innovative technology for purifying drinking water contaminated by toxic metal pollutants. The present focus on arsenic removal in the developing countries is the use of iron containing compounds because they are both economical and effective.

II THEORETICAL PART

II THEORETICAL PART

2.1 CHEMISTRY OF ARSENIC

Arsenic is a metalloid element, with a chemical symbol As, has two allotropes: grey (density 5.73 g/cm^3 at 300 *K*) and the yellow forms (1.97 g/cm at 300 *K*). The grey form is the most common and more stable, the atomic number of arsenic is 33 and atomic weight 74.92 g/moL. It sublimes at 617 °C. Its electronic configuration is [Ar]^{18} 4s^2 3d^{10} 4p^3. It occurs in several oxidation states (-3, 0, +3, +5) under different redox conditions. It oxidizes rapidly in oxygenated media to form AsO_3^{3-} [arsenite, As(III)], or AsO_4^{3-} [arsenate, As(V)] depending on the pH and redox potential of its surrounding. Substitution of oxygen atoms with methyl group leads to the formation of monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) [5,6]. In table 2.1 common inorganic and organic arsenic species are noted. The inorganic species tend to be more prevalent in water than the organic arsenic species [7]. While the organic species (methylated arsenic) are commonly considered to be of little significance in waters compared with the inorganic species [2,8,9,10]. Table 2.2 shows the approximate values for the *pKa* of arsenic species.

Table 2.1 Common inorganic and organic As species [4]

Name	Synonyms	Oxidation State	Chemical Formula
Arsenate	As(V)	+5	AsO_4^{3-}
Arsenite	As(III)	+3	AsO_3^{3-}
Methylarsonic acid	Monomethylarsonic- - acid, MMA	+5	$CH_3AsO(OH)_2$
Dimethylarsinic acid	Cacodylic acid, DMA	+5	$(CH_3)_2AsO(OH)$
Trimethylarsine oxide	TMAO	+5	$(CH_3)_3AsO$
Tetramethylarsonium ion	TETRA	+3	$(CH_3)_4As^+$
Arsenobetaine	AsB	+3	$(CH_3)_3As^+CH_2COO^-$
Arsenocholine	AsC	+3	$(CH_3)_3As^+CH_2CH_2OH$

Table 2.2 Approximate values for the *pKa* of arsenic species

Speciation	Equation	*pKa*
As(V)	$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$	2.24
	$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}$	6.69
	$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}$	11.5
As(III)	$H_3AsO_3 \rightleftharpoons H^+ + H_2AsO_3^-$	9.20
	$H_2AsO_3^- \rightleftharpoons H^+ + HAsO_3^{2-}$	12.1
	$HAsO_3^{2-} \rightleftharpoons H^+ + AsO_3^{3-}$	13.4
MMAs(V)	$H_2AsO_3(CH_3) \rightleftharpoons H^+ + HAsO_3^-(CH_3)$	4.49
	$HAsO_3^-(CH_3) \rightleftharpoons H^+ + AsO_3^{2-}(CH_3)$	8.77
DMAs(V)	$HAsO_2(CH_3)_2 \rightleftharpoons H^+ + AsO_2^-(CH_3)_2$	6.14

2.1.1 Arsenic species in water

Arsenic of geological origin is found in groundwater used for drinking-water supplies in several parts of the world. Arsenic occurs in several different species depending upon the pH and oxidation potential of the water; inorganic arsenic occurs in two valence states, inorganic arsenic “arsenite As(III) and arsenate As(V)” mostly found in natural waters, for both ground waters and surface waters While the methylated species would rarely be present in water supplies [2]. Organic arsenic forms may be produced by biological activity, mostly in surface waters, but are rarely quantitatively important such as MMAs(V) and DMAs(V) are predominant in water and sediments [3,8,9], and both organic arsenic DMAs(V) and MMAs(V) stable in oxidizing system [3].

One of the most important sources of arsenic is leaching of naturally occurring arsenic into water aquifers resulting in run off of arsenic into surface waters. Drinking water is derived from a variety of sources depending on local availability: surface water (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rain water. Several anthropogenic activities including coal combustion, irresponsible disposal of mine tailings, glassware and ceramic industries, petroleum refining, dyes and pesticides contribute to elevated arsenic levels in the water. The WHO guideline for arsenic in drinking water is 10μg/L. The development of simple and easy methods for determination of arsenic in water becomes a priority in research. New inexpensive methods which can provide acceptable quantitative results are very important for research studies in the field of analytical chemistry. In Fig. 2.1 the structural difference between arsenate and arsenite in waters is shown.

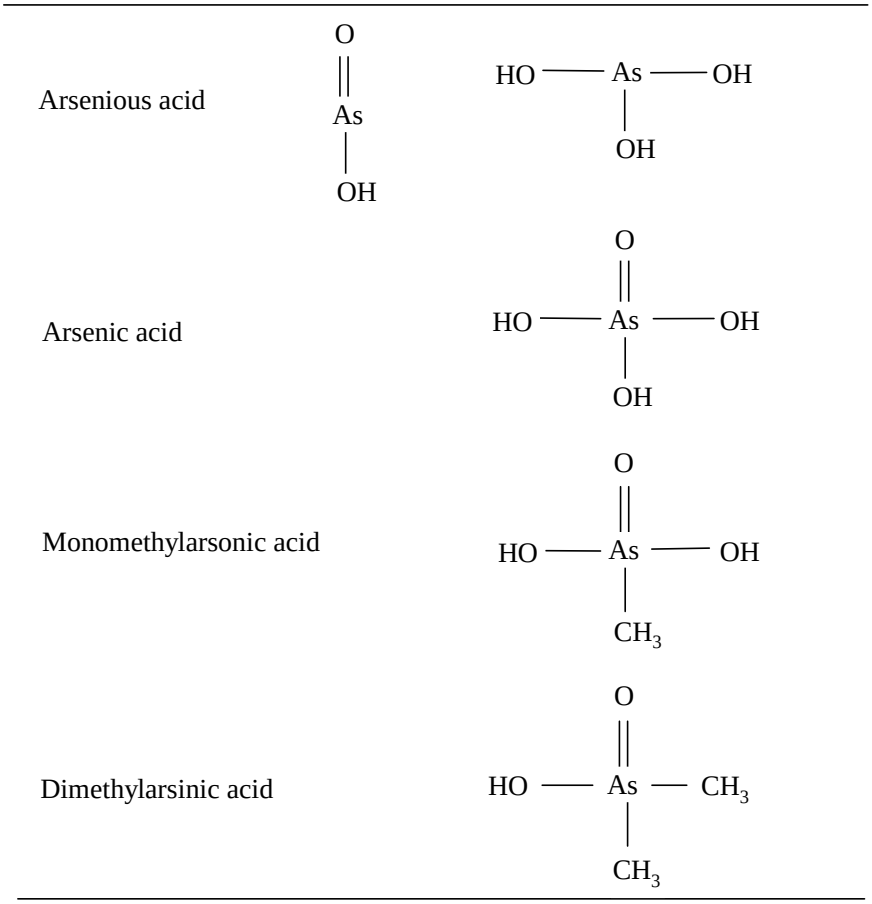

Fig. 2.1 Arsenic species in water [3,8]

2.1.2 Effect of pH and Eh on the distribution of arsenic species in water

pH and redox potential (Eh) play the primary and (the most) important role in determining and separating arsenic species. As(V) species are dominant under oxidizing conditions, and As(III) is thermodynamically stable under mildly reducing conditions. Thus As(V) is more likely to occur in surface waters and As(III) tends to occur more frequently in ground waters. As(III) is more mobile because it is present as a neutral form at the pH of most natural (<pH 9) [11] so it is less strongly adsorbed on mineral surfaces. Under oxidizing and aerated conditions, the predominant form of arsenic in water is arsenate. Under reducing conditions arsenate should be the predominant in arsenic compounds. The rate of conversion is dependent on the Eh and pH of the water[12-14]. In brief, at moderate or high Eh, arsenic can be stabilized as a series of pentavalent (arsenate) oxyanions, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} [13,15], as it is shown in Fig.2. 2.

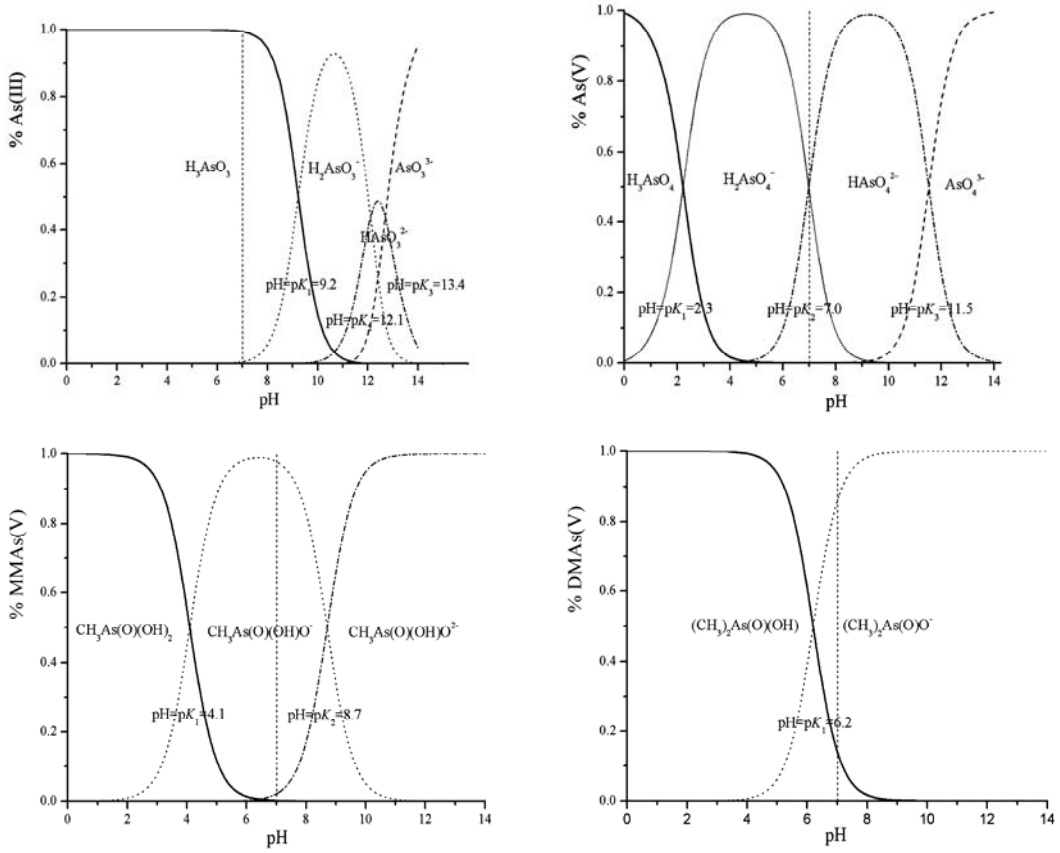

Fig. 2.2 Stability and speciation of arsenic compounds, As(III), As(V), DMAs(V) and MMAs(V), as a function of pH. [8,16]

The arsenic compounds with low molecular weights are highly susceptible to dissolution of the organic material and the formation of complexes, and on this basis, the disposal of arsenic

will change depending on the circumstances of reductions provided by the organic matter. The free ion positive for arsenic is lost directly from the water because of its association with organic matter and this limits the movement of arsenic in the water and prevents its spread. Generally the concentration of arsenic in water is high during the period of discharge, when the grain size of sedimentary soft and organic content in water is high.

2.2 ANALYTICAL METHODS FOR THE DETERMINATION OF ARSENIC IN WATER

There has been several review articles on the speciation of arsenic in variety samples; with emphasis on arsenic measurement techniques. These reviews focus on, (i) determination of total content of arsenic and (ii) speciation analysis. The total concentration of arsenic in drinking water (mostly traces of arsenic, level of µg/L or less) can be detected only by sophisticated analytical techniques as inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GF-AAS). For iAs species the hydride generation atomic absorption and fluorescence spectrometry (HG-AAS and HG-AFS) methods are applicable.

The speciation analysis of arsenic usually requires the coupling of proper sample preparation with two analytical techniques: first, a technique to separate the chemical forms of arsenic, and second, a sensitive detection for measurement.

Three steps are required for arsenic speciation: the extraction of arsenic from the sample, the separation of the different arsenic species and their detection/quantification. The extraction procedure should be as mild and complete as possible.

There are a variety of chemical methods that are used for determination of arsenic species using different techniques. The most important techniques used to determine arsenic are:

- ICP-MS - Inductively coupled plasma mass spectrometry
- GF-AAS - Graphite furnace-atomic absorption spectrometry
- HG-AAS - Hydride generation-atomic absorption spectrometry
- HG-AFS - Hydride generation-atomic fluorescence spectrometry
- ICP-AES - Inductively coupled plasma atomic emission spectrometry
- ICP-OES - Inductively coupled plasma optical emission spectrometry
- HG-ICP-OES - Hydride generation-inductively coupled plasma atomic emission spectrometry
- HPLC-ICP-MS - High performance liquid chromatography linked to inductively coupled plasma mass spectrometry

- HPLC-ICP-AES - High performance liquid chromatography linked to inductively coupled plasma atomic emission spectrometry
- SEC-ESI-MS - Size exclusion chromatography coupled to electrospray ionization mass spectrometry
- HS-SDME-ET-AAS - Headspace single drop micro extraction coupled to electro thermal atomic absorption spectrometry
- ASV,CSV - Electrical voltametric

2.2.1 Analytical methods for the determination of total arsenic in water

The most widely applied analytical techniques for total arsenic determination are ICP-MS [17, 18], ICP-OES [19] and ICP-AES [20]. The main advantages of ICP-MS over ICP-AES are isotope analysis capability of high precession and lower detection limits. The results obtained by ICP-AES are comparable to determinations, with low detection limit 0.1 µg/L [21]. However the determination of low concentrations of arsenic in real samples suffers from low sensitivity due to the poor ionization efficiency in ICP.

2.2.1.1 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP–MS is classified among the U.S. organizations- approved analytical methods for arsenic. In this instrument the atoms converted to the positive ions are separated and evaluated by MS. The advantage of the instrument:

- Provides very low detection
- A fast, precise and accurate
- Good sensitivity to most of the elements
- Multi-element analytical technique for the determination of trace elements
- plasma provides a high temperature, which reduces the matrix interference
- In some cases could be better than GF-AAS
- Isotopes measurement

The technique was commercially introduced in 1983 and has acceptance in many laboratories. Inductively coupled plasma ICP is a method of producing ions (ionization) that will dissociate a sample into its atom ions and cause them to emit light at a characteristic wavelength by exciting them to a higher energy level. This is accomplished by the use of an inductively coupled plasma source with a mass spectrometer as a method of separating and detecting the ions. An ICP contains a sufficient concentration of ions and electrons to make the gas

electrically conductive. The resulting detection limits are very low, and they usually range from 1.0-10 µg/L.

2.2.1.1.1 Mechanism

Inductively coupled plasma (ICP) for spectrometry is sustained in a torch that consists of three quartz concentric tubes, the end of this torch is placed inside an induction coil supplied with a radio-frequency electric current. The argon gas will pass in the central channel of ICP (ICP Torch) through the quartz tube and exit from the tip. The tip of the quartz tube is surrounded by induction coils that create a magnetic field at the end of torch with oscillating current generator. The AC current that flows through the coils is at a frequency of about 30 *MHz* and a power level around 2.0 *kW*. The stream of argon gas that passes the coil has been previously seeded with free electrons from a Tesla discharge coil. The magnetic field excites these electrons and they then have sufficient energy to ionize the argon atoms by collision of argon atoms forming argon ions, these ions begin to collide with other atoms of the Argon forming an argondischarge or plasma.The mechanism system of Agilent 7500ce ICP-MS is shows in Fig. 2.3.

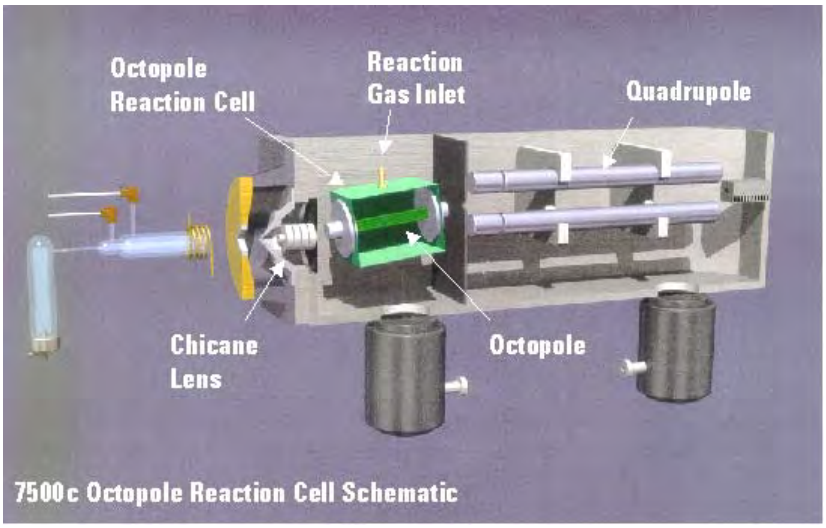

Fig. 2.3 Octopole reaction cell in Agilent 7500ce ICP-MS.

A second flow of argon (around 1.0 liter per minute) is usually introduced between the central tube and the intermediate tube to keep the plasma away from the end of the central tube. The sample entered in the form of liquid or dissolved solid to the nebulizer transformation, in aerosol turned into a gas atom which is ionized to the plasma using nebulizer or atomizer (a spray of small sample droplets carried by a stream of Argon gas).

1. Plasma temperature between 6000 *K* 10000 *K* is considered to be the best source of ions.
2. Ions generated by the ICP is the positive ions (M^{+} or M^{+2})
3. Ions, which are preferably negative, such as F^{-}, I^{-}, Cl^{-}, are very difficult for direct measurement by ICP-MS
4. Detection limit is important, and depends on the type of sample, the amount of sample and interferences

After converted a sample into metal ions, traveling in the argon sample stream at atmospheric pressure (1-2 *torr*) into the low pressure region of the mass spectrometer (<1.0 x 10^{-5} *torr*), and all this through intermediate vacuum created by two faces or cones *(*sampler and skimmer), which is a suppression of the metal disks with a small hole (~ 1.0mm) in the center. The purpose of these cones is to sample the center portion of the ion beam coming from the ICP torch, the shadow stop is to stop the photons coming from the ICP, which have intense light source. Total dissolved solids of samples must not exceed 0.2% because it close the hole of skimmer and samplers which leads to further measurement reduce of the sensitivity of the instrument and performs maintenance on non-periodic or stop the instrument.

For this reasons we need always to dilute of the sample. The ions coming from the skimmer are focused by the suitable electrostatic lenses for the positive ions. The lenses must also be positively charged even for no attraction with metal ions, and sending the ions to the direction of MS. Different types of ICP-MS systems have different types of lens systems. The simple instrument consists of a single lens, while for high resolution the instruments operate with 12.0 lenses. Upon entering the ions to mass spectra they are separated by their mass to charge ratio. The mass-analyzer is usually a quadrupole which separates the ions according to their mass-to-charge-ratio (m/z). The quadrupole consists of 4.0 parallel rods in length between 15-20 cm and 1.0 cm in diameter divided in two pairs in an electrical field [22]. Two opposite rods have an applied potential of (dc voltage +ac voltage) and the other two rods have a potential of -(dc +ac). The applied voltages affect the trajectory of ions traveling down the flight path centered between the four rods. For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole filter and all other ions are thrown out of their original path.

The normal quadrupole provides resolution which is sufficient for most routine applications and research work, but when the resolution is not sufficient the interference may occur during

metal analysis such as estimation of arsenic, calcium, iron and strontium. While the high resolution type called (HR) ICP-MS which is expensive it can be use for remove interference.The **detector** purpose is to detect, amplify and measure the analyte ions passing through the mass spectrometer. The most commonly used type of detector in ICP-MS is an electron multiplier, although in some instruments a photomultiplier tube is used. The most elements can be analyzing by ICP-MS are presented in the Fig. 2.4.

2.2.1.1.2 Spectral Interferences

Spectroscopy interferences are divided into two categories depending on the origin of the interference. Molecular or polyatomic ions may also cause overlapping. The possible sources of these interferences are the precursors in (1) plasma gases, (2) entrained atmospheric gases, (3) water and acids used for dissolution and (4) sample matrix [23]. Argon, oxygen and hydrogen combined with other elements present in sample matrix are thus the basic components of polyatomic ions. The intensities of these species can be reduced by adjusting the instrumental design and operating conditions such as nebulizer gas flow rate, plasma potential, spacing between load coil and sampler cone if the origins of the interferences are due to the plasma and entrained atmospheric gases

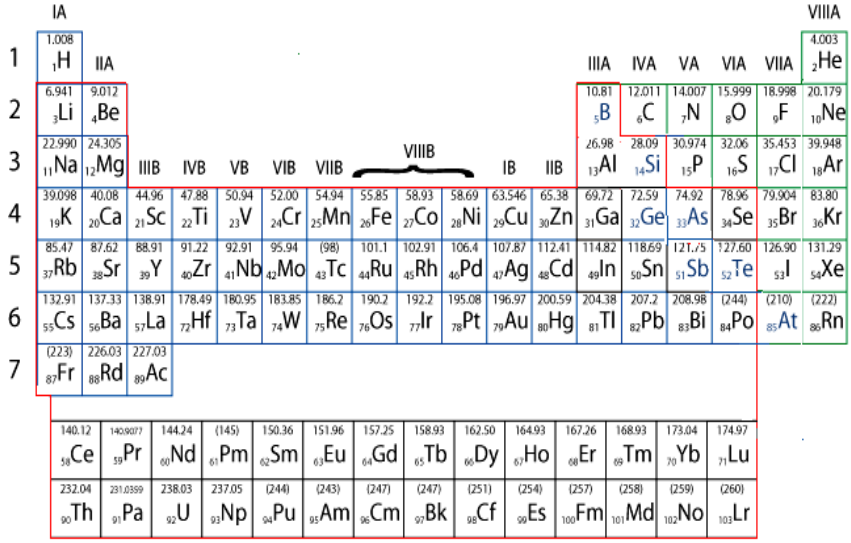

Fig. 2.4 Approximate range of elements that can be analyzed using the 7500ce ICP-MS. Carbon, phosphorous, and sulfur can be analyzed with high sensitivity in specific matrices using GC-ICP-MS.

2.2.1.1.3 Agilent 7500ce ICP-MS

The Agilent 7500ce is a quadrupole ICP-MS with an octopole reaction system for interference reduction and an electron multiplier detector that operates simultaneously in pulse counting and analog modes.

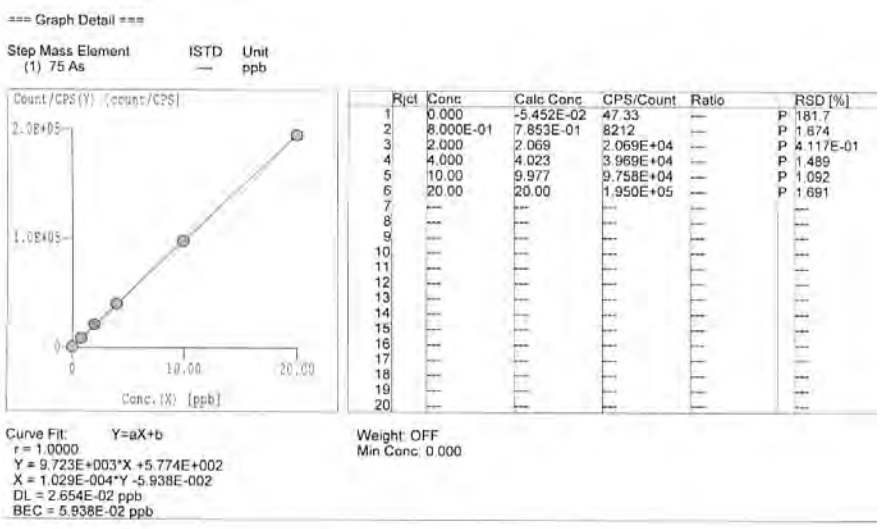

Fig. 2.5 Agilent 7500ce ICP-MS calibration curve used in this study

The instrument is capable for:

1. Trace element concentration for more than 90% of the elements of the periodic table without any interference where the detection limit is less than ppt, depending on each element
2. Isotopic ratios of elements
3. Can be coupled with speciation methods such as gas chromatography and ion chromatography to estimate the metals speciation
4. Provides a very low quantification limit for analysis of the arsenic and the detection limit is less than 0.2 µg/L

Agilent 7500ce is suitable for removal of multiple polyatomic that occurs during the determination of arsenic, selenium, chromium, vanadium and iron.The ICP-MS calibration curve which is used for determination of arsenic in this thesis is presented in the Fig. 2.5.

2.2.1.2 Spectrophotometric Methods

These methods are based on conversion of arsenic to the colored compound [24-30] such as molybdenum blue [31-33], or silver diethyldithiocarbamate [34-36]. While some study based on the reaction of As(III) with potassium iodate in acid medium to liberate iodine, which oxidizes variamine blue to form a violet coloured species [37]. The arsenomolybdate chemistry is highly sensitive but the basic chemistry is sensitive to silicate and more importantly phosphate. Because only As(V) and not As(III) responds to this chemistry, As can be determined by a different method where the reaction is run with and without pre-

reduction of As(V) to As(III); P(V) is not reduced under such conditions. In a sample where As(III) and As(V) both exist, it is possible in principle to run the sample (a) such as, (b) with pre-oxidation, and (c) prereduction. These respectively measure P(V)+As(V), P(V)+As(V)+As(III), and only P(V), from which all three can be calculated. The limitation of obtaining a small number from the difference of two large numbers of course remains. Dhar et al. [31] in which good comparability with a reference method was established for real samples. In this laboratory, the arsenomolybdate chemistry has been used in a different manner to measure As(III), by eluting unretained As(III) from the interstices of an anion exchange resin column, oxidizing it, and carrying out the molybdate chemistry. Total As could be measured only after in-line pre-reduction of the sample [38], making for an undeniably complex arrangement. Another attractive photometric approach is to convert the As to AsH_3 and concentrating the AsH_3 thus liberated into a suitable oxidant receiver such as $KMnO_4$ or triiodide and determining it by direct colorimetry or after the molybdate reaction [39-41]. This approach can be attractive because borohydride based reduction can exploit pH control to generate AsH_3 from all As species or from As(III) alone [42-45]. Recently these two key concepts were exploited to a sensitive, speciation-capable field instrument [46]. However, the issues of large sample volume, difficulties in automating sample handling remained.

2.2.1.3 Electrochemical Methods

The affordability, sensitivity and ease of fabrication of electrochemistry based field deployable instruments are noteworthy, much work has been done in this area. Electrical voltametric where some experiments have very low detection limit [47,48]. The anodic stripping voltammetry (ASV) methods using platinum and gold electrodes [49,50], and cathodic stripping voltammetry (CSV) method using a glassy-carbon electrode [51,52] have been used. Determination of total As is performed by reducing As(V) to As(III) using sodium *meta* bisulfite/sodium thiosulfate reagent, the limits of detection achieved was 0.02 µg/L done by Forsberg et al. [53]. Sadana [51] determined arsenic in drinking water with Cu(II) by differential pulse cathodic stripping voltammetry (DPCSV) using hanging mercury drop electrode (HMDE) as working electrode and Ag/AgCl as reference electrode, the optimized analytical conditions are 0.75M hydrochloric acid, 5.0 ± 1 mg/mL Cu^{2+} concentration and –0.6*V* deposition potential. The detection limit of this method is 1 ng/mL. Gibbon et al. [54] used (CSV), the experimental was study at pH 9.0 for determination of As(III), while As(III)+As(V) detected by square-wave ASV (at pH 1.0), the detection limit was 0.5 nM

with a 60s deposition time, this method is suitable for waters of pH 7.0-12, the analytical range was 0.07-7500 µg/L. Profumo et al. [55] used a (CSV) method for determination of As(III) by forming a copper-arsenic intermetallic at HDME during the preconcentration step. Cu(II) 50 mg/L final concentration, was added to sample. The best results were obtained by using 0.45M HBr as supporting electrolyte.

2.2.1.4 Gutzeit Method

Currently commercially available field assays are all based on the Gutzeit method, developed over 100 years ago. How well these kits work have been passionately discussed. Significant concentrations of arsine are produced and ~50% of this can escape the device. Hydrochloric acid and zinc dust is used to reduce all As species to arsine. Alternatively, $NaBH_4$ is used instead of Zn. To avoid interference from any H_2S produced, the liberated gases first pass through a lead acetate soaked filter. The AsH_3 passes on to an $HgBr_2$ -impregnated filter, turning it yellow to brown, depending on the amount of arsenic present

2.2.2 Analytical methods for the determination of arsenic species in water

2.2.2.1 Speciation of arsenic compounds

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

One of the important points of speciation analysis is to preserve the integrity of the sample and the species of interest during sampling, sample storage and pretreatment, such as dissolution, extraction and preconcentration. Any treatment that would result in a shift of equilibrium or in a destruction or transformation of one species into another must be carefully avoided.

Speciation is furthermore an important tool when investigating the chemicals form and bioavailability of elements where the information of the total element concentration may be insufficient.

IUPAC definitions [56]

1. Chemical species. Chemical elements: Specific form of an element defined as to isotopic
2. Composition, electronic or oxidation state, and/or complex or molecular structure.

3. Speciation analysis. Analytical chemistry, Analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample.
4. Speciation of an element, speciation. Distribution of an element amongst defined chemical species in a system.
5. Fractionation. Process of classification of an analyte or a group of analytes from a certain sample according to physical (e.g. size, solubility) or chemical (e.g. bonding, reactivity) properties.
Selectivity and sensitivity are two important factors for a successful speciation analysis. These two issues can be achieved using on-line coupling of chromatographic or electrophoresis technique with an element selective detector (atomic absorption, emission, fluorescence, or mass spectrometry, inductively coupled plasma. or microwave induced plasma.

Arsenic species can be readily transformed by such events as biological activity, changes in redox potential, or pH. Speciation analysis of arsenic usually requires the coupling of proper sample preparation with two analytical techniques: first a technique to separate the chemical forms of arsenic and second a sensitive detection. In order to Speciation and measure different arsenic species numerous analytical methods of separation and detection have been proposed it becomes necessary to provide a careful definition of the word species in this context. Chemical compounds that differ in isotopic composition, conformation, oxidation or electronic state, or in the nature of their complexed or covalently bound substituents, can be regarded as distinct chemical species.
Separation science is the most important an analytical technique science used in speciation of arsenic, it depends on the extraction and separation of compounds to get pure component can be estimated easily without interference. Separating the components in a substance is usually one of the first steps in identifying its components. All mixtures can be separated and identified by the distinguishing chemical or physical properties of the components. The separation technique chosen depends on the type of mixture (anion, cation, polar and nonpolar, act…) and its characteristics. After a mixture is separated the components can easily determine without interference. Researchers can match the properties of the unknown substance to those properties of a known substance. Separation has been simply defined as a method in which a mixture is divided into at least two components having different compositions, or two molecules with the same composition but different stereo chemical structure [57]. After the separation and preconcentration the component is transferred to the

(instrumentation, voltametric, gravimetric act) analysis for the detection and determine the concentration.

A number of methods can be used for separation of particles. These methods are often referred to as mechanical separation processes. A well-known example is screening, or elutriation, where particles are separated according to the size and shape. The most methods that can be used for separation of component are, precipitation, crystallization, sedimentation, centrifugation, extraction, adsorption, ion exchange, diffusion, and thermal diffusion, chromatography [57]. The separation science plays an important role in chemical analysis for:

- Removal of the interference which is affecting the analytical procedure
- Isolative the unknown component to select and analyze
- Determination and analysis of complexes in different samples

The Simple component can be easily separated and measured, but for some of the complexes compounds, physical and chemical separation is difficult and hence choosing the appropriate method depends on the type and complexity and quantity of the sample

2.2.2.2 Hydride Generation atomic absorption/Atomic fluorescence spectroscopy

Formation of the hydrides of antimony, arsenic, bismuth, germanium, lead, selenium, tellurium and tin by reaction with sodium tetrahydroborate affords an excellent method for the separation of these elements as gases from a wide range of matrices. Excellent low limits of detection are attained when this separation method is combined with atomization of the hydride in a heated quartz tube in the optical axis of a conventional atomic absorption spectrometer but there are many interferences to contend with both at the hydride generation stage and in the atomization process.

Hydride generation was first used as sample introduction technique in atomic spectrometry [58] for determines arsenic; Braman et al. [59] used sodium tetrahydroborate as reductant for the generation of arsine in 1972. In 1978 Thompson and coworkers used ICP-AES for determination of arsenic, antimony, bismuth, selenium and tellurium, with their hydrides being generated in the reaction with $NaBH_4$ in a continuous flow-reaction system then from 1978 [60]. (HG) methods involve four successive steps depending on the technique used:

- The hydride is generated by chemical reaction between the sample and reducing agent
- Hydride that formed is collected in a reaction batch.
- hydride is entrained in a gas stream into the atomizer

- The hydride atomizer to form atomic vapor, absorption and the results can be obtained [61,62].

To increase the signal it is important that, the rapidly produce of hydride gas, collection and transferred to atomizer as possible. For determination of arsenic: with As(III) as the analyte and $NaBH_4$ as the reductant:

$$3BH^-_4 + 3H^+ + 4H_3AsO_3 \longrightarrow 3H_3BO_3 + 4AsH_3 + 3H_2O \qquad (2.1)$$

The standard methods approved detection methods are all based on atomic spectrometry hydride generation [63-65], which connected with some detector such as atomic fluorescence spectrometry (AFS) or atomic absorption (AAS) [66,67]. The most important disadvantage of the technique for arsenic determination is the requirement for pre-concentration in order to increase sensitivity. In this technique the As(V) and As(III) must be converted (reduced) to arsine AsH_3. A mixture of sodium borohydride $NaBH_4$ and HCl are employed as reducing agents to generate AsH_3 from [68,69]. As(V) is first reduced to As(III) followed by convert to AsH_3. The reduction reagents $NaBH_4$ and KBH_4 have proved to be exceptionally reliable reagents for the conversion of the sample to volatile forms [70]. Generally l-cysteine has proved to be very useful for preventing iron interferences, which are commonly present at high concentration in many types of samples. Atomic spectrometry can readily provide detection limits in the sub-µg/L range and although better methods of sample preservation have been developed [71]. Subsequent As oxidation state speciation in the laboratory is often questioned [72,73]. HG technique has been advocated as the best value in terms of the cost/performance ratio [74].

The AAS and AFS are the most important previous techniques for determination of arsenic species after obtaining the AsH_3. The hydride generation procedure can be also used for differential determination of As(III) and As(V) based on the fact that As(III) reacts with tetrahydroborate at a higher pH than As(V).

Whereby sodium or potassium tetrahydroborate is used as reduction reagent for arsine, AsH_3 production As(III) and As(V) give AsH_3, MMAs(V) ($CH_3AsO(OH)_2$), gives (CH_3AsH_2), DMAs(V) ($(CH_3)_2AsO(OH)$) gives ($(CH_3)_2AsH$). The formation of arsines is pH dependent. This indicates that arsenic species must be fully protonated before reduction to corresponding arsine so As(III) reacts with tetrahydroborate at a higher pH than As (V). The procedure can be used for differential determination of As (III) and As(V). One of the main basic advantages on hydride generation methods is that, it provides the chemical reaction between metals and

reducing agent without matrix interference, efficient, low detection limit used in determining the inorganic and organic arsenic.

- Interference in Chemical Hydride Generation

The Interferences effects of inorganic compounds are the main problem for hydride generation of pure MH_3 by $NaBH_4$ in the sample. That interference by inorganic compound is divided into three groups

- There is a strong oxidizer,
- Ions of heavy metals and noble gases,
- Other species including ions of other hydride forming elements.

Three mechanisms have been suggested to explain the effects of these elements: tetrahydroborate depletion; formation of insoluble species between the interferent ion and the analyte after the hydride has formed; and decomposition of hydrides on metal borides, or on colloidal metals formed by the reduction of the interferent ion [75]. The main interference effect is tetrahydroborate depletion mechanism based on the competition between interference ions and the analyte for reduction by tetrahydroborate and it was first suggested by Pierce et al. [76]. Meyer et al. [77] suggested the formation of insoluble species between the interferent ion and the hydride. Welz et al. [78] proposed that this mechanism was overwhelmed by the decomposition of hydrides on colloidal metals and this decomposition was effective at lower interferent ion concentrations. Smith [79] proposed that the interferences in chemical hydride generation were based on the reduction of the interferent ion to its metallic form and the co-precipitation of the analyte or adsorption and decomposition of the hydride formed.

Several studies and researches conducted for determination of arsenic using hydride generation AAS/AFS. Yano et al. [80] determined arsenic species in drinking water by three methods using HG-AAS. The first method based without any pre-reduction, second method was based on the microwave reduction of As(V) by 10% of KI and the third method involves microwave digestion for mineralizing of organic arsenic used NaOH and $K_2S_2O_3$. The good results were obtained for determination of As(III), also for determination of As(V) after it is reduced to As(III), while organic arsenic species were determined quantitatively by the third method. Nielsen et al. [81]. In this study a volume-based flow injection (FI) procedure is described for the determination and speciation of trace inorganic arsenic, As(III) and As(V), via hydride generation-atomic absorption spectrometry of As(III).The determined the As(III) and As(V), via (HG-AAS) as As(III). The determination of total arsenic is obtained by on-line reduction of As(V) to As(III) by means of 0.50% (w/v) ascorbic acid and 1.0% (w/v) potassium iodide in 4.0M HCI. The combined sample and reduction solution is initially

heated by flowing through a knotted reactor immersed in a heated, oil bath at 140°C, The injected sample volume was 100 µL. while the total sample consumption per assay was 1.33 mL. The detection limit for the on-line reduction procedure was 37 ng/L and at the 5.0 pg/L. Leal et al. [70] used MSFIA (multi-syringes flow injection analysis) connected with (HG-AFS). The method based on used four syringes equipped with a three-way solenoid commutation valve on each head. Syringe S1 contained 6.0% hydrochloric acid valve E1, S2 contained the 0.2% $NaBH_4$. Controlled valve E2, S3 contained pre-reduction solution (10% KI, 0.2% ascorbic acid) valves E3 and S4 were used as loading samples with valve E4 as a dispense sample. Opened and closed valves depend on the progress of determination of arsenic; the detection limit of the proposed technique was 0.05 µg/L.

2.2.2.3 Chromatography methods

Chromatography is a common name for several separation methods in chemical analysis based by distribute the components between two phases, one of which does not move (stationary phase) and the other that moves (mobile phase). The process used to separate molecules based on physical/chemical separation techniques of the ions or molecule mass, charge, affinity for ligands or substrates and hydrophobic interactions. The discovery of chromatography is attributed to Tswett, who in 1903 was the first to separate leaf pigments on a polar solid phase and to interpret this process

- Chromatography can separate the very low concentrations of ions of small volume and give the high sensitivity results such as arsenic species [14,17,20,82]
- Chromatography can separate soluble and volatile compounds easily by choosing the experimental condition of adsorbent material and the mobil phase.
- Chromatography is used to separate the pigments and colors components
- Chromatography can separate complex compounds, such as proteins (amino acid) simply with purity separation and high precision
- Chromatography costs are not high and it does not need to large and complex equipment [14,17,18].

Various modes of chromatography have been use in the development research, where the column chromatography first discovered by [83]. Liquid chromatography is similar to liquid–liquid extraction, where two phases are liquids. The extraction process can be explained as follows: when two liquids are shaken together to achieve an extraction of a component of

interest in a separator funnel, the sample proportionate itself into the two phases based on its distribution coefficient:

$$\text{Distribution cofficient K} = \frac{\text{Concentration of sample in phase 1}}{\text{Concentration of sample in phase 2}} \qquad (2.2)$$

The stationary phase in chromatography is similar in function to the raffinate in extraction and the mobile phase is equivalent to the extractant. Then the chromatography is the general term for a broad range of physical/chemical separation techniques, which depend on the distribution of a substance between a mobile and a stationary phase. Chromatographic techniques are classified by the aggregate state of both phases.

2.2.2.3.1 The most common chromatography methods

There are different forms of chromatography, they are all based on the principle that the compounds separated are dispersed between two phases; one of them is mobile while the other is stationary. In Table 2.3 and 2.4, the most common chromatographic methods are reviewed.

Table 2.3 A review of the most common chromatographic methods

Gas Liquid chromatography
Analytical scientific technique to separate a volatile mixture components of a very small sample and to determine the amount of each component in the sample by using suitable detection methods. The stationary phase is a nonvolatile liquid coated onto a porous support or onto the walls of a capillary column. The mobile phase is an inert carrier gas, for example, helium and argon. The separation process depends on the vapor pressure of each component in the sample. The component, which has a high vapor pressure delayed exit from the column. This depends a mainly on the molecular weight of the component.. The sample is detected by nondestructive detectors such as thermal conductivity or destructive detectors, as exemplified by the flame ionization detector.
Liquid–liquid chromatography
Liquid-liquid chromatography is a chromatography separation technique in which the mobile phase is a liquid usually a solvent (hexane) or a simple binary mixture of solvent (polar and nonpolar) and the stationary phase is also a liquid (must insoluble in the liquid mobile phase). The liquid stationary phase is supported on some suitable material such as a silica gel. The system is inherently unstable, as the stationary phase will always have some solubility in mobile phase and, as a consequence, will eventually be stripped from the support. Thin Layer chromatography and column chromatography is similar to partition chromatography only that the stationary phase has been replaced with a bonded rigid silica or silica based component onto the inside of the column.. The analytes that are in the mobile phase that have an affinity for the stationary phase will be adsorbed onto it and those that do not will pass through having shorter retention times. Both normal and reverse phases of this method are applicable can be used in this type of chromatography the stationary phase in the form of granules of resin as in HPLC [84].

Table 2.4 The most common chromatographic methods related to the mechanism

Partition Chromatography
This form of chromatography is based on a thin film formed on the surface of a solid support by a liquid stationary phase. Solute equilibriates between the mobile phase and the stationary liquid, analyte interacts with mobile and stationary phase, differential interaction leads to selectivity. Interactions are: Proton accepting ability, Dipole interaction, Proton Donor, e- pair donating ability, Van der Waals dispersion forces.
Size Exclusion Chromatography
Exclusion relates to separation based on the size of the molecule in the sample. An exclusion mode of chromatographic separation does not allow the sample to enter the stationary phase based on size or shape. The liquid or gaseous phase passes through a porous gel which separates the molecules according to its size. Large molecules unretained, in the column and the small molecules retained. The medium size will differentiate be a time of retaining within the column between large size and small size.
Affinity Chromatography
Affinity chromatography involves the use of ligands that attach to the media and that have binding affinity to specific molecules or a class of molecules. Ligands can be bio-molecules, like protein ligands or can be synthetic molecules. Both types of ligand tend to have good specificity. But protein ligands have the disadvantage that they are expensive and mostly denature with the use of cleaning solutions, whereas synthetic ligands are less expensive and more stable.

2.2.2.3.2 Ion exchange chromatography

Ion exchange resins are widely used in the field of analytical chemistry and their quality (chromatographic techniques). Ion-exchange would provide a powerful analytical tool by separates and preconcentration compounds such as arsenic species [85,86], based on net surface charge [17,20]. Molecules are classified as either anions (having a negative charge) or cations (having a positive charge) [87]. Many study research have been written on the analytical applications of ion-exchange [88,89]. The many papers have now been published

on specific application, all the paper are based on the use of a column through witch a solution of the substance being analyzed is based [85].

Ion exchange resins are commonly divided to cation exchange chromatography and anion exchange (Muromac® 2×8, 100–200 mesh in Cl-form) [20], depending on the functional group of stationary phase. Anion exchangers can be classified as either weak or strong. The charge group on a weak anion exchanger is a weak base, which becomes deprotonated and, therefore, loses its charge at high pH. DEAE-cellulose (Diethylaminoethyl cellulose) is an example of a weak anion exchanger, where the amino group can be positively charged below pH ~ 9.0 and gradually loses its charge at higher pH values. A strong anion exchanger it is a strong base, which remains positively charged throughout the pH range normally used for ion exchange chromatography (pH 1.0-14) such as M500 resin witch loaded with chloride can be used for many analytical application [17].

Cation exchangers can also be classified as weak or strong. A strong cation exchanger contains a strong acid (such as a sulfopropyl group) that remains charged from pH 1.0–14, whereas a weak cation exchanger contains a weak acid (such as a carboxymethyl group), which gradually loses its charge as the pH decreases below 4.0 or 5.0.

To optimize binding of all charged molecules, the mobile phase is generally a low to medium conductivity (i.e., low to medium salt concentration) solution. The adsorption of the molecules to the solid support is driven by the ionic interaction between the oppositely charged ionic groups in the sample molecule and in the functional ligand on the support. The strength of the interaction is determined by the number and location of the charges on the molecule and on the functional group. By increasing the salt concentration (generally by using a linear salt gradient) the molecules with the weakest ionic interactions start to elute from the column first. Molecules that have a stronger ionic interaction require a higher salt concentration and elute later in the gradient. The binding capacities of ion exchange resins are generally quite high. This is of major importance in process scale chromatography, but is not critical for analytical scale separations.

The stationary phase consists of a substrate such as a polystyrene-divinylbenzene polymer or silica which has an ionic functional group such as quaternary ammonium or sulfonate. Ion exchange chromatography is compatible with element selective detectors such as an ICP-MS [17]. Also can be utilized for the purpose of sample cleanup prior to analysis and sample preconcentration [17]. For ion chromatography, the packing material used in the column mostly consists of organic polymers, because they are stable over a large pH range. The used

resin bears a functional group with a fixed charge. Each functional group is closely accompanied by the respective counter ion from the eluant, therefore the group appears neutral to the outside. For anion exchange chromatography, the exchange function of the resin is a quaternary ammonium group. Anion-exchange chromatography can separate inorganic and organic arsenic mono- and di-methylated species, which have an anionic character. Other organic species, such as (AsC), (TMAO) and ($TMAs^{+}$) are neutral or cationic, and may also have hydrophobic properties due to their alkyl group, they should be separated by cation-exchange or reversed-phase chromatography. The coupling of liquid chromatography with inductively coupled plasma mass spectrometry (HPLC–ICP-MS) and hydride generation atomic fluorescence spectrometry (HG-AAS/AFS) are the most highly-recommended techniques for speciation and total As determination, respectively.

The choose of resin for separate the arsenic species needs the particular specifications such as to provide a good capacity, and not to affect with acidity of the sample such as Lewatit Mono Plus M500. The following reversible equilibrium processes take place:

$$R_2 — HAsO_4 + 2Cl + 2H^+ \rightleftharpoons 2R — Cl + H_3AsO_4 \qquad (2.3)$$

Several studies developed an useful method for the preparation of the functional resins (selective resin) for the separation /preconcentration and determination of arsenic species in solution samples such as water, by a simple modification of ion-exchange resin with appropriate reagents [17,20,82]

$$4Fe^{2+}(aq) + O_2 + 10H_2O \rightleftharpoons 4Fe(OH)_3(s) + 8H^+ \qquad (2.4)$$

$$FeOH^+ + HAsO_4^{2-} \longrightarrow FeOH^+ \text{------} HAsO_4^{2-} \qquad (2.5)$$

2.2.2.3.3 Classic column chromatography

The classic column chromatography is used widely as selective analytical method in most laboratories introduced by Tswett in 1906. Glass columns with inner diameter of 1.0 to 5.0cm and a length of 50 to 500cm were applied. In our work we used 2.0cm diameter and a 20cm length [13,17,18]. The basis of chromatography is a liquid mobile phase to separate very low concentration of component such as arsenic [17,20]. This technique is inexpensive procedure in chemical analysis and provides a highly efficient separation and determination of very low concentrations of the arsenic and other component [90].

Some researchers achieved speciation of arsenic by the principle of ion chromatography and complexmetric sorption. Calzada et al. [91] proposed the use of the alga *Chlorella vulgaris* for the separation of As(III) from the other arsenic species, the arsenic concentration was determined by HG-AAS. Koh et al. [92] bonded *Saccharomyces cerevisiae* onto the controlled pore glass covalently, which showed selective preconcentration of As(V) over As(III), the effluent was directly connected to HG-ICP-AES. The optimum pH for the retained arsenic at the column was pH 7.0. As(V) and As(III) were completely separated in a few minutes with the flow rate of 1.5 ml/min, 3.0M nitric acid was adequate for the elution of As(V). Jitmanee et al. [20] developed for the simultaneous pre-concentration and determination of As(III) and As(V) in freshwater samples, two mini columns with a solid phase anion exchange resin Muromac® 2×8, 100–200 mesh in Cl-form placed on two 6.0 way valves were utilized for the solid-phase collection/concentration of As(III) and As(V) respectively by controlled the pH value the As(III) could be retained on the column after its oxidation to As(V) species by used $KMnO_4$, the ICP-AES was used as detection equipment, the limit of detection for both As(III) and As(V) were 0.1 µg/L. Pantsar-Kallio et al. [86] proposed a new method for separation and determination of As(III) and As(V) in water sample using Ion exchange-ICP-MS and the method can also be used for determination the DMAs(V) and MMAs(V), as well as the sum of AB arsenic species present in the water sample, the detection limits are 0.4–0.5 mg/L. In Fig. 2.6 a scheme of using classic column chromatography for separation of arsenic species is presented.

Yalçin and Le [87] used and tested the retention and elution characteristics of different sorbent materials for As(III), As(V), MMAs(V) and DMAs(V). The authors reported that alumina retained all four arsenic species, whereas strong cation exchange resin was used for DMAs(V) eluted with 1.0M HCl and a silica-based anion exchanger was used for MMAs(V) and As(V) while MMAs(V) was eluted with 60 mM acetic acid and As(V) was eluted with 1.0M HCl. As(III) remained in solution. Flow injection hydride generation atomic fluorescence spectrometry (FI-HG-AFS) and hydride generation atomic absorption spectrometry (HG-AAS) were used as detector.

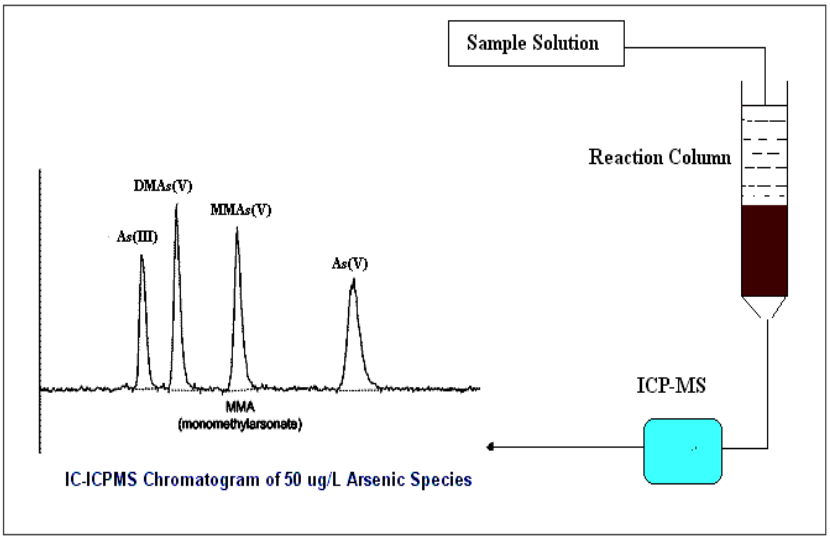

Fig. 2.6 Scheme for separation arsenic species using classic column chromatography

Simon et al. [85] described an on-line decomposition method based on UV photooxidation for the analysis of organoarsenic species by coupling cation exchange chromatography and atomic fluorescence spectrometry with hydride generation. In this study, aqueous pyridine solutions were used as mobile phase and fully compatible solutions, such as potassium nitrate, nitric acid and sodium hydroxide solutions were used in order to reduce the inhibition of signal by mobile phase.

2.2.2.3.4 Solid phase extraction

In solid-phase-extraction (SPE), the sample is solved in liquid and loaded on a column with a solid phase (sorbent). The analytes interact with the sorbent and the liquid depending on the interactions; the analytes are either retained in the column or eluted with the liquid phase [93]. The sorbent is usually made of silica, where functional groups are attached to optimize the interactions with the analytes. Different functional groups can be chosen according to the properties of the analytes

There are 4 different types of solid phase extractions:

1. Reversed phase extraction, extract non-polar analytes from a water-based solution.
2. Ion-exchange extraction, extract ionic analytes from a water-based solution.
3. Normal phase extraction, extract polar analytes from an organic solution.
4. Mixed-mode extraction, extract analytes with both hydrophobic and ionic properties.

Speciation methods include solid-phase extraction (SPE) [94-98] with strong cation- and anion exchange columns or with electrophoresis. Other packing materials commonly utilized

include hydrocarbons mixed-mode and various non-polar silica beads. SPE is also used for pre-concentration of certain species of arsenic that could be retained in the columns and provides high accuracy of separation of arsenic species before measurement by some detector.

C. Yu et al. [99] studied the determination of arsenic species at different pH value, the authors found that, at pH 5.6 the various species of arsenic have with different charges, and the percentage of arsenic retained in the columns is higher for most species studied, compared with pH 2.0, 3.5 and 9.0. AsC and $TMAs^+$ are cations and can be retained in cyanopropyl (CN), ethylbenzene sulfonic acid (SCX-3), propylcarboxylic acid (CBA), and mixed-mode (MM, containing C18, $–SO_3$ - and –NR3 +) cartridges. In addition, AC was also retained on primary secondary amine (PSA) cartridges. As(V) and MMAs(V) which are anionic species, and were fully retained on the strong anion-exchange column (SAX, also known as quaternary amine) and hydrophobic and anion exchange column (HAX, composed of C8 and –NR3 +) cartridges containing SAX sorbent and also the M-M cartridge. In addition, As(V) has very strong acidity relative to MMAs(V), and therefore it was completely retained on PSA and aminopropyl (NH_2) cartridges which are weaker anion-exchange columns. Arsenobetaine was completely retained on both the SCX-3 and M-M columns while SCX-3 was the only column that retained DMAs(V) strongly. Chen et al. [90] used micro-column packed with 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTS) modified ordered mesoporous silica, the As(V) was retained in the column, eluted by 1.0 mol/L HCl and estimated by ICP-OES, the total arsenic was estimated after oxidizing As(III) to As(V) by 50 µmol/L of $KMnO_4$ for 10 minutes. Xiong et al. [100] used microcolumn on-line coupled with (ICP-OES), trace amounts of As(V) species was separated and preconcentrated from total As at pH 6.5 by a conical microcolumn packed with cetyltrimethylammonium bromide (CTAB)-modified alkyl silica sorbent in the absence of chelating reagent. The species adsorbed by CTAB-modified alkyl silica sorbent were quantitatively desorbed with 1.0 mol/L HNO_3. Total inorganic arsenic was extracted after oxidation of As(III) to As(V) with $KMnO_4$. The assay of As(III) was based on subtracting As(V) from total arsenic. The limits of detection were 0.15 µg/L for As(V), the calibration graphs of the method for As(V) was linear in the range of 0.5–1000.0 µg/L with a correlation coefficient of 0.9936. Hsieh et al. [82] determined the As(III) by formed complex with 2,3-dimercaptopropane-1-sulfonate (As(III)-DNPS) in ammonium acetate buffer at pH 5.0 -5.5, the complex was selectivity retained on the Sep-Pak C_{18} cartridges and then eluted with methanol, after addition of Ni^{2+} (2.0 mg), a portion 20 µL was introduced into (GF-AAS). The L-cysteine used in this study as pre-

reduction As(V) to As(III). The experiment quantitatively determination of the As(III), and it calculated As(V) by difference between total arsenic and As(III). Shemirani et al. [101] described A new approach for developing a cloud point extraction-electrothermal atomic absorption spectrometry for determination of arsenic. The method is based on phase separation phenomenon of non-ionic surfactants in aqueous solutions, after reaction of As(V) with molybdate towards a yellow heteropoly acid complex in sulfuric acid and increasing the temperature to 55°C, analytes are quantitatively extracted to the non-ionic surfactant-rich phase (Triton X-114) after centrifugation. An amount of 20 µL of this solution plus 10 µL of 0.1% $Pd(NO_3)_2$ were injected into the graphite tube and the analyte determined by electrothermal atomic absorption spectrometry. Total inorganic was extracted similarly after oxidation of As(III) to As(V) with $KMnO_4$.

2.2.2.3.5 High performance liquid chromatography (HPLC)

High performance liquid chromatography/Ion chromatography is considered to be an indispensable tool in a modern analytical laboratory. Complex mixtures of organic, protein, anions or cations can usually be separated and quantitative amounts of the individual ions can be measured in a relatively short time. Higher concentrations of sample ions may require some dilution of the sample before introduction into the "HPLC ion chromatographic instrument". Ion chromatography (IC) can be classified as a liquid chromatographic method, in which a liquid permeates through a porous solid stationary phase and elutes the solutes into a flow-through detector

Instrument component

Structure of a (HPLC/IC) unit is simply shown in Fig. 2.7

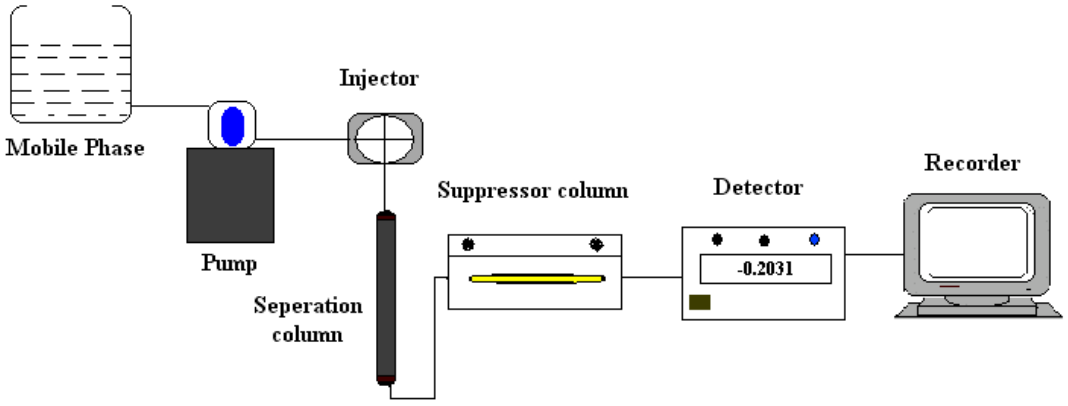

Fig. 2.7 Ion analysis (HPLC) components

– The column is packed with (stationary phase), on the surface of particles of the solid so as to reduce the corridors of diffusion and move through the middle static, and this of course increases the speed of the separation process. It has been possible using this method load among the static in the form of a thin layer of material gel silica or ion-exchanger such as a polystyrene-divinylbenzene polymer or silica which has an ionic functional group such as quaternary ammonium or sulfonate.

– The Use of the short columns (10- 25cm) has been proven that the higher efficiency and capacity of the largest community of static corticosteroids, the basis of this instrument (method) is how to select the column, which will provide the quantified separation without any interference effect , while sometimes needs to select more than one separation column for the sample (Cation and Anion) , Example for separation of arsenic species at the pH values less than 7.0 the DMAs(V) in the cation form [102], while the As(V) and MMAs(V) are in the anion form, the choice of column separation is very important, some column were used for separation arsenic species such as, Hamilton PRP-X100 anion-exchange column [103], Shiseido Capcell Pak C_{18} [104], Agilent introduced a G3288-8000, 4.6 x 250mm plus G3154-65002 Guard [105] and anion-exchange column (Ion Pac AS 7, Dionex) [106]. Ions in solution can be detected by measuring the conductivity of the solution. In ion chromatography the mobile phase contains ions that create background conductivity making it difficult to measure the conductivity due only to the analyte ions as they exit the column. This problem can be greatly reduced by selectively removing the mobile phase ions after the analytical column and before the detector. This is done by converting the mobile phase ions to a neutral form or removing them with an eluent suppressor which consists of an ion-exchange column or membrane. The mobile phase is often HCl, HNO_3, HCO_3^{2-}, sodium acetate and sodium nitrate which can be neutralized by an eluent suppressor that supplies OH^-. The Cl^- or NO_3^- is either retained or removed by the suppressor column or membrane. The same principle holds for anion analysis, the mobile phase is often NaOH or $NaHCO_3$, and the eluent suppressor supplies H^+ to neutralize the anion and retain or remove the Na^+.

Ion-exchange chromatography is the most extensively used type of chromatography separates arsenic compounds based on charge. Anion exchange resins designed to separate negatively charged arsenic compounds, and cation resins designed to separate positively charged arsenic compounds. In order to separate arsenic species anions and cations in a single run, a column switching system involving a combination of anion-exchange and reversed-phase separation has been developed as a major component of (HPLC) instrument. The charge of the arsenic compound is controlled by the pH of the mobile phase passing through the column [107].

High performance liquid chromatography (HPLC) has been the preferred a separation technique for arsenic speciation. Majority of the papers published on arsenic speciation in the past few years used (HPLC) as the basis of separating the species [108], this is usually coupled with mass spectra detector [109,110], (HG) [111], sensitive optical spectroscopic detection system such as (AFS) [112], (AAS) [113,114], (ICP-MS) [115], ion-pair reversed-phase chromatography (IP-RP-HPLC) [116,117], and (IE-HPLC) [118,119]. That most studies agree with the use of HPLC which provided high efficiency of separation for very low concentration of the arsenic species, many of researchers agreed to couple (HPLC) with (ICP-MS) for measurement.

HPLC-ICP (MS / OES)

Xie et al. [120] developed a sensitive new method for the determination of seven inorganic and organic arsenic species in human urine using ion exchange chromatography combined with inductively coupled plasma mass spectrometry**.** As(III), As(V), MMAs(V) and DMAs(V), were selectively separated by an anion exchange column using sodium hydroxide gradient elution, while MMAs(III), DMAs(III) and AsB were separated by a cation exchange column using 70mM nitric acid as the mobile phase. In this study high repeatability and low detection limits 0.10–0.75 ng/mL were achieved. Vassileva et al. [121] used (IC-ICP-MS) for separation and determination As(III)), As(V), MMAs(V), DMAs(V) and AsB, the proposed method has been successfully applied to the analysis of groundwater and extracts of contaminated soils. No interference of ^{40}Ar, ^{35}Cl and ^{75}As was observed when natural water samples were analyzed; the detection limits for the arsenic species are in the range 0.4–0.8 µg/L. Pizarro et al. [122] in this study arsenic species were quantified by (HPLC), (anionic and cationic chromatographic column) coupled to (ICP-MS), the As(III), As(V), MMAs(V) and DMAs(V) was quantified measured in rice and soil whereas AsB, DMAs(V) and an unknown arsenic species were quantified in chicken tissue. AsB (major component) and one non-identified arsenic species were quantified in fish tissue. Demesmay et al. [123] used an (ICP-MS) detector coupled to an (HPLC) system for determine of As(III), As(V), MMAs(V), DMAs(V), AsB and AsC, by used an anion-exchange column with a mobile phase of phosphate buffer with 2.0% acetonitrile. Morita et al. [124] used (HPLC) to separate mixtures of arsenic compounds on anion and cation exchange columns using phosphate buffer. The ICP is used as a selective detector by observing As emissions at 193.6 nm. The detection limit was 2.6 ng. In Fig. 2.8 scheme of the general process of separation by using HPLC technique is presented.

HPLC-HG-AAS / AFS

Lopez et al. [126] used an anion column with 17 mM phosphate at pH 6.0 as the mobile phase. The effluent of the (HPLC) was merged with a persulphate stream before entering the thermo-reactor consisting of a loop of PTFE tubing dipped in a powdered-graphite oven heated to 140°C. After cooling in ice-bath, hydrochloric acid and sodium borohydride are added on-line to generate the arsine. Coelho et al. [127] determined of As(III), DMAs(V), MMAs(V) and As(V) in beers by (HPLC-HG-AAS/AFS). Arsenic species were separated by anion-exchange chromatography with isocratic elution using KH_2PO_4/K_2HPO_4 as mobile phase.

The Solution of sodium tetrahydroborate 4.0% (m/v) and 2.0 mol/L hydrochloric acid were used, the detection limit was found to be 0.12, 0.20, 0.27 and 0.39 µg/L for As(III), DMAs(V), MMAs(V) and As(V), respectively.

The main problem with (HPLC) technique is that it is expensive and it is not available in every laboratory. Fig. 2.8 shows the coupled HPLC and ICP-MS used for determination of arsenic species.

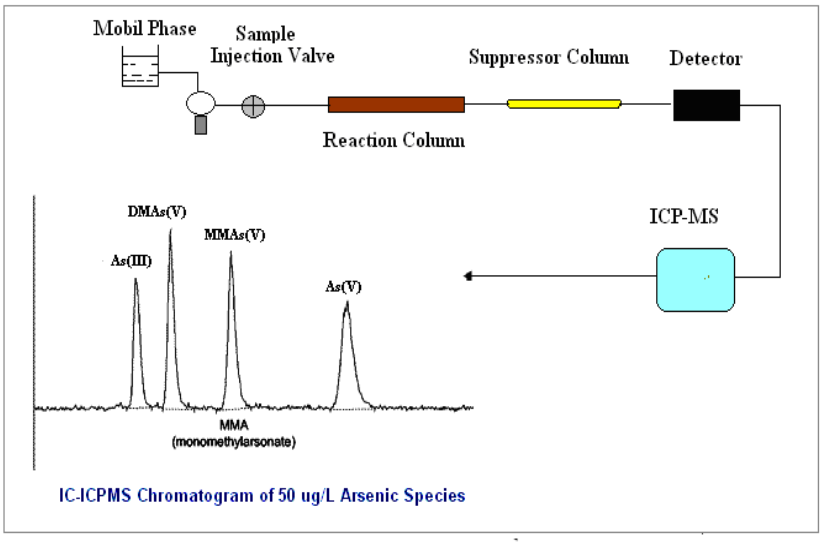

Fig. 2.8 Scheme of separation and determination of arsenic species by using HPLC System

2.2.3 Analytical methods for the preconcentration of arsenic species from water

The researchers focused their research in order to obtain pure substances and ions easy direct and with high percentage recovery without interference. Several methods techniques can be applied for separation the components and preconcentration of ions such as arsenic [125], which resides at very low concentrations in samples. Some of the most preconcentration

methods are: evaporation, recovery of trace components by solvent extraction filtration or centrifugation or sorption methods. The eluent used to elute the ions from the preconcentration column to the analytical column usually does not interfere with the separation process. This approach is widely used as [20] because it is simple, provides enrichment factors, and is easy to automate and operate. There have been very few studies involving preconcentration ion chromatography techniques [128], able to detect ng/L concentrations of anions and cations in 20-130 mL of high-purity water through the application of a preconcentration ion chromatography technique.

Table 2.5 A review of some procedure for (Extraction / Separation) of arsenic speciation

Reference	**Reagent**	**Method of separation**	**Method of Detection**
B. Issa et al. [14]	HY-Ag-Cl	Reaction	,,
B. Issa et al. [17]	SBAE	Ion Exchange	ICP-MS
B. Issa et al. [18]	HY-Fe	Reaction	,,
Jitmanee et al. [20]	Anion. Exc.	,,	,,
Dhara et al. [31]	AM	,,	,,
Sandhu et al. [35]	SDDC	Extraction	UV.Vis
Chatterjee [36]	AgDDTC/$CHCl_3$	,,	,,
Shemiran et al. [101]	molybdate/ Triton-Cp	,,	,,
S. Chen et al. [95]	APDC /CNFs	Solid Phase Extraction	ICP-MS
Anthemidis et al.[93]	APDC	,,	HG-AAS
Chen et al. [90]	APTS	,,	ICP-OES
Hsieh et al. [82]	DMPS/Sep-Pak C_{18} cartridges	,,	GF-AAS
Zhang et al. [94]	Eggshell	,,	HG-AFS
H. Wu et al. [96]	APDC / SWCNTs	,,	HG-DC-AFS
Staniszewski [97]	Silica gel	,,	TXRF
Xiong et al. [100]	CTAB	,,	,,
Rahman et al. [102]	MRT	,,	GF-AAS

Note: APDC: Ammonium pyrrolidinedithiocamate, CNFs: Carbon nanofibers, DNPS: 2,3-dimercaptopropane-1-sulfonate, APTS: 3-(2-aminoethylamino)propyltrimethoxysilane, CTAB: Cetyltrimethylammonium bromide (coated with silica), DDTC: Diethyldithiocarbamate, SBAR: Strong base anion resin, Hy-Fe: Iron hybride resin, Hy-AgCl: Silver resin, AM:,Ammonium molybdate, Triton-Cp : Non ionic surfactants, SWCNTs: single-walled carbon nanotubes, MRT: Polymeric organic materials-ion –selective, TXRF; Total reflection X-Ray fluorescence

Arsenic sometimes presents in more than two oxidation states and in the form of different chemical species. Often need to estimate one species and do not want to estimate the other species, in this case can use preconcentration technique to provide highly efficient in preconcentration obtaining, one ion species or ions to be analyzed only the exclusion of the others. Must obtain a pure quantity so can be estimated easily and directly, by given real concentrations without interference. Table 2.5 presents a review of some procedure for (Extraction / Separation) of arsenic speciation

2.2.4 Analytical methods for the preparation of samples for speciation analysis

Sample preparation is an important step in order to separate the analyte from the matrix and to avoid chemicals matter which may react with the metal ions or chemical reagents and interfere with the analyte during measurements. The most commonly used methods for the sample treatment are (1) dry ashing: offers the advantage of complete elimination of the organic matter leading to high pre-concentration factors, it done by ashing at atmospheric pressure is known as dry ashing; programmable furnaces may be used for this purpose (2) wet digestion: is performed by using concentrated acids including nitric acid, perchloric acid, hydrogen peroxide and mixture of acids in open or closed vessels. It is possible to apply convective or microwave heating during wet digestion. When open vessels are used, loss of volatile analytes and contamination may occur and they require constant operator attention (3) ultrasound-assisted extractions: is commonly used for biological, environmental and agricultural solid sample pre-treatment because the energy provided accelerates some steps such as dissolution, fusion and leaching and (4) microwave assisted treatment.

Nowadays microwave heating is the most commonly used technique for treatment of a variety of samples. It has proved to be the most suitable digestion method for complex matrices including oxides, silicates and organic substances. It decreases digestion times, increases analyte recoveries also for volatile elements and reduces cross contamination and consumption of reagents leading to improvement in detection limits and overall accuracy of analysis.

2.2.4.1 Acid Digestion. (Total arsenic content)

The use of mineral acids in the digestion of various solid samples, for extract high concentration of arsenic, is an attempt to estimate the total arsenic. It has been used widely in many studies; most of these studies have achieved good results in the estimation of total arsenic. Apart from classical wet digestion, dry ashing or fusion techniques were most

frequently applied in the past. Microwave assisted heating of samples with acids in closed pressurized digestion systems has gained importance during the last years as a fast and effective method of sample preparation. Nitric acid and hydrochloric acid are the most frequently used in the methods of digestion such as: Frank et al. [129] digested plant and peat samples with high purity of nitric acid in a high-pressure microwave autoclave at 240°C ,subsequently measured using (HG-AAS) or (ICP-SF-MS). Baba et al. [130] provided better extraction efficiency by use of 68% HNO_3 than water, 50% methanol, or 2.0M trifluoroacetic acid in rice grain and straw samples, while the extraction of arsenic from soil sample with 68% HNO_3 provided better extraction efficiency than H_2O, 1.0M H_3PO_4, or 1.0M NaOH. Ketavarapu, et al. [131] extracted of total arsenic from samples of freeze-dried carrots by 5.0 mL of ultrapure nitric acid overnight, the samples were digested using a microwave system at 50% power output. The programmable microwave was set at 100psi pressure at 125°*C* temperature limits with a total run time of 60min. Forehand et al. [132] used concentrated hydrochloric acid for digesting samples of the sandy soils and allow the mixture to stand at room temperature for at least 12h. Maria Barra et al. [133] described method for the determination of As(III) As(V) and total arsenic in soils. 3.0mL of HCl :HNO_3 (3 : 1) solution were added and mixed well, the sample irradiated at 50% power for 3.0min, the solution irradiated once again at 70% power for 3.0min, 1.0 mL of H_2O_2 30% solution was added using a third step of digestion during which the sample was irradiated in the closed vessel at the 70% power for 3.0min. The sample microwave-assisted distillation both total and inorganic arsenic were determined by hydride generation-atomic fluorescence spectrometry (HG-AFS). Jiang et al. [134] extracted total arsenic From human Hair in this study the sample was transferred into three PTFE vessels, and 5mL of concentrated HNO3 was added to each vessel, respectively, the vessel solution was then closed and placed in a re-programmed microwave oven. Dagnaca et al. [135] extracted of arsenic species from mussel tissues by using low power focused microwaves. Sample was placed in an open reflux vessel and focused microwaves are applied, digestions were carried out and the appropriate digestion program was adjusted by addition of concentrated nitric acid and hydrogen peroxide. Davidowsk et al. [136] used the microwave-assisted digestion,(PTFE-TFM digestion vessel liners), 6.0 mL of concentrated HNO_3 and 0.5 mL of concentrated HCl were added to baby food and fruit juice. Schaeffer et al. [67] determined the total concentration of arsenic in seafood, freeze-dried powder were weighed into PTFE bombs and were digested with 2.0mL HNO_3 and 2.0mL H_2O_2 in a pressure-cooker for 1.0h. The bombs were cooled,

and the solutions were diluted to 10 mL with ultrapure water. The measurement was achieved by (ICP-MS).

In Some studies organic arsenic species are converted into the inorganic arsenic species. Ringmann et al. [137] converted the DMAs(V), tetraphenylarsenium chloride (TPAC), phenylarsonic acid (PAS) and AsB to inorganic arsenic species by $S_2O_8^{2-}$ with HF in biological and sediment samples. However some researches converted samples in the ash form and then dissolved the dry residue in acid solution to determine arsenic in milk and eggs samples [113]. Mar Gonzalez et al. [138] determined of total arsenic by precipitating As(V) from 10ml of digested sample using a weakly acid silver solution, the Ag_3AsO_4 precipitate was dissolved with 0.5 ml of 6.0M ammonia. While the digestion of arsenic in palm oil, margarine and mayonnaise samples were prepared in soluble form they were subjected to dry pyrolysis (ashing) in the presence of $MgNO_3$, followed by dissolution of the dry residue in 10 mL of 2.6 mol/L H_2SO_4, or they were subjected to hydrolysis with acid extragent, by boiling for 10min. The studied achieved by Sevaljevic et al. [139]. Most of the studies have agreed that the samples need to be dry, crushed and screened to obtain a form of soft powder [89,110,134,137,138]. Although in some studies the authors agreed to add HF after digestion to remove silica [130,131]

Generally the most commonly used procedure for the extraction of arsenic species from samples is acid extraction (mostly combined with solvent extraction, water, alcohol and phosphate extractions). The extraction step is still one of the most critical steps. The extraction involves some problems related with the extraction efficiency, conversion and destruction of the arsenic species.

2.2.4.2 Extraction methods

Extraction is one of the most important procedures for determination of arsenic species without any changing of oxidation state. There are many studies that focused on the process of extraction. Shi et al. [140] used sequentially procedure extraction of arsenic by water, 1.0% HCl and 1.0% NaOH and 0.6M KH_2PO_4 from soil samples. In this study the 0.6 mol/L KH_2PO_4 achieved highest efficiency extraction after 3.0h. Bissen et al. [141] achieved a highly quantified extract of As(III) and As(V) in soil with ammonium oxalate pH = 3, milli-Q water pH = 5.8, sodium bicarbonate pH = 8, and sodium carbonate pH = 11.0 The highest amount of extracted arsenic was found at the highest pH value. Extracted of As(V), AsB, MMAs(V), and DMAs(V) in samples of mussel tissues by (methanol / water) was

investigated by Dagnaca. et al. [135] the solution was placed in an open reflux vessel, focused microwaves were applied at suitable conditions, after decantation the sample extract was centrifuged at 2500 rpm for 10min and the liquid phase was evaporated to complete dryness under an IR lamp. The time of evaporation was close to 4.0h. The dry extract was dissolved in 10 mL of water and filtrated, the arsenic compounds were separated with anion-exchange liquid chromatography and detected by ICP-MS. Pizarro et al. [122] used of (metanol / water) for the extraction arsenic species from rice, chicken and fish, the mixture was maintained at 55°C, for 10h and then treated in an ultrasonic focalized bath for 5.0min and centrifuged at 6000 rpm. While the best extraction efficiency and easiest handling was provided by the 1:1 1M phosphoric acid for soil. The As species were separated by HPLC shows in Figure 2.9. Vergara et al. [142] found that the efficiency of orthophosphoric acid extraction was shown to depend more upon the nature of the material analysed than on acid concentration, excellent (90–100%) recoveries of total As being obtained for the sediment and the sludge reference materials samples whereas yield did not exceed 62% for the soil. The comparison of the matrix effect on determination of arsenic is presented in table 2.6

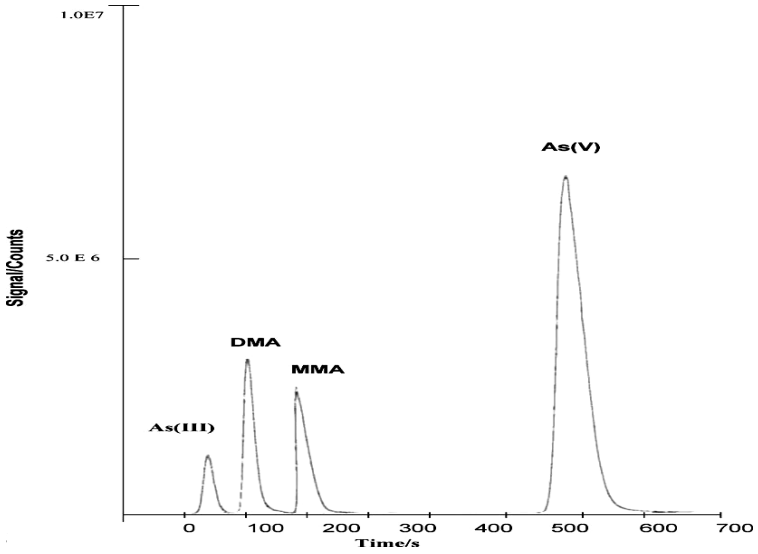

Fig. 2.9 HPLC–ICP-MS chromatograms (anionic column) [129]

2.3 EVALUATION OF ANALYTICAL RESULTS

Validation can be defined as:

Establishing documented evidence which provides high degree of certainty when proposing new methods of chemical analysis to test the efficiency analytical methods.The properties of the method are revealed by determining the following validation parameters:

2.3.1 limit of detection (LOD)

LOD is the lowest concentration where an analyte can be detected. It can be calculated by dividing the area of the signal with the area of the noise, and this ratio (signal to noise ratio, S/N) should be ≥ 3.0 [143]. The signal of the noise is the height of the baseline. Detection limits of arsenic species by some different methods are presented in table 2.7

2.3.2 limit of quantification (LOQ)

LOQ is the lowest concentration where an analyte can be quantified. It can be calculated in the same way as LOD, but the S/N should be ≥ 10 [143].

If the signal to noise ratio is low, it is difficult to say how much of the signal is due to the analyte, and how much is due to the matrix, thus a reliable quantification would be difficult. There are no requirements for the LOQ or LOD value in doping analysis, but the value should fit the purpose.

2.3.3 Upper limit of quantification (ULOQ)

ULOQ, upper limit of quantification, is the highest concentration where the analyte can be quantified, before having a saturated signal. At this point, the calibration curve will go from being linear to parabolic.

2.3.4 Linearity

Linearity is the ability of the method to give a linear calibration curve in a given concentration range. The ratio is given by the response of the analyte which is divided by the response of the internal standard, and allows a plot at different concentrations. The linearity of the equation is described by *R*, the regression coefficient [143]. *R* should be as close to 1.0 as possible.

2.3.5 Specificity

The specificity is the ability of the method to detect and quantify the analyte in presence of contaminations in the sample. The signal of the analyte should not be interfered.

2.3.6 Range

This is the interval between the lower and the upper concentration where the method can quantify the analyte with a suitable accuracy, precision and linearity.

2.3.7 Relative standard deviation

Relative standard deviation (RSD), which is the standard deviation of the results divided by the mean value of the same results, and multiplied by 100. A low RSD indicates a good precision.

Table 2.6 The comparison of the matrix effect on determination of arsenic

Reference	Matrix	Effect
B. Issa [14,17,18]	Common ions in water	No Influence
Nielsen [81]	Cu(II), Co(II), Ni(II) and Se(IV) at excesses of 60, 160, 140 and 500 times, respectively	Decrease in the signal of 5%
Yano [80]	Fe(III) up to 1000-fold amount of As	No Influence on reduction
Hsieh [82]	Ca(II), Mg(II), Fe(II), Mn(II), Na(I) and Cl^- up to 50, 400, 0.5, 200, 900 and 1400 mg/L respectively	Recoveries 95-99%
Xiong [19]	Common ions in water	Tolerance
Sandhu [35]	Cr(IV), Co(II), Cu(II), Mo(V), Ni(II), PO_4^{3-} and NO_3^-, 0.8 mg/L for each	No Influence
Morita [32]	PO_4^{3-} removed by anion Exchange a silica removed by used HF as masking Fe(III) is masked with EDTA	Not affect the by other of elements
Leal [70]	Fe 200, Cu 1000, Pb 1000, Cr 200, Co 1000, Ni 1000, Zn 25, Hg 700, Cd 25 and Se 400 (µg/L)	No Influence
Anthemidis [93]	Cu(II), Co(II), Cd(II), Cr(III), Fe(III), Ni(II), Pb(II) and Se(IV) concentrations up to 100µg/L Hg(II) up to 30 µg/L	No Influence
Chen [94]	Common ions in water	No Influence
Shemirani [101]	Ca(II), Mg(II), Co(II), Ni(II), Fe(II), Cd(II) and Pb(II). 1000 times higher than As(V)	No Influence
Vassileva [121]	Up to 400 mg/L solution of Cl^-	No Influence

2.3.8 Accuracy

Accuracy represents the closeness between the theoretical value and the calculated value. Hence, this parameter considers the uncertainty and the precision of the method. The uncertainty can be determined by calculation of the theoretical values in the sample by using a calibration curve. The calculated- and the theoretical value are plotted in a curve. The linearity and the slope of the curve demonstrate the correlation ship between these values; a linear curve with a slope of 1 suggests a good correlation between these.

2.3.9 Robustness

The robustness is an assessment on the ability of a method to stay unaffected by minor changes in the procedure, i.e. small variations in pH. This is to make sure that the analysis is not affected by variations that might occur in a sample preparation [143].

2.3.10 Standard Deviation

A measure of the dispersion of a set of data from its mean, the more spread apart the data, the higher the deviation. Standard deviation is calculated as the square root of variance.

2.3.11 Precision

The measurement of the reproducibility of results, It is evaluated by performing replicate experiments under the same conditions. It is defined as an agreement between the numerical values between two or more measurements.

Table 2.7 The comparison of the detection limits of arsenic species by different methods

Reference	Method	As(III), µg/L
B. Issa et al. [14,17,18]	ICP-MS	0.24
Jitmanee et al. [20]	ICP-MS	0.1
S. Chen et al. [95]	ICP-MS	0.0045
Xiong et al. [19]	ICP-OES	0.15
Chen et al. [90]	ICP-OES	0.05
Nielsen et al. [81]	HG-AAS	0.1
Anthemidis et al. [93]	HG-AAS	0.02
Leal et al. [70]	HG-AFS	0.05
Zhang et al. [98]	HG-AFS	0.001
H. Wu et al. [96]	HG-DC-AFS	0.0038
Hsieh et al. [82]	GF-AAS	0.11
Rahman et al. [102]	GF-AAS	0.06
Shemiran et al. [101]	GF-AAS	0.01
Morita et al. [32]	UV.Vis	4.0
Staniszewski [97]	TXRF	0.01

2.4. REVIEW OF THE ARSENIC SPECIATION RESEARCH ON SCIENCE DIRECT

Review of the percentage of publications on the science direct site concerning for determination of arsenic species by using different methods and techniques in the last four years is presented in Figs. 2.10 and 2.11.

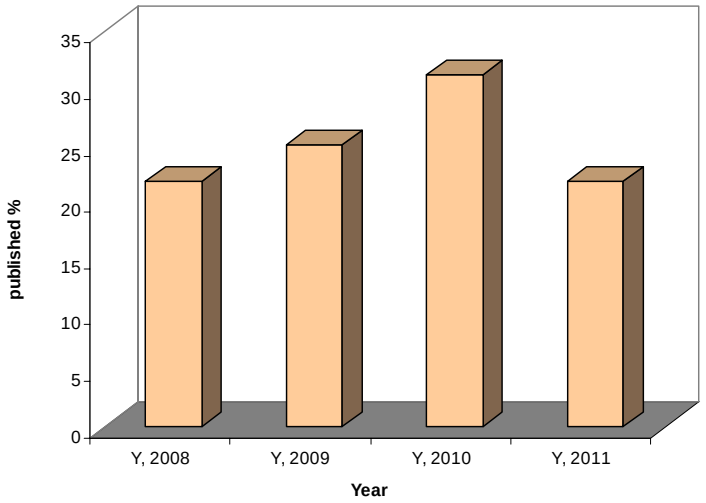

Fig. 2.10 The percentage of the total research for determination of arsenic species in the last four years

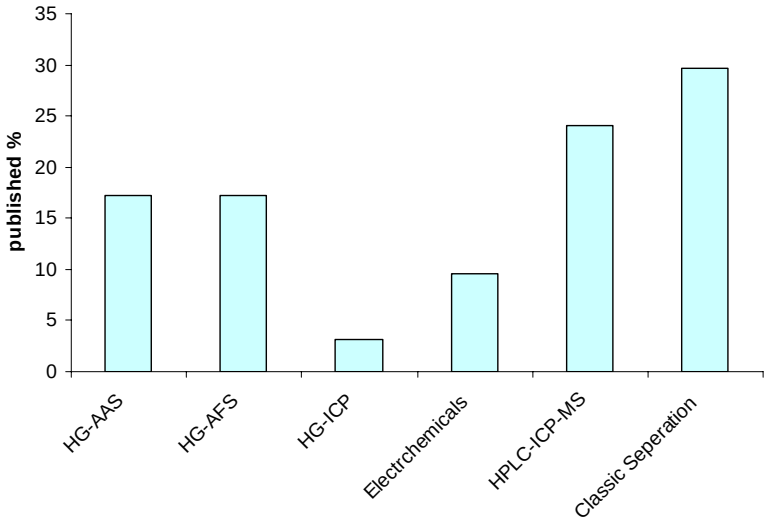

Fig. 2.11 The percentage of the development of methods for determination of arsenic species in the last four years

2.5 THEORETICAL APPROACH IN ANALYSIS OF SYSTEM FOR THE ION EXCHANGE AND SORPTION OF ARSENIC FROM WATER

A large number of countries in the world have paid attention to the removal of arsenic from drinking water. The removal methods vary and depend on the technique and the search for

inexpensive methods. The most of the treatment methods are based on the use of chemical compounds and also depend on the acidity of the water where the pH value plays a key role for the process of removing arsenic. On the other hand, the choice of the appropriate way associated with concentration of arsenic in water is also important to use the method utilized in the selective removal of arsenic without interference with other ions.

- Coagulation, precipitation: one of the methods for removing arsenic and some other ions, so that it uses an array of materials such as aluminum salt, ferric chloride, ferric sulfate and it is not sufficient without the use of filtering to get a good water quality.
- Ion exchange: there is a wide range of commercially strong-base anions. Exchange resins are available; the selective resins for removing arsenic are one of the most important requirements so as to provide high removal. Using this kind of technique depends on the pH values of water. As(III) at neutral pH is in the form of a molecular and it does not provide any removal by this technique. It needs to oxidize as an initial processing while As(V) in the form of ion can be removal.
- Activated aluminum advantage of these materials with high surface area: more than 200 m^2g^{-1} provides very high arsenic adsorption.
- Membrane methods are used largely to remove all dissolved substances in water and they also provide good removal of arsenic. Techniques that are mostly used are reverse osmosis, nanofiltration, and electrodialysis.
- Other methods use by the group of oxides such as Mn-oxide and iron oxide. A very high availability to remove arsenic also includes the use of natural and commercial materials such as zeolites, zero-valent iron, bauxite and hematite, laterite, wood charcoal, iron-oxide coated sand and hydrous granular ferric oxide. The use of oxides in the removal of arsenic is following a bonding between metal and arsenics presented in Fig. 2.12.

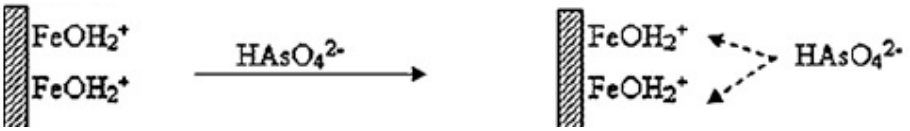

Fig 2.12 Schematic presentation of reaction between arsenic species and iron

- Oxidation: The methods of oxidation are not intended to remove arsenic from drinking water, but intended to transform the arsenic species from As(III) to As(V) so that the transformation is necessary for the treatment process and the removal of arsenic from water, the materials commonly used agents oxidizing are: $KMNO_4$, chlorine, H_2O_2, ozone.

2.5.1 Batch system, capacity, kinetics and adsorption isotherms

Adsorption is commonly defined as the concentration of a substance at an interface or surface. The process can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The interface of interest in water and wastewater treatment is the liquid-solid interface.

The pH of a solution can have a significant effect upon adsorption at the liquid-solid interface. The pH will determine whether the ionized or unionized sorbate species will exist in solution as well as the degree of ionization of surface functional groups.

Metal sorption kinetics are influenced by sorption reactions and the mass transfer steps that govern the transfer of metal ions from the bulk of the solution to the sorption sites on the surface and inside adsorbent particles, i.e. external and intra-particle diffusion

According to Langmuir equations, sorption takes place at specific homogenous sites with in the adsorbent. To determine the maximum adsorption capacity of the adsorbent, Langmuir isotherm model was used in this study. The adsorption isotherm followed Langmuir equation:

$$q_e = \frac{q_{max}\, C}{b + C} \qquad (2.6)$$

where:

q_e = the amount of arsenic adsorbed, (μg As/g adsorbent)

C = equilibrium concentration of arsenic (μg/L) in the solution.

q_{max} = the maximum adsorption of arsenic, (μg/g)

b = adsorption constant

The kinetics of the adsorption process can be studied by carrying out a separate set of adsorption experiments at constant temperature to follow the adsorption with time. The adsorption rate can be determined quantitatively and tested by the pseudo-first-order and pseudo-second-order models. This information is useful for further applications of system design in the treatment of natural water and waste effluents.

2.5.2 Flow system, capacity and breakthrough curves

Breakthrough curves give an indication of when the column is completely saturated. When this happens, the concentration of target going in equals to the concentration of target coming out. It gives an indication to when to stop the loading depending on how much bed remains unused and how much of the product is lost. Breakthrough curves are normally used to

measure the dynamic capacity of a media. The column is loaded with analyte solution at a specific concentration and flow rate. The loading is stopped at a specific percentage breakthrough and the analyte is eluted to get the dynamic capacity. The capacity can be increased by either decreasing the flow rate or hence increasing the contact time in the column or by increasing the length of the column, which also increases the contact time in the column [144]. Increasing the flow rate normally decreases the dynamic capacity. This is mainly due to the fact that using a faster flow rate decresaes the rate of mass transfer of the analyte to the interior adsorption sites of the matrix. In other words. The extent of the decrease in the mass transfer rate depends on the particle size and the pore size of the adsorbents. When comparing different types of media, adsorbent that tend to show good mass transfer properties will have a higher dynamic capacity at higher flow rates. Some media which have poorer mass transfer properties will tend to show a higher dynamic capacity at longer contact time and might have a higher equilibrium binding capacity overall [144]. The higher concentration can be used in order to decrease the breakthrough time.

III EXPERIMENTAL PART

III EXPERIMENTAL PART

3.1 REAGENTS, APPARATUS AND MATERIALS

3.1.1 Reagents

In the experimental work, the following chemicals were used: $Na_2HAsO_4 \cdot 7H_2O$ p.a. Aldrich (Munich, Germany); $NaAsO_2$ p.a. Riedel de Haen (Buchs, Switzerland); DMAs(V) $HAsO_2(CH_3)_2$ p.a. Sigma-Aldrich (St. Louis, MO, USA), MMAs(V) $Na_2AsO_3CH_3$ $6H_2O$ p.a. Sigma-Aldrich, H_2SO_4 p.a. Sigma-Aldrich, Silver nitrate ($AgNO_3$) 99.9999% Trace Metals Basis p.a. Sigma-Aldrich, Hydrochloric Acid HCl —Trace-metal grade- purified- concentrated, reagent-grade, Merck (Darmstadt, Germany), Nitric acid HNO_3—Trace-metal grade purified concentrated, reagent-grade p.a. Fluka, Sodium Hydroxide NaOH—grade, p.a. Merck, Sodium Borohydride Sigma-Aldrich.

Ultra-pure water resistivity less than 18 MΩ/cm, produced by a Millipore Milli-Q system was used throughout the experimental work.

3.1.1.1 Arsenic compounds

An As(III) stock solution (3750.0 mg/L) was prepared by dissolving sodium arsenite (4.9460 g As_2O_3 +1.30 g NaOH) in deionized water in a 1.0 L volumetric flask and refrigerated in an amber bottle. Under these conditions, this working stock solution was found to be stable for at least one year. An As(V) working stock solution was made by dissolving of 4.1600 g $Na_2HAsO_4 \cdot 7H_2O$ in 1.0 L of deionized water (1000.0 mg/L stock solution), which was preserved with 0.50 % HNO_3.

A monomethylarsenate, MMAs(V), working stock solution was made by dissolving of 389.3 mg $Na_2AsO_3CH_3 \cdot 6H_2O$ in 1.0 L of deionized water (100.0 mg/L stock solution). A dimethylarsenate, DMAs(V), working stock solution was made by dissolving of 184.0 mg $HAsO_2(CH_3)_2$ in 1.0 L of deionized water (100.0 mg/L stock solution).

3.1.1.2 Water samples

Water samples were collected according to [145] from home taps, lakes and wells of the Vojvodina Region, Serbia (southern boundary of the Great Pannonia Plane) 1.0 L of water samples are collected directly into cleaned polyethylene bottles using sample handling technique, according to [145] Appendix 1.

For determination of total arsenic all samples were filtered through a 0.45µm membrane filter, acidified to pH 2.5 with HNO_3 and stored in a refrigerator at 4.0 °C in polyethylene bottles.

For determination of arsenic species, all the sampling was performed according to a simple sampling procedure without addition of any reagent for stabilization according to Segura et al. [146], arsenic species in water are stabile under neutral conditions for a period of 4 months if they are placed in polypropylene bottles in a refrigerator. Before ICP-MS measurements, the samples were acidified with 5.0 % HNO_3.

3.1.2 Apparatus

3.1.2.1 Inductive coupled plasma mass spectroscopy (ICP-MS Agilent 7500ce spectrometer, Waldbronn, Germany)

3.1.2.2 Hydride generation atomic absorption HG-AAS, PerkinElmer Analyst 200, MHS 15 (Waltham, MA, USA)

3.1.2.3 High sensitivity, low detection limits ion chromatograph product of metrohm type 861 Advanced Compact IC MSM II combines with effective suppression techniques Herisau/Switzerland, Separation Column METROSEP A SUPP 5-150 (6.1006.520), 4.0 x 150 mm, No. 7612576, Part. size 5.0 µm, eluent 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$, flow 0.70 mL/ min, temperature 20.0°C, pressure 7.5 *MPa*

3.1.2.4 A laboratory pH meter, Metrohm 827 (Zofingen, Switzerland), was used for the pH measurements. The accuracy of the pH meter is ± 0.01 pH units. Prior to measurement, a three-point calibration of the meter was performed using standard buffers of pH 4.0, 7.0, and 10 purchased from consort in accordance with the procedure provided by the manufacture

3.1.2.5 A Laboratory shaker (Rotamax 120, Heidolph Instruments, Kelheim, Germany) was used for stirring of solutions during exchange process.

3.1.3 Glassware Cleaning Procedures

All bottles, glassware and columns were first brush was used to remove any material stuckto the sides. All bottles, glassware and columns were then triple rinsed with distilled water before being submerged in a 10% nitric acid solution and allowed to soak overnight. Proceeding the acid bath, bottles and glassware were then triple rinsed with de-ionized water (Ultra-pure Water system (ultra-pure water) and allowed to air dry. Cleaned bottles were stored with lids and placed in to prevent recontamination prior to use.

3.2 ANALYTICAL METHODS AND INSTRUMENTATION

3.2.1 ICP-MS method and procedure

Arsenic was analyzed by the Inductive coupled plasma mass spectroscopy ICP-MS method following the method 200.8 [147] using an Agilent 7500ce spectrometer (Waldbronn, Germany) equipped with an Octopole Reaction System. Calibration at levels 1.0–20 µg/L was performed with external standards, Fluka arsenic standard solution (Product No. 01969), Fluka (Buchs, Switzerland) by appropriate dilution. The slope of the calibration curve was 0.9999. The calibration blank and standards were prepared in 2.0 % nitric acid for all measurements. A tuning solution containing Li, Mg, Co, Y, Ce and Tl (Agilent) at concentrations in the µg/L level, was used for all instrument optimizations. The Optimal operating conditions is presented in the table 3.1

Table 3.1 Optimal instrumental operating conditions (ICP-MS Agilent 7500ce).

Operation parameters	
RF frequency (MHz)	27
RF power (W)	1500
Plasma gas flow (L/min)	15
Nebulizer gas flow (L/min)	0.9
Sample uptake rate (rps)	0.3
Data acquisition	
Acquisition mode	Peak hopping
Dwell time (ms)	100
Integration time (s)	0.1-0.3/point
Repetition	3 (FullQ)
Interference correction	As= 1*(75C)- 3.175* [(77C)-0.815*(82C)] where ′m′ C is the total ion count at m/z ′m′ (ref 23 – EPA 200.8)

The concentration of As(III), DMAs(V) and oAs in the water samples were measured by applying ICP-MS method under optimal instrumental (Agilent 7500ce) operating conditions. The linear range was found to be 0.030-20.00 µg/L. Method detection limit (MDL) determination was based upon seven replicate measurements of a series of spiked calibration blanks. Each blank solution was spiked with analytes at concentrations between 2 and 5 times the calculated instrument detection limit (IDL). The MDL was calculated by multiplying the standard deviation of the seven replicate measurements by the appropriate Student's test value

based on a 99% confidence level (t¼ 3.14 for six degrees of freedom). Each arsenic species was measured separately. MDL for all arsenic species was 0.030 ppb, MDL (spiking level) was 0.500 µg/L.

The accuracy of the method was evaluated by analyzing of reference material NRC SLRS4 (National Research Council Canada, Canada) with low elemental concentrations of the elements of interest. Nominal value for As in NRC SLRS4 was 0.68±0.06 µg/L, the measured value was 0.65±0.02 µg/L. None of the arsenic species measured in this work has certified values. Values for the total arsenic for reference material applied were in good agreement with the certified value, the calculated recovery 95.6% was satisfactory. The repeatability, as relative standard deviation RDS(%) was calculated from seven replicate measurements at the 10 µg/L of each arsenic species. For total arsenic measurements, RDS(%) was 1.7. RDS (%) for separated species: As(III), DMAs(V) and oAs including the separation step was determined, it was 1.3, 1.5 and 1.8 respectively.

The proposed separation scheme was also applied to the analysis of local water samples (tap, river and wastewater) and was validated by spiking the samples with known amounts of arsenic species. The recoveries from spiked solutions were varied in the range 88.4±4.0%–102.4±2.0%.

3.2.1.1 Interferences during the ICP-MS measurements

The major interference for arsenic determination by ICP-MS is the polyatomic species $^{40}Ar^{35}Cl^{+}$, which is sometimes formed in the plasma and has the same *m*/*z* value as the only naturally occurring ^{75}As isotope. Drinking water samples have a relatively high level of chlorine and the procedure with the SBAE resin even increases the level of chlorine (due to exchange with Cl^{-} ions during exchange process), hence the $^{35}Cl^{+}$ ion should be monitored in addition to the $^{75}As^{+}$ signal during each run. The determination of arsenic in the presence of chloride was accomplished by a procedure suggested in the literature [148]. The option to use SBAE resin in R-OH was avoided due to significant influence of pH to separation on the resin.

3.2.1.2 Analytical figure of merit and application

Analytical characteristics of the proposed method is given in table 3.2, and the experimental limit of detection (LOD) was 0.20 µg/L for As(III) and As(V). The sensitivity achieved is adequate for arsenic determination in non-polluted water samples.

Table 3.2 Analytical characteristics of the proposed method

Characteristics	iAs (total inorganic arsenic)	oAs (total organic arsenic)
Calibration	$A = 1.016x10^4[iAs] + 4.671x10^2$	$A = 1.022x10^4[oAs] + 4.785x10^2$
	R = 0.9999	R = 0.9996
Linear analytical range	1-80 µg/L	1-80 µg/L
Detection limit	0.2 µg/L	0.2 µg/L

A: absorbance and [As] expressed as µg/L; n - number of measurements; *R* - correlation coefficient.

3.2.2 HG-AAS method and procedure

Method using a PerkinElmer Analyst 200, MHS 15 (Waltham, MA, USA) was applied following the standard procedure (Method 1632) [149]. The technique using MHS-15 chemical vapor generation system (Perkin-Elmer), coupled to the AA spectrometer. Arsenic hollow cathode lamp (Perkin-Elmer) operated at 6mA was used. Measurements were carried out at the wavelength of 197.2nm. Argon 99.9% was used as the carrier gas. The calibration curves (1.0-20 µg/L) for Arsenic were established with solutions prepared from a 1000 µg/L certified stock solution. Reduction of As(V) to As(III) was performed with potassium iodide solution and ascorbic acid in moderately concentrated (5.0 mol/L) HCl solution. Time for reduction was 30 minutes. 10ml of reduced water samples were analyzed using, ccorrelation coefficient = 0,997736.

The experimental limit of detection using hudride generation AAS was (LOD) was 0.5 µg/L. The sample solutions were filtered through a Millipore 0.45 µm membrane filter (Bedford, MA, USA) before injection.

3.3 SET-UP FOR ION-EXCHANGE AND SORPTION PROCESS AND PROCEDURES

3.3.1 Ion exchange and sorption resin

Resins used in presented experiments were: 1) SBAE resin, Lewatit MonoPlus M 500, Lanxess (Leverkusen, Germany), a gel-type, strong base anion exchange resin based on a styrene-divinylbenzene copolymer with uniform, spherical (monodispersed), light yellow particles, mean bead size of 0.61 mm; 2) HY-Fe resin, a hybrid macroporous monodispersed polystyrene-based resin, FO36, Lanxess with spherical, brown particles, mean bead size of 0.35 mm [150] and 3) HY-AgCl resin, silver loaded ion exchange resin, a new resin synthesized in our lab according the procedure proposed in US Patent [151].

3.3.2 Preparation of HY-AgCl resin, silver loaded ion exchange resin

Commercial SBAE resin, Lewatit MonoPlus M500, Lanxess (Leverkusen, Germany) was activated by silver nitrate solution according to procedure described previously [151]. The activation was accomplished in batch system: 10 g of resin was washed with deionized water, and then 200 mL of 3.0 mol/L of silver nitrate solutions was added. The exchange process was accomplished according to the following procedure: stirring 150 rpm, a room temperature, pH 8, time of reaction 4 h. Precipitate of a silver-chloride was formed to the resin according to:

$$R–Cl^- + Ag^+ + NO_3^- \rightleftharpoons R–AgCl + NO_3^-$$

Silver loaded exchange resin was filtrated and washed thoroughly with deionized water to remove residual $AgNO_3$ (chloride test), and dried at room temperature. After drying HY-AgCl, resin was sieved and stored away from light. Properties of HY-AgCl were as follow: particles mean bead size 560 μm; density 1.1 g/mL, silver content $1.73 \cdot 10^{-3}$ mol/g.

IV RESULTS AND DISCUSSION

IV RESULTS AND DISCUSSION

4.3 PRELIMINARY INVESTIGATION OF ION-EXCHANGE AND SORPTION PROCESSES OF ARSENIC SPECIES IN BATCH SYSTEM

preliminary investigations were accomplished by applying standard batch system in order to compared and proved the efficiency of the SBAE, HY-Fe and HY-FeCl resin and to find out the main influences for their separation abilities and determination of arsenic species.

4.3.1 Effect of pH values on ion-exchange and sorption processes

4.3.1.1 Effect of pH on Ion-exchange SBAE for separation and determination of iAs

The experiments were focused on separation and speciation of iAs by the strong base resin (in order to determine As(III) and As(V) species in water samples)

The effect of pH on the separation and speciation of arsenic by the sorption process with SBAE resin was investigated in a batch system. The mass of resin (m = 1.0 g), concentration of both arsenic species (C_{As} = 100 mg/L), volume of water solution (V = 100 mL), temperature (t= room temperature), contact time (τ = 60 min) and shaker speed (w = 150 rpm) were constant during the experiments. The pH value was varied between 2.0 and 12. For each pH value, the percentage of arsenic, bonded to SBAE, was calculated and the results are presented in Fig. 4.1.

The experimental results confirmed that the inorganic arsenic (iAs) separation by SBAE was highly affected by the pH value, for the As(V) species, the ion exchange process was observed at pH > 4.0, but significant efficiency was reached at pH > 6.0. At higher pH values divalent As(V) ions prevail and a higher separation efficiency was exhibited. As(III) did not bond to the SBAE resin at pH < 8.0 due to the existence of neutral molecules of As(III) below this pH value. With this feature the SBAE resin is a convenient material for the separation of As(III) and As(V) species. As(V) could be bonded totally to the SBAE by adjusting the pH value, As (III) determined easily without interference.

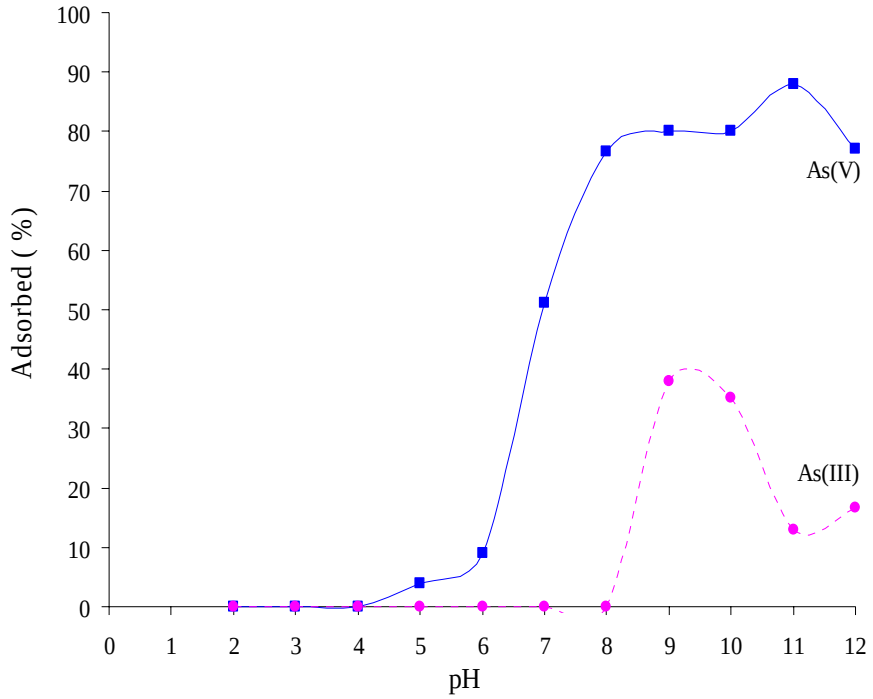

Fig. 4.1 The effect of pH in separation of iAs on the SBAE, Conditions: $C_{As(III)}$ = $C_{As(V)}$ = 100.0 mg/L, m_{resin} = 1.00 g, t = 20 °C, V = 100 mL, τ= 60 min, w = 150 rpm, n = 5

4.3.1.2 Effect of pH on hybrid resin HY-Fe for preconcentration of total arsenic

Preconcentration of all iAs species to the HY-Fe resin in order for determine of total iAs as an analyte or to remove iAs as an interference in analytical determinations. The Fig. 4.2 showed that the inorganic arsenic species (iAs) separation from water by the HY-Fe resin was not affected by the pH value, suggesting that HY-Fe is efficient for the preconcentration and mutual interference removal of molecular and ionic forms of both As(III) and As(V).

At equilibrium (C_{As} = 100 mg/L, V = 100 mL, room temperature, τ = 24 h, w = 150 rpm), pH value was between 2.0 and 12. The results confirmed that under neutral conditions, which are a feature of natural and drinking water, both of inorganic species were bonded according to the reaction in schematic Fig.4.3 at pH value 5.0-10. However, preconcentration and determination of total arsenic species could be preformed At pH value between 6.5 to 8.5.

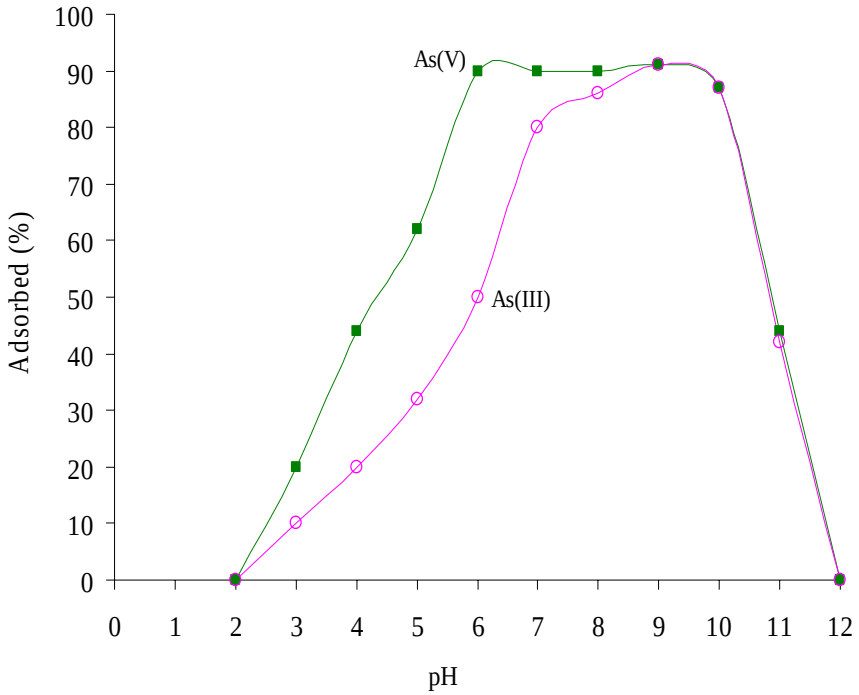

Fig. 4.2 The effect of pH in preconcentration of total iAs on HY-Fe, Conditions: $C_{As(III)} = C_{As(V)} =$ 100.0 mg/L, m_{resin} = 1.00 g, t = 20 °C, V = 100 mL, τ= 60 min, w = 150 rpm, n = 5

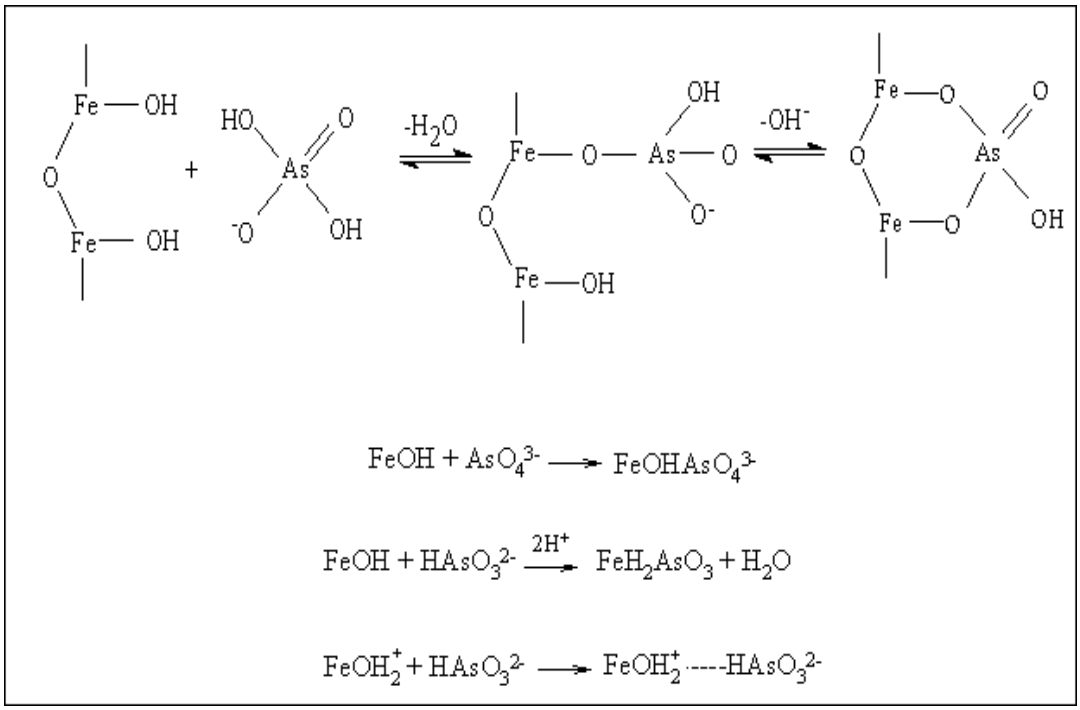

Fig. 4.3 Schematic reactions of arsenic species with HY-Fe

4.3.1.3 Effect of pH on HY-AgCl for separation and determination of oAs species

In order to elucidate the influence of pH values of water to separation ability of HY–AgCl resin in the preliminary investigations some experiments were accomplished in a batch system. The procedure at the following conditions: mass of resin (m = 1.0 g), concentration of all arsenic species (C_{As} = 500 µg/L), volume of water solution (V = 100 mL), temperature (t= room temperature), contact time (τ = 60 min) and shaker speed (w = 150 rpm) were constant during the experiments. The results are presented in Fig. 4.4

The presented results in figure 4.4, confirmed that the separation of inorganic and organic arsenic species by HY–AgCl resin is highly affected by the initial pH of working solution. The organic arsenic species are not bonded with HY–AgCl. It can be ascribed to the steric interference with a surface groups, repulsive forces prevent to some extent entrance inside the meso and micropores [152]. As(III) and As(V) species were bonded with HY–AgCl at pH value 4.0–12, but the maximum sorption was noticed at pH 9.0. With this specific feature, the HY–AgCl resin is a convenient material for the separation of iAs and oAs (V) species at pH 9.0

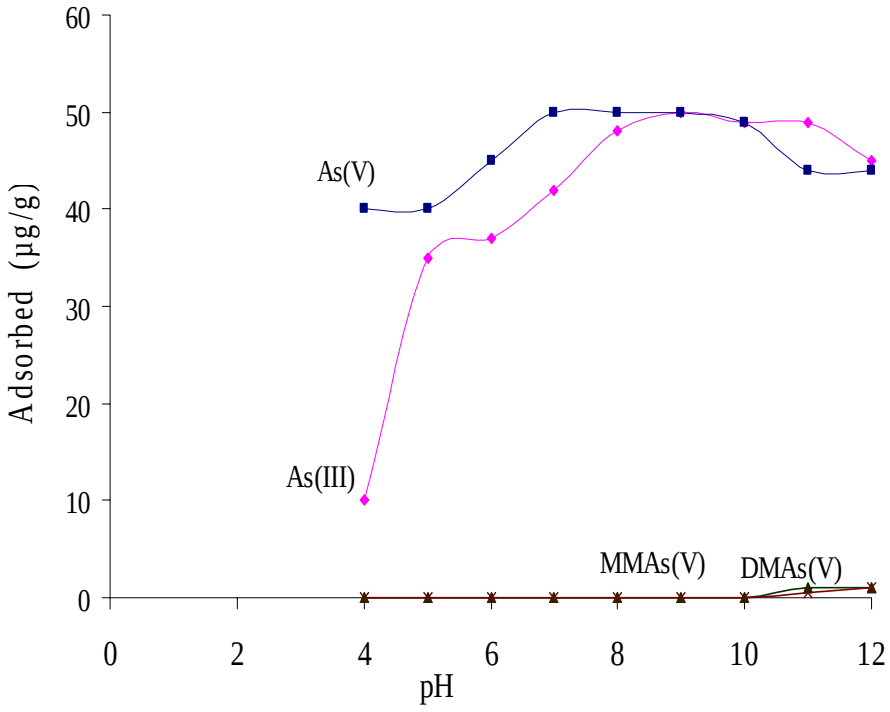

Fig. 4.4 The effect of pH in separation of oAs on HY-AgCl resins,

Conditions: $C_{As(in\ all\ species)}$=500 µg/L, m_{resin}=1.0 g, t=20 ^{o}C, V=100 mL, τ=2hr, w=150 rpm

4.3.1.4 Effect of pH on HY-Fe for separation and determination of DMAs(V)

The influences of pH on the separation of arsenic species iAs and oAs was studied in a pH rage from 2.0 to 12, the results are given in Fig. 4.5. Separation of the iAs and oAs species was conducted, using HY-Fe and SBAE resins, in a batch system procedure at the following conditions: mass of the resin (m = 1.0 g), sample volume (V = 100 ml), concentration of both oAs and iAs C_{As}=(100 mg/L), contact time (τ = 60 mim) and shaker speed (w = 150 rpm) at room temperature. All capacities measurements were done in triplicate.

The results presented at Fig. 4.5, show that the pH of solution plays an important role in the control of arsenic species which is beneficial for the arsenic separation. SBAE can be high efficiency used for separation and determination of As(III) and As(V). Bonding capacities of SBAE with respect to MMAs(V), DMAs(V) and As(V) species increase starting from pH 5.0 and reach maxima at pH 11.0. However The SBAE bonded all arsenic species at neutral pH value except As(III) - as mentioned in Figure 4.5.

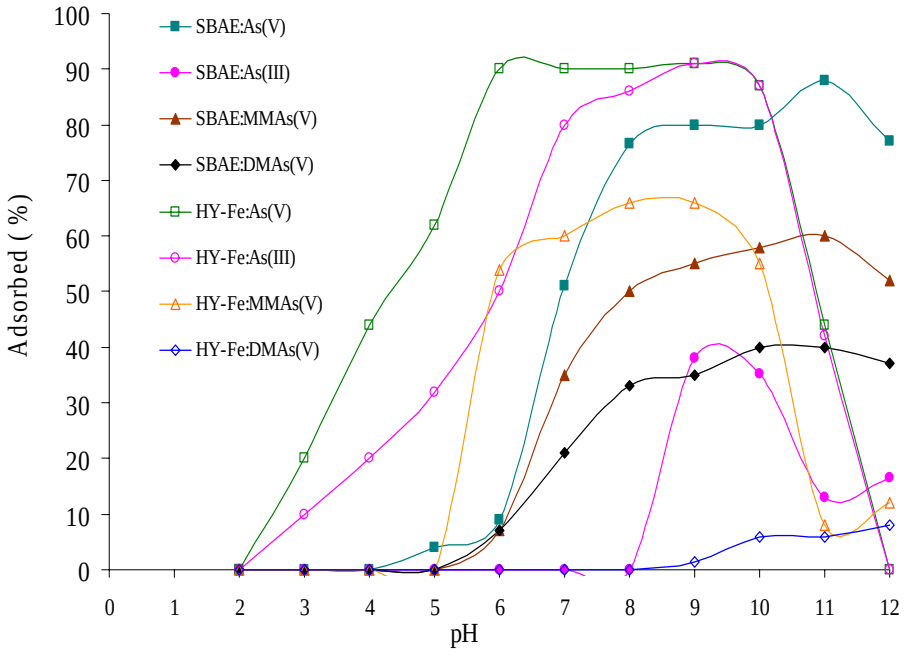

Fig. 4.5 The effect of pH in separation and preconcentration of iAs on SBAE and HY-Fe resins Conditions: $C_{As(III)} = C_{As(V)} = C_{MMAs(V)} = C_{DMAs(V)}$ = 100.0 mg/L, m_{resin} = 1.00 g, t = 20 °C, V = 100 mL, τ = 60 min, w = 150 rpm

The DMAs(V) exist as neutral species, or even as cation in strongly acidic media [102], at pH < 6.0 Fig. 4.5, at pH 7.0 DMAs(V) is not bonded at HY-Fe, while MMAs(V) shows significant affinity to HY-Fe resin surface. Significant sorption capacity of MMAs(V) was

observed in a pH range from 6.0 to 10.0 and at lower pH molecular forms become dominant and less attracted by positive resin surface. Low DMAs(V) sorption capacity at pH > 8.0 could be due to steric interference of two methyl and resin surface groups, and those repulsive forces prevent entrance inside meso- and micropores [152]. Arsenate adsorption on iron-oxide involves ligand exchange reaction with surface hydroxyl group, which result in different surface complexes, *e.g.*, monodentate *vs* bidentate, mononuclear *vs* binuclear. Arsenite adsorbs *via* ligand exchange reaction as well forming mono- and binuclear complexes. At higher surface coverage bidentate binuclear complex is a preferential type of binding which could be a reason of low affinity of DMAs(V) toward HY-F resin surface [153,154].

However, iAs and MMAs(V) separation from water by the use of HY-Fe resin was not affected by the pH value suggesting that HY-Fe is efficient for the retained of molecular and ionic forms of both As(III), As(V), as well MMAs(V). While DMAs(V) did not bond to the HY-Fe resin at pH < 8.0. From that point of view HY-Fe resin could be used, without interference with other arsenic species, in the pH range from 6.0 to 8.0 for separation and determination of DMAs(V).

Generally, preconcentration of iAs and MMAs(V) species to the HY-Fe resin could be performed in order to determine DMAs(V).

4.4 PRELIMINARY INVESTIGATION OF ION-EXCHANGE AND SORPTION PROCEDURE OF ARSENIC SPECIES IN FLOW SYSTEM

The fixed bed flow system employed laboratory columns of diameter 2.00 cm. The flow rate, *Q*, mass of resins, *m*, and empty bed volume, *EBV*, were adjusted to obtain optimal time of contact, τ, for the ion exchange/sorption.

The exchange/sorption capacity was determined according to the following equation:

$$q = \frac{C_i - C_f}{m} V \qquad (4.1)$$

where: q - sorption capacity (mg/g), C_i - initial arsenic concentration (mg/L), C_f - final arsenic concentration (mg/L), V – volume of model solution (L) and m - mass of resin (g).

4.2.1 Determination of capacity of ion-exchange and hybrid resins

4.2.1.1 Determination of ion-exchange SBAE on separation of inorganic arsenic species

Before analytical application, resin was exposed to the preliminary investigations in standard fixed bed flow system. In order to find out the capacities and the efficiency of the resins for the separation and determination, the collection purposes high arsenic concentration of 5000

µg/L, was tested. Each arsenic species was tested and analyzed separately. In all experiments the conditions were: $C_{As(III)} = C_{As(V)} = 5000$ µg/L, pH = 7.5, $m_{resin} = 6.0$ g, $Q = 1.66$ mL/min, *EBV*= 12.5 mL. Breakthrough point (the point when the arsenic concentration is equal or higher than 10 µg/L was an optimal criteria for the comparison of different sorbents.

The main results obtained with resin and iAs species in deionized and modified tap water are presented in Fig. 4.6. The result presented that the SBAE resin in flow system bonds more than 370 µg/g of As(V), while As(III) is not bonded at all. The results presented that the SBAE can be used as separation method for As(III) and As(V) and can be simply measured of As(III).

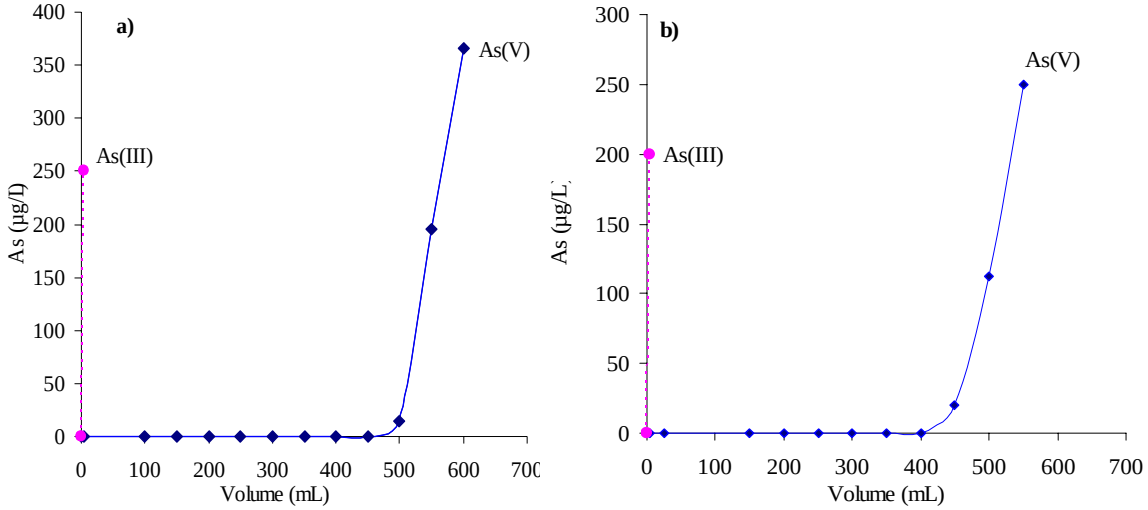

Fig.4.6. Breakthrough curves for iAs species in deionized and modified tap water on SBAE: a) deionized water; b) modified tap water (influence of common inorganic ions)

4.2.1.2 Determination of hybrid resin HY-Fe on separation of total inorganic arsenic species

In order to find out the capacities and the efficiency of the HY-Fe for the preconcentration and determination of total inorganic arsenic, high arsenic concentration of 5000 µg/L, was tested. In all experiments the conditions were: Concentration of both arsenic were $C_{As(III} = C_{As(V)} = (5000$ µg/L), pH = 7.5, mass of resin was (m_{resin}= 6.0 g), flow rate (Q = 1.66 mL/min) and *EBV* = 12.5 mL, n = 3

The results in the Fig. 4.7 presented that, the HY-Fe resin bonds more than 4150 µg/g of As(III) and more than 3500 µg/g of As(V) over a wide range of pH values. The capacities of the resins were slightly lower when modified tap water was tested. The quantity of bonded arsenic was calculated only up to the breakthrough point. These high capacities of resins are

very convenient for development of analytical procedures for water sample. These results are also promising for solid phase extraction technologies and some specific pretreatment systems described in the literature [20,99,155].

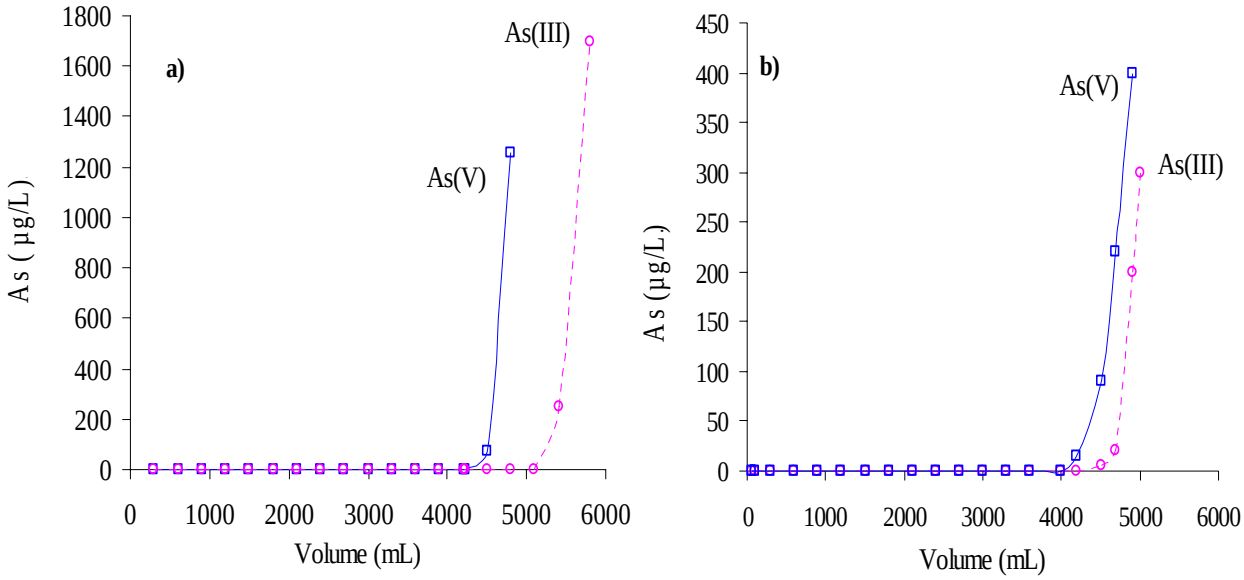

Fig.4.7. Breakthrough curves for iAs species in deionized and modified tap water on HY-Fe: a) deionized water; b) modified tap water (influence of common inorganic ions)

4.2.1.3 Determination of hybrid resin HY-AgCl on separation of organic arsenic species

Capacities and the efficiency of the resins for the separation and determination the collection purposes preliminary were investigated in a standard fixed bed flow system. Each arsenic species was tested and analyzed separately. The concentration of all species was prepared in order to have final arsenic concentration of 500 µg/L. In all experiments, the conditions were: $C_{As(III)} = C_{As(V)} = C_{DMAs(V)} = C_{MMAs(V)}$ 500 µg/L, pH = 9.0, m_{resin} = 6.0 g, Q = 1.25 mL/min and EBV = 12.5 mL, n = 3. Breakthrough point (the point when the arsenic concentration is equal or higher then 10 µg/L) was an optimal criteria for the comparison of different resins. The results obtained with model solutions of iAs and oAs species are presented in Fig.4.8.

Retention behaviors of the arsenic species on resins were estimated comparing the species concentration in the sample solution loaded in resin columns with the concentration in the solution, which passed through the columns. Data evaluation showed that the most significant finding of this experimental part was the following

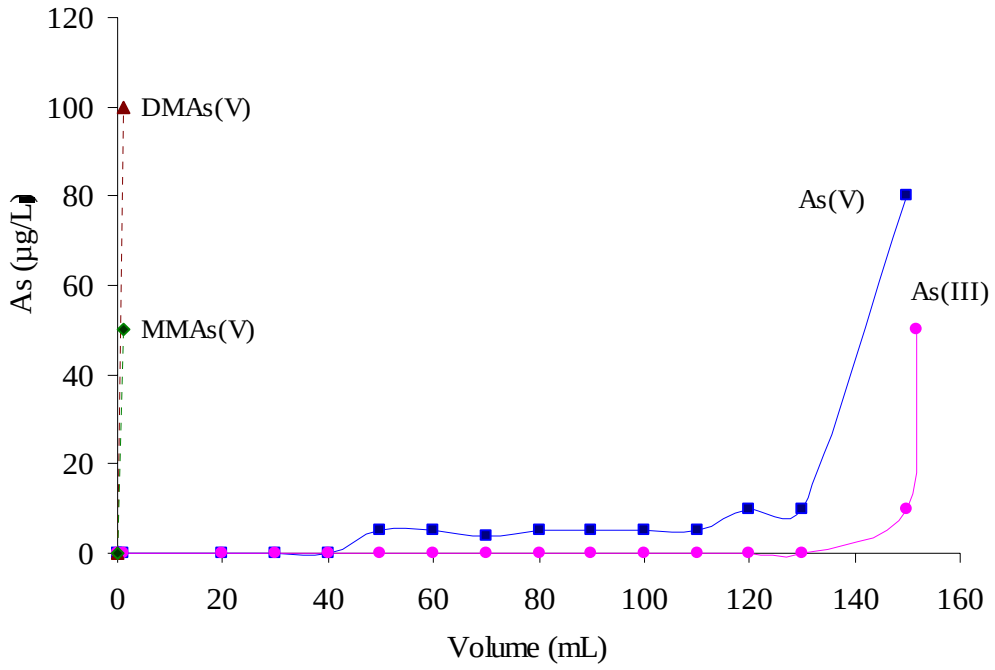

Fig. 4.8 Breakthrough curves for iAs and oAs species in deionized water on HY-AgCl.

The HY−AgCl resin bonds only iAs species [As(III) and As(V)] allowing oAs species to pass through. It could be ascribed to the chemical reaction between iAs species and silver-chloride onto HY−AgCl, at pH values near 9.0. At this pH value, MMAs(V) and DMAs(V) exist in ionic forms, but they did not exhibit the affinity to silver−chloride as active agent of HY−AgCl resin. It is interesting that DMAs(V) is recognized as a cation in acidic medium [102]. The HY−AgCl resin in batch system bonds, at pH=9.0, more than 950 µg/g of As(III) and more than 1500 µg/g of As(V). The capacity of the HY−AgCl resin in a flow system was low, 80 µg/g of As(V) and 85.0 µg/g of As(III). The capacity of HY−AgCl is an order of magnitude lower than those of other resins, but the resin was stable and efficient for arsenic separation in the case when real water sample were tested. This result is promising and worthy for the development of a specific determination, pretreatment separation system and SPE cartridges.

4.2.1.4 Determination of hybrid resin HY-Fe on separation of dimethylarsenate

In order to establish method for separation and determination of DMAs(V), it was necessary to determine the capacity and the efficiency of HY-Fe resins in a fixed bed flow system.

Model solution was prepared from deionized water, conditions: $C_{As(III)} = C_{As(V)} = C_{MMAs(V)} = C_{DMAs(V)}$ = 5000 µg/L, pH 7.0-7.5, m_{resin} = 6.0 g, Q = 1.66-2.0 mL/min and EBV = 12.5 mL. The breakthrough point is the point when the arsenic concentration is equal to or higher than 10 µg/L, which is a good criterion for determination of resin capacity as well for resin comparison. The results of capacities determination for HY-Fe resins are shown in Fig. 4.9.

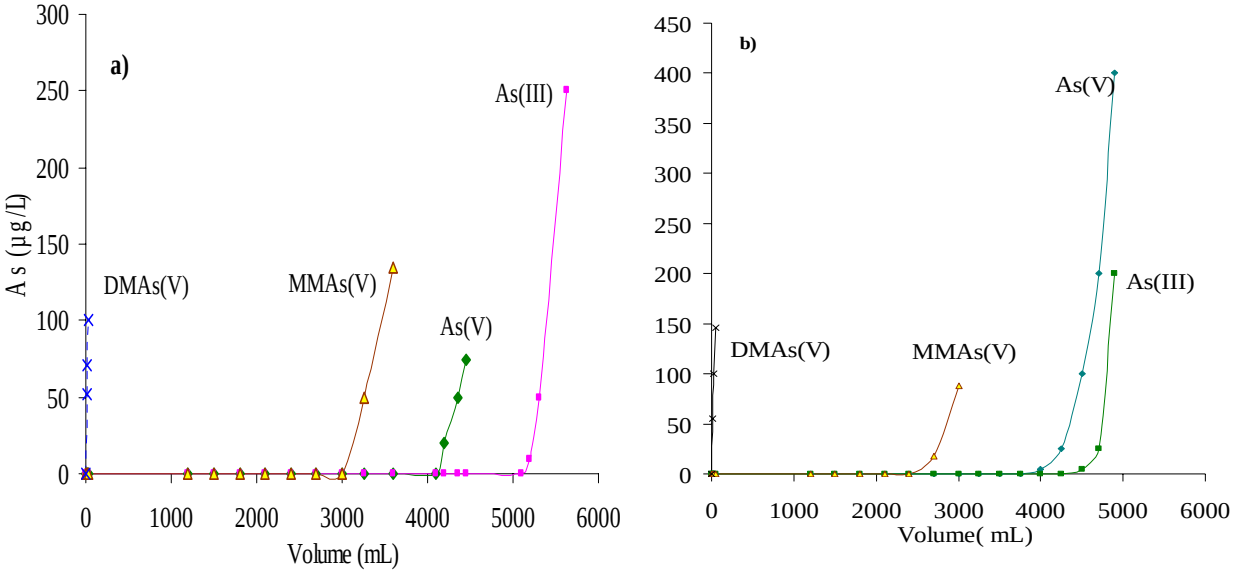

Fig. 4.9 Breakthrough curves for iAs and oAs species in deionized and modified tap water on HY-Fe resin: a) deionized water and b) modified tap water.

The capacity of HY-Fe resin, in a fixed bed flow system, for the samples prepared in deionized water was 1500 µg/g for MMAs(V), 4150 µg/g for As(III) and 3500 µg/g for As(V) at pH 7.0. Analogous experiments conducted with modified tap water gave results of slightly lower capacities (less than 10%). The high capacity provides a good area for research, especially for the separation and determination of DMAs(V) in different water samples.

4.3 CONCENTRATION, SEPARATION AND DETERMINATION OF ARSENIC SPECIES (iAs AND oAs) IN FLOW SYSTEM ON ION-EXCHANGE AND HYBRID RESIN WITH STANDARD ARSENIC MODEL SOLUTION IN DEIONIZED AND WATER MODIFIED WITH COMMON INORGANIC IONS

4.3.1 Concentration, separation and determination of iAs on SBAE.

A large number of experiments have been conducted to estimate the arsenic in standard solution samples according to the proposed procedures are presented in tables 4.1, 4.2, 4.3

and 4.4. Standard solutions of arsenic were prepared by the proposed procedure, the separation condition were: m_{resin} = 6.0 g; t = 20 °C; Q = 1.66 mL/min, EBV = 12.5 mL, τ = 7.5 min, V_{sample} = 20 mL, n = 5 at pH 7.5. All standard solutions were measured by ICP-MS and HG-AAS method. The concentrations investigated ranged from very low, near to the drinking water (5.0 μg/L) to relatively high (100, 200 or even 300 μg/L), which are close to real water samples from the Vojvodina region.

The standard solution were prepared according to the tables, table 4.1 Presents the result of determination of As(III) without any additions of As(V), while the ratio between As(III) and As(V) species were 1:1 presented in table 4.2. Table 4.3 and 4.4 show the results of As(III) at lower /higher than content of As(V) which is also related to real water samples. Table 4.5 shows the effect of ions naturally present in water.

The results in Table 4.1, 4.2 and 4.3 confirmed that the As(III) as a nonionic species was not retained on the SBAE resin under the proposed conditions, whereas As(V), which is present as anionic species, was retained on the resin. After separation by SBAE, only As(III) species were present in the water and measured with ICP-MS/ HGAAS, The good recoveries percentages for all samples were obtained for determination of As(III).

The proposed method described has proven to constitute an effective approach for the determination of As(III) and As(V) in standard solution samples.

The methods could be applied for determination of inorganic arsenic species in water samples.

Table 4.1 Results of determination of As(III) by separation procedure with SBAE applied to standard arsenic solutions without adding As(V)

Sample	As concentration, μg/L				
	Standard solutions analyzed			**Measured**	
	As(III)	As(V)	Total As	Total As±σ	Recovery % As
1	5.00	0.00	5.00	5.10±0.08	102.0
2	10.0	0.00	10.0	9.88 ± 1.3	98.80
3	15.0	0.00	15.0	15.2±2.5	101.3
4	25.0	0.00	25.0	25.5 ± 1.4	102.0
5	50.0	0.00	50.0	48.9 ±2.0	98.00

Table 4.2 Results of determination of As(III) by proposed methods with SBAE applied to standard arsenic solutions in the presence of As(V)

Sample	As concentration, μg/L				
	Standard solutions analyzed			**Measured**	
	As(III)	As(V)	Total As	Total As±σ	Recovery % As
1	5.00	5.00	5.00	5.20±0.98	104.0
2	10.0	10.0	20.0	10.8 ± 2.5	108.0
3	15.0	15.0	30.0	14.54±2.2	97.0
4	20.0	20.0	40.0	20.5 ± 1.7	102.6
5	22.5	22.5	45.0	22.0 ±0.8	98.0
6	25.0	25.0	50.0	24.4± 2.0	97.6
7	30.0	30.0	60.0	28.5± 1.2	95.0
8	40.0	40.0	80.0	40.9 ± 1.2	102.2
9	50.0	50.0	100.0	48.9 ± 1.9	97.8
10	50.0	100	150.0	49.0± 2.1	98.0
11	10.0	75.0	85.0	10.0± 0.7	100.0
12	75.0	75.0	150.0	75.5±1.0	100.6
13	100.0	100.0	200.0	104 ± 1.5	104.0
14	150.0	150.0	300.0	150 ± 3.8	100.0

Table 4.3 Results of the proposed methods for determination of As(III) by SBAE applied to standard arsenic solutions in the presence different concentration of As(V)

Sample	As concentration, µg/L				
	Standard solutions analyzed			**Measured**	
	As(III)	As(V)	Total As	Total As±σ	Recovery % As
1	5.00	8.00	13.0	5.20±0.98	104.0
2	5.00	10.0	15.0	4.70±0.40	94.0
3	5.00	12.5	17.5	4.85±1.20	97.0
4	5.00	15.0	20.0	4.95±2.00	99.0
5	5.00	20.0	25.0	10.8 ± 2.5	108.0
6	5.00	25.0	30.0	5.15±0.52	103.0
7	5.00	30.0	35.0	5.10±0.70	102.0
8	10.0	5.00	15.0	9.89±1.2	99.0
9	10.0	15.0	25.0	9.80±.85	98.0
10	10.0	20.0	30.0	10.11±1.3	101.0
11	20.0	40.0	60.0	21.0±2.1	105.0
12	50.0	100.0	150.0	50.12±2.3	100.4
13	10.0	5.00	15.00	10.2±1.1	102.0
14	100.0	150.0	250.0	97.5±2.5	97.6

The analytical data of the proposed separation procedure for the two standard arsenic solutions are presented in table 4.4. The concentrations of arsenic species were related to relatively low (sample #1: $C_{As(III)}$ = 10.0 and $C_{As(V)}$ = 30.0 µg/L) and the average concentration (sample #2: $C_{As(III)}$ = 20.0 and $C_{As(V)}$ = 80.0 µg/L) of arsenic found in natural waters. In order to establish the separation procedure, the concentration of As(III) in the effluent was tested by the ICP-MS and HG-AAS technique.

According to the results presented in table 4.4, good agreement between the ICP-MS and HG-AAS measurements was observed in determined of As(III). The standard deviations of the determination of As(III) in the two standard samples by both techniques were in the range from 0.50 to 1.10 µg/L. The maximal relative standard deviation (RSD), was about 5.6%.

Table 4.4 Analytical data of the proposed separation procedure using SBAE resin and determination of As(III) species in standard solutions by the ICP-MS and HG-AAS technique

As measurements				
Standard solution analyzed	#1.		#2.	
	As(III)	As(V)	As(III)	As(V)
Concentrations of standards (µg/L)	10.0	30.0	20.0	80.0
Measured after separation on SBAE, As(III) ICP-MS	10.20		20.4	
Mean				
Standard deviation (µg/L)	0.47		1.10	
%RSD	4.61		5.40	
Confidence limit (t = 2.36 for 95% certainty	10.2±0.39		20.4±0.92	
Measured after separation on SBAE, As(III) AAS-HG				
Mean	9.70		19.7	
Standard deviation (µg/L)	0.50		1.10	
%RSD	5.20		5.60	
Confidence limit (t = 2.36 for 95% certainty)	9.7±0.42		19.7±0.92	

Table 4.5 Results of the proposed methods for determination of As(III) by SBAE applied in modified water

Sample	As content, standard addition	Inorganic ions added, mg/L				**Measured**	
	As(III)	SO_4^{2-}	Cl^-	NO_3^-	HCO_3^-	As(III)±σ	Recovery % As
1	5.00	10.0	10.0	10.0	10.0	5.05±0.3	101.0
2	5.00	25.0	25.0	25.0	25.0	5.2±0.21	104.0
3	10.0	50.0	50.0	50.0	50.0	9.8.±2.5	98.0
4	10.0	100.0	100.0	50.0	150.0	9.86 ±1.0	98.6
5	50.0	100.0	100.0	100.0	110.0	51.5±2.5	103.0

Table 4.5 shows the effect of ions naturally present in water on the efficiency of proposed method and ability to measure the low concentrations of arsenic species. Many experiments has conducted by adding different concentrations of ions to a sample of As(III).

The results showed that there was no effect on the proposed method for determination of As(III) in the presence of common ions in the water until the concentration reached to 100 mg/L for each of the sulfate, chloride, nitrate, and bicarbonate. These results give clear evidence that the proposed method can be applied for different water types.

4.3.2 Concentration, separation and determination of total iAs on HY-Fe resin

4.3.2.1 Preconcentration and determination of total arsenic in deionized water and modified water

The use of HY-Fe resin for preconcentration and determination of total inorganic arsenic species were investigated, in standard solutions by the proposed procedures. The results are presented in table 4.6. The standard solutions of arsenic were prepared by the standard procedure, separation conditions by HY-Fe were: m_{resin} = 6.0 g; temp. = 20 °C; pH = 7.50: Q = 1.66 mL/min, EBV = 12.5 mL, τ = 7.5 min, V_{sample} = 20 mL, n = 5. All standard solutions were measured by ICP-MS and HG-AAS instruments. The concentrations investigated ranged from very low, near to the drinking water (10.0 µg/L) to relatively high (300 µg/L), which are close to real water samples from the Vojvodina region. The ratio between As(III) and As(V) species was 1:1 /or the random concentration ratio between As(III) and As(V) which is also related to real water samples (table 4. 6)

The use of HY-Fe resin provided a high efficiency preconcentration of As(III) and As(V) based on the bonded of iAs species with HY-Fe resin, then the arsenic eluted and measured by ICP-MS / HG-AAS without any matrix interference.

Results show that the method can be efficiency used for determination of iAs with out interference. Also the proposed method can be used to prevent interference of arsenic ions in the case of determination of the other elements.

Analytical data for the preconcentration procedure of all iAs species and for the desorption of arsenic from the HY-Fe resin are presented in table 4.7. The conditions for sorption and desorption of iAs from HY-Fe resin are also listed.

Two standard solutions were prepared with concentrations of arsenic species which were related to extremely low ($C_{As(III)}$ = 2.0 and $C_{As(V)}$ = 8.0 µg/L) and average ($C_{As(III)}$ = 20.0 and $C_{As(V)}$ = 80.0 µg/L) concentrations of arsenic in natural waters. The data shown in table 4.7 confirmed that arsenic species could be efficiently preconcentrated and determined and removed from water.

Table 4.6 Results of the preconcentration and determination of total inorganic arsenic species applied in standard arsenic solutions

Sample	As concentration, μg/L				
	Standard solutions analyzed			**Measured**	
	As(III)	**As(V)**	Total As	Total As±σ	Recovery % As
1	5.00	5.00	10.0	10.1±0.11	101.0
2	5.00	10.0	15.0	15.3±0.23	101.5
3	5.00	50.0	55.0	60.0±2.5	108.0
4	10.0	5.00	15.0	14.6 ±1.2	97.0
5	10.0	100.0	110.0	104.5±3.2	95.0
6	10.0	10.0	20.0	20.2± 1.6	101.0
7	40.0	40.0	80.0	78..0± 0.2	97.5
8	50.0	50.0	100.0	105.8 ± 1.7	105.8
9	50.0	150.0	200.0	200.0± 2.3	100
10	100.0	100.0	200.0	209.0 ± 2.6	104.5
11	150.0	150.0	300.0	296.5± 3.2	98.8
12	100.0	200.0	300.0	297.3±1.8	99.0

Table 4.7 Analytical performance data of the proposed preconcentration procedure using HY-Fe resin and determination of the total concentration of As in standard solutions

As measurements				
Standard solution analyzed	1.		2.	
	As(III)	As(V)	As(III)	As(V)
Concentrations of standards (μg/L)	2.00	8.00	10.0	90.0
Measured after separation on HY resin				
Maen	10.15		105.8	
Standard deviation (μg/L)	0.09		1.70	
%RSD	0.89		1.61	
Confidence limit (t = 2.36 for 95% certainty	10.15 ±0.08		105.8±1.42	

Conditions for desorption from HY-Fe resin: pH> 11.00, *V*-sample =50mL.

The benefit of the removal in the analytical sense is the separation and the possibility to concentrate all arsenic species on a small amount of ion exchange/sorption material (m = 6 g). The content of arsenic bonded to the resin was desorbed by a 1:1 mixture of 1.0M NaOH and

1.0M NaCl solutions using at least 3EBV of solution for evaluation. In this way, an even higher sensitivity was attained; the standard deviation of the arsenic determinations was in the range from 0.09 to 1.70 µg/L. As particulate iron is incorporated in the HY-Fe resin, the concentration of iron in the effluent was also determined by ICP-MS measurements. It was found that the concentration of iron in the effluent was no higher than 1.0 µg/L, proving that iron cannot be easily eluted from the resin.

The effect of ions naturally present in water on the efficiency of proposed method were studied, four samples of modified water were prepared table 4.8, the different concentration of common inorganic ions (SO_4^{2-}, NO_3^-, Cl^- and HCO_3^{1-}) were added to different concentration of As(III) and As(V) species which were related to ($C_{As(III)}$ = 2.0, 5.0, 10.0 and 25.0 µg/L and $C_{As(V)}$ = 5.0, 10.0, 25.0 and 50.0 µg/L).

The result in table 4.8 confirmed that the arsenic species could be efficiently preconcentrated and determined and removed from water in presence of high concentration of inorganic ions. The results were recovered 96.6 – 100 %. The very high efficiency analysis was obtained.

Table 4.8 Results of the proposed methods for determination of total arsenic applied in modified water

Standard solutions analyzed							**Measured Arsenic**	
Sample	As content, standard addition		Inorganic ions added, mg/L				Found in effluent	
	As(III)	**As(V)**	SO_4^{2-}	Cl^-	NO_3^-	HCO_3^-	Total As±σ	Recovery (%)
1	2.00	5.00	25.0	25.0	10.0	25.0	7.0±0.8	100.0
2	5.00	10.0	50.0	50.0	25.0	50.0	14.3±1.0	95.3
3	10.0	25.0	75.0	75.0	50.0	75.0	35.0±2.2	100.0
4	25.0	50.0	100.0	50.0	100.0	100.0	72.5±1.5	96.6

4.3.3 Concentration, separation and determination of oAs on HY-AgCl resin

To validate the proposed method several samples of deionized water were spiked with different iAs and oAs concentrations to check efficacy of the proposed method for determination of organic arsenic species. Procedure was based on the use of standard samples with addition of differents concentration of iAs and (oAs species in the range of 5.0 µg/L to

35 µg/L) to approach concentration of arsenic in natural water. Table 4.9 shows the selected experiments for estimation of the organic arsenic species without any additions of inorganic arsenic species, while the concentration of oAs were lower /higher than concentration of iAs species are presented in table 4.10, which is also related to real water samples. Table 4.11 shows the effect of ions naturally present in water on the determination of oAs.

The separation condition for all experiments were: m_{resin} = 10 g; t= 20 °C; pH = 9.0; Q = 1.25 mL/ min, EBV = 12.5 mL, τ = 7.5 min, V_{sample} = 20 mL, n = 5

The result confirmed that the oAs was not retained on the HY-AgCl resin under the proposed conditions, while the iAs were retained at neutral pH value on the resin. After separation by HY-AgCl only oAs species were present in the water, and can be measured without interference from iAs.

Table 4.9 Analytical data of the separation and determination of total oAs species using HY-AgCl resins in standard solutions without adding inorganic arsenic species

Sample	Standard solutions analyzed: As content standard addition, µg/L					**Measured,**	
	oAs		iAs			Result (µg/L)	Recovery (%)
	DMAs(V)	**MMAs(V)**	As(V)	As(III)	Total oAs	oAs±σ	oAs
1	5.00	5.00	0.00	0.00	10.0	9.80±0.4	98.0
2	5.00	10.0	0.00	0.00	15.0	15.1±0.96	100.6
3	15.0	5.0	0.00	0.00	20.0	20.54±2.2	102.7
4	10.0	10.0	0.00	0.00	20.0	19.3 ±2.5	96.5
5	20.0	15.0	0.00	0.00	35.0	34.0±0.93	97.1

The results in tables 4.9 and 4.10 confirmed that the organic arsenic species could be efficiently determined in presence of high concentration of iAs. The results were recovered 96.0 – 103.3 % and relative standard deviation was 2.2% - 5.6%. The very high efficiency analysis was obtained.

Table 4.10 Analytical data of the separation and determination of oAs species using HY-AgCl resins in standard solutions in the presence of iAs species

Sample	Standard solutions analyzed: As content standard addition, µg/L					**Measured,**	
	oAs		iAs			Result (µg/L)	Recovery (%)
	DMAs(V)	**MMAs(V)**	As(V)	As(III)	Total oAs	oAs±σ	oAs
1	5.00	5.00	10.0	5.00	10.0	9.6±0.44	96.0
2	5.00	5.00	20.0	5.00	10.0	10.2±0.68	102.0
3	10.0	5.00	20.0	10.0	15.0	15.5±1.5	103.3
4	10.0	10.0	40.0	20.0	20.0	19.5 ±1.8	97.5
5	20.0	15.0	50.0	30.0	35.0	35.0±0.33	100.0
6	5.00	5.0	100.0	50.0	10.0	9.85±0.55	98.5
7	5.00	0.00	100.0	50.0	5.00	5.0±0.13	100.0
8	0.00	5.00	100.0	50.0	5.0	5.1±0.13	102.0

In analytical chemistry is important to investigate all the evidence that proves efficiency of the proposed method. The modified water samples were prepared by added the common ions in different concentrations to the oAs. The excremental samples and results were presented in the table 4.11

The results obtained very good recoveries were varied in the range 98-104%. The use of Ag-Cl provides accurate results and low detection limit, which gives a very important feature of the method even in the presence of high concentrations of common ions in natural water.

Table 4.11 Analytical data of the separation and determination of oAs species using HY-AgCl resins in modified water

Sample	Standard solutions analyzed: oAs content standard addition, µg/L		Inorganic ions added, mg/L				**Measured,** Result (µg/L)	Recovery (%)
	MMAs(V)	**DMAs(V)**	SO_4^{2-}	Cl^-	NO_3^-	HCO_3^-	oAs±σ	% As
1	5.00	5.00	25.0	25.0	10.0	25.0	10.0±0.3	100.0
2	5.00	5.00	50.0	50.0	25.0	50.0	9.8±0.21	98.0
3	10.0	5.00	75.0	75.0	50.0	75.0	14.5 ±2.5	97.0
4	10.0	10.0	100.0	50.0	100.0	100.0	20.8±1.0	104.0

4.3.4 Concentration, separation and determination of dimethylarsenate DMAs(V)

Validation of the proposed method for the water, several samples of deionized water were spiked with different iAs and oAs concentrations to check efficacy of DMAs(V) separation and determination. Testing was based on the use of standard samples spiked with iAs and oAs in the concentration range of 5.0 -100 µg/L to approach concentration of arsenic in natural water. The separation condition were pH = 7.5, m_{resin} = 6.0 g, Q = 1.66 mL/min, EBV= 12.5 mL. The results of samples analysis prepared in deionized water, without and with addition of different concentration of DMAs(V), MMAs(V), As(V) and As(III), are shown in Tables 4.12, 4.13 and 4.14.

Table 4.12 Analytical data of the separation and determination of DMAs(V) species using HY-Fe resins in standard solutions

As concentration (µg/L)					**Measured**	
	Standard solutions analyzed				Result (µg/L)	Recovery (%)
Sample	**DMAs(V)**	MMAs(V)	As(V)	As(III)	DMAs(V)±σ	DMAs(V)
1	**5.00**	0.00	0.00	0.00	4.85±0.4	98.0
2	**10.0**	0.00	0.00	0.00	10.1±0.66	101.0
3	**15.0**	0.00	0.00	0.00	15.04±1.4	100.2
4	**25.0**	0.00	0.00	0.00	25.0±2.20	100.0
5	**100 .0**	0.00	0.00	0.00	96.0±1.32	96.0

Results in table 4.12 showed that the good recoveries percentages of 96- 101% were obtained and relative standard deviation RSD were 1.1 to 7.5 % for standards solution 1, 2, 3, 4 and 5. The results of analysis of standard samples prepared in deionized water containing different concentrations of DMAs(V) and MMAs(V) are shown in Table 4.13. Good recoveries were found in the samples at DMAs(V) concentration of 5.0, 10, 50 and 100 µg/L, and relative standard deviation RSD were 3.2, 2.6, 4.6 and 2.4%, respectively.

The results of analysis of standard samples prepared in deionized water containing different concentrations of DMAs(V) MMAs(V), As(V) and As(III) shown in Table 4.14. The results showed that the Good recoveries of 95.0 – 106 % were obtained with relative standard deviation RSD values of 1.69 to 4.4%.

Table 4.13 Analytical data of the separation and determination of DMAs(V) species using HY-Fe resin in standard solutions in the presence of MMAs(V)

As concentration (µg/L)			**Measured**	
	Standard solutions analyzed		Result (µg/L)	Recovery (%)
Sample	**DMAs(V)**	MMAs(V)	DMAs(V) ±σ	DMAs(V)
1	**5.00**	5.00	5.00±0.10	100.0
2	**5.00**	7.50	5.20±0.08	104.0
3	**5.00**	10.0	4.60±0.50	92.00
4	**5.00**	15.0	4.86±0.42	97.20
5	**10.0**	5.00	10.2±1.20	102.0
6	**10.0**	10.0	9.00±0.17	90.00
7	**10.0**	20.0	10.35±1.00	103.50
8	**10.0**	50.0	9.95±1.40	99.50
9	**50.0**	50.0	52.73 ± 2.5	104.5
10	**100.0**	100.0	104.8±2.50	104.8

Table 4.14 Analytical data of the separation and determination of DMAs(V) species using HY-Fe resins in standard solutions containing MMAs(V), As(V) and As(III)

Standard solutions analyzed					**Measured,**	
Sample	As content standard addition, µg/L				Result (µg/L)	Recovery (%)
	DMAs(V)	MMAs(V)	As(V)	As(III)	DMAs(V) ±σ	DMAs(V)
1	**5.00**	5.00	5.00	5.00	4.75±0.06	95.0
2	**5.00**	5.00	10.0	5.00	5.15±0.06	103.0
3	**5.00**	5.00	20.0	10.0	5.21±0.06	104.2
4	**5.00**	10.0	20.0	20.0	4.80±0.20	96.0
5	**5.00**	5.00	50.0	10.0	4.70±0.12	94.0
6	**5.00**	10.0	100.0	20.0	5.10±0.05	102.0
7	**10.0**	10.0	20.0	10.0	10.10±1.2	101.0
8	**20.0**	40.0	100.0	50.0	18.80±0.21	94.0
9	**20.0**	50.0	50.0	50.0	21.33±1.6	106.0
10	**50.0**	20.0	100.0	50.0	52.50±2.2	105.0

The effects of different concentration of ions which are naturally present in water were investigated. The presence of interference ions showed negligible effect on the determination

of DMAs(V) as long as concentration of common ions in water reached to 100 mg/l, the results are presented in table 4.15

Table 4.15 Results of the proposed methods for determination of DMAs(V) applied to modified of water

Sample	Standard solutions analyzed						**Measured**	
	As content, standard addition		Inorganic ions added, mg/L				Found in effluent	
	DMAs(V)	MMAs(V)	SO_4^{2-}	Cl^-	NO_3^-	HCO_3^-	Total As±σ	Recovery (%)
1	2.50	2.50	25.0	25.0	10.0	25.0	2.5±0.2	100.0
2	5.00	5.00	50.0	50.0	25.0	50.0	4.6±0.32	92.0
3	10.0	5.00	75.0	75.0	50.0	75.0	10.2. ±3	102.0
4	25.0	15.0	100.0	50.0	100.0	100.0	25.8±0.8	103.2

The method is simple, easy and achieved good evidence and proof that can use in accuracy determination of very low concentrations of DMAs(V) in different type of liquid sample the method can be used without influence from the other arsenic species

4.4 INTERFERENCES ON DETERMINATION OF iAs AND oAs SPECIES IN WATER

4.4.1 Interference effect on determination of As(III) and As(V)

4.4.1.1 Effect of organic arsenic species

In order to elucidate the influence of oAs species for determination of iAs species some experiments were accomplished with methylated arsenic compounds, MMAs(V) and DMAs(V). The presence of oAs compounds in natural waters is the result of anthropogenic activities and natural sources [20]. The methylated arsenic species are weak acids, they are similar to the iAs species with the respect to the relative stabilities of their oxidation states in the environment. Methylated species of As(V) are stable in oxidized system while methylated species of As(III) are unstable and readily oxidized [156]. The presence of both MMAs(V) and DMAs(V) compounds originate from natural sources, and these oAs compounds are found ubiquitously in surface waters. However, oAs compounds appear to contaminate the groundwater as a result of pesticide use [157]. In this part of work only methylated organic species of oAs(V) were tested as the influence to iAs species separation and determination.

The results obtained with model solutions of iAs and oAs species are presented in Figure 4.10.

- The capacities of both resins (SBAE and HY-Fe) for iAs species, in the presence of oAs species, were not significantly decreased (less than 10%).
- The SBAE resin was efficient in bonding of both tested oAs species. It was observed that MMAs(V) and DMAs(V) have similar sorption behavior to As(V). Maximum adsorption of both species occurs in neutral and base conditions. The adsorption decreases as pH decreases, which corresponds with the prevailing molecular forms of MMAs(V) and DMAs(V) at lower pH:

$$H_2AsO_3CH_3 \rightleftharpoons H^+ + HAsO_3CH_3^- \rightleftharpoons H^+ + AsO_3CH_3^{2-} \quad (4.2)$$

$$HAsO_3(CH_3)_2 \rightleftharpoons H^+ + AsO_3(CH_3)_2^- \quad (4.3)$$

- The HY-Fe resin was efficient for bonded of all arsenic species except for DMAs(V). It was observed that DMAs(V) was not efficiently sorbed under any of the experimental conditions in this study. The smaller amount of DMAs(V) sorption on HY-Fe resin could be ascribed to the additional methyl group and to its molecular geometry which decreases spatial compatibility with surface sorption sites and HFO particles inside the HY-Fe resin.

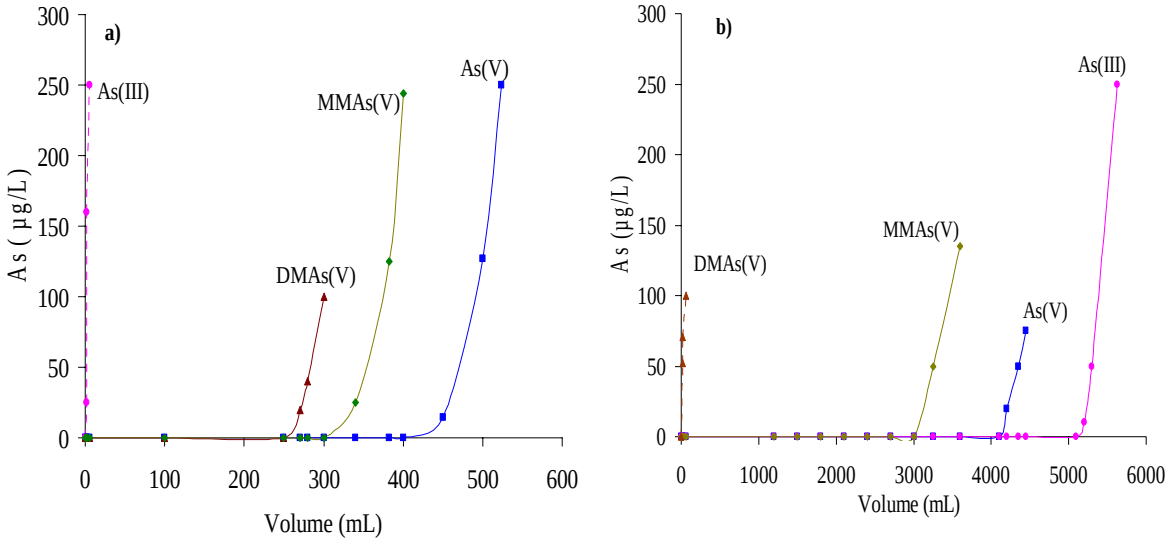

Fig. 4.10 Breakthrough curves for iAs and oAs species in deionized water on a) SBAE and b) HY-Fe resins, Conditions: $C_{As(III)}$) = $C_{As(V)}$ = $C_{MMAs(V)}$ = $C_{DMAs(III)}$ = 5000 µg/L, pH = 7.5, m_{resin} = 6.0g, Q = 1.66 mL/min, EBV = 12.5 mL, n = 3

However in natural samples and water supplies for drinking water, which were the object of interest organic compounds were not observed. However, it can be concluded that in the accidental presence of oAs species in water, the capacities of both resins for iAs species will not be significantly decreased and iAs species could be still determined. For the determination of all arsenic species, iAs and oAs, the other more sophisticated procedures should be applied

4.4.1.2 Effect of Inorganic ions

Sulfate, chloride, hydrogen-carbonate and phosphate ions in water are considered competing ions. The influence of these ions on separation and determination ofAs(III) and as(V) by ion exchange/sorption efficiency was investigated using a model solution containing these ions in the concentration ranges corresponding to those present in tap water. In some tap water matrices, the concentration of these anions was added to tap water were presented in table 4.16. The concentration of inorganic ions were added to tap water from 10 up to 100 mg/L of sulfate, chloride, phosphate and bicarbonate, but the obtained results indicated no significant influence on the capacity of both examined resins for determination of inorganic arsenic species. It was expected that sulfate ions would noticeably decrease the resin efficiencies. However, in the applied sulfate concentration range, the efficiencies of the analyzed resins towards arsenic remained the same, which is particularly beneficial for application with real drinking water samples.

Table 4.16 The concentration (mg/L) of anions in tap water determined by HPLC

Test	TDS	Cl^-	SO_4^{2-}	F^-	NO_3^-	Br^-
Tap water	331.2	15.01	32.92	0.106	3.55	1.074

4.4.2 Interference of inorganic ions on determination of dimethylarsenate DMAs(V)

The ions commonly present in the tap water: chloride, sulfate, fluoride and nitrate could have a potential interference in the proposed analytical method. Study of DMAs(V) separation and determination in presence of ions naturally present in drinking water was investigated using drinking water samples spiked by gradual addition of appropriate anion (Cl^-, SO_4^{2-}, F^- and NO_3^-) in a concentration ranging from 10 to 100 mg/L. Ions interference was studied using a 10 µg/L solution of DMAs(V) spiked with different interference ions concentration, at pH 7.0, in order to find out level of noticeable signal depression table 4.17. Presence of interference ions showed negligible effect on the DMAs(V) determination reproducibility as long as total dissolved salts (TDS) were less than 450 mg/L.

Table 4.17 Concentration of interfering ions in modified tap water samples determined by HPLC

Modified Tap water	Inorganic ions concentration, µg/L					As concentration(µg/L)
	TDS	Cl^-	SO_4^{2-}	F^-	$NO3^-$	**DMAs(V)** ±σ
	450	49.93	68.0	0.179	3.44	**9.5** ±1.1

Interferences such as chloride and sulfate ions could be tolerated up to concentration of 100.0 mg/L. A severe problem associated with the determination of As by ICP-MS is the interference from a polyatomic species at *m*/*z* = 75. The chloride present in the sample reacts with the working gas, resulting in the formation of $^{40}Ar^{35}Cl^+$ (*m*/*z* = 75), the signal which could interfere with those of the As species, leading to inaccurate results. The determination of DMAs(V) in the presence of chloride was accomplished according to the procedure suggested in the literature [148]. Significant signal depression was observed for fluoride and nitrate anion at level of 0.2 and 3.2 mg/L, respectively. These results could not have large influence on the method such as fluoride and nitrate in drinking water are of lower concentration than the detection limit.

4.4.3 Interference of inorganic ions on determination of oAs species

Chloride and sulfate ions in a concentration ranging from 10 to 100 mg/L presented no interferences, for arsenic concentration up to 100 µg/L. The resins also provides the advantage of reducing the chloride ion of the sample in the effluent which reduces the problems with polyatomic species $^{40}Ar^{35}Cl^+$ which could be formed in the plasma and has the same m/z value as naturally occuring ^{75}As isotope. According to this result, the combination of these three resins can be recommended for the separation processes and quantitative determination of iAs and oAs in real water samples.

4.5 EFFECT OF TEMPERATURE ON DETERMINATION OF iAs AND oAs SPECIES

It is important to investigate the effect of temperature on the efficiency of the proposed methods. To find out an efficient method of separation and determination of arsenic species, procedure was based on the use of standard samples which were spiked with differents concentration of arsenic species. The separation procedure conducted several experiments at different temperatures 40°C and 80°C. The results obtained in table 4.18, 4.19, 4.20 and 4.21 showed that, at 40°C there is not any effect or change in quantification analysis of arsenic, the results were covering between 102-106 % for all type of resins, which is not different from

the selection experiments at room temperature. At 80°C, the results for determination of arsenic species were not improved and were not good, due the (degradation of three type of resins) (Figure 4.11.)

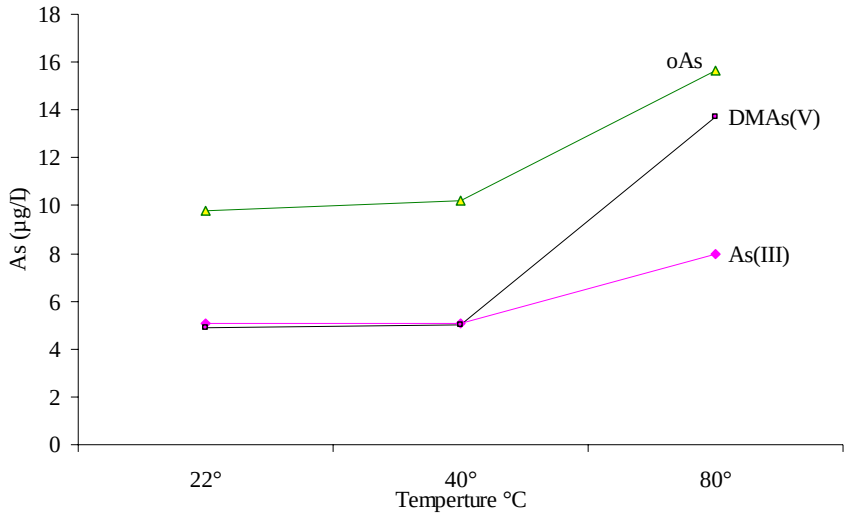

Fig. 4.11 The effect of temperature on determination of arsenic species

Table 4.18 Result for determination of As(III) in standard solution by proposed method using SBAE at different temperatures (40°C and 80°C)

Sample	As content standard addition, µg/L		Measured (40°C) µg/L	Measured (80°C) µg/L
	As(III)	As(V)	As(III)±σ	As(III)±σ
1	**5.00**	5.00	5.10 ±0.22	8.0 ± 0.12
2	**10.0**	10.0	10.5 ±0.65	14.0± 0.69
3	**5.00**	50.0	5.30±0.23	35.7±0.94

Table 4.19 Result for determination of iAs species in standard solution by proposed separation method using HY-Fe at different temperatures (40°C and 80°C)

Sample	As content standard addition, µg/L		Measured (40°C) µg/L	Measured (80°C) µg/L
	As(III)	**As(V)**	Total iAs±σ	Total iAs±σ
1	**5.00**	**5.00**	10..85± 0.13	2.70± 0.6
2	**10.0**	**10.0**	19.90± 0.32	4.4± 0.16
3	**5.00**	**50.0**	55.20±0.23	26.0±2.33

Table 4.20 Result for determination of oAs species in standard solution by proposed method using HY-AgCl at different temperatures (40°C and 80°C)

Sample	As content standard addition, µg/L				Measured(40°C) µg/L	Measured (80°C) µg/L
	MMAs(V)	**DMAs(V)**	As(III)	As(V)	oAs±σ	oAs±σ
1	**5.00**	**5.00**	5.00	5.00	10.0± 0.8	15.7± 0.06
2	**5.00**	**5.00**	10.0	10.0	10.1± 0.42	15.0± 0.88
3	**5.00**	**5.00**	10.0	20.0	9.80± 0.6	28.0±1.12

Table 4.21 Result for determination of DMAs(V) in standard solution by proposed method using HY-Fe at different temperatures (40°C and 80°C)

Sample	As content standard addition, µg/L				Measured, (40°C) µg/L	Measured, (80°C) µg/L
	MMAs(V)	**DMAs(V)**	As(III)	As(V)	DMAs(V) ±σ	DMAs(V) ±σ
1	5.00	**5.00**	5.00	5.00	5.0±0.6	13.7± 0.61
2	5.00	**10.0**	10.0	50.0	10.3±0.22	66.0± 1.23
3	10.0	**25.0**	10.0	50.0	24.55±1.1	76.0± 3.2

4.6 ANALYTICAL PROPERTIES OF NEW PROCEDURES FOR PRECONCENTRATI--ON, SEPARATION AND DETERMINATION OF As(III), As(V), MMAs(V), DMAs(V) SPECIES IN STANDARD SOLUTION

The difference in retaining different arsenic species by three types of resins enables to propose a selective separation method before the measurements of concentration of each arsenic species. The procedure for separation and determination of four arsenic species in water was peformed in two steps.

First step is always the measurement of total inorganic arsenic in samples (C_{As}). It was done directly without adding any reagent (only standard acidification of the sample with 5.0% HNO_3 and filtration) by ICP–MS. The second step comprehends a procedure for separation and determination of arsenic species in water. The scheme for selective separation with

subsequent quantitative measurement of the arsenic species by ICP–MS technique is shown in Figure. 4.12

Separation columns were prepared (diameter of 2.0cm) by packing with three investigated resins (m=6.0 g), and washing with deionized water. Sample of water was adjusted at adequate pH value by using 0.01M HNO_3 or 0.01M NaOH, and passed through the column at flow rate of 1.25–1.66 mL/min. The total volume of the effluent was 100 mL and it was used, with pH adjustment, for injection directly into ICP–MS.

The concentrations of each species was measured directly or calculated by the difference between the total arsenic concentration determined in first step and concentration of species determined in second step. The sampling was performed according to a simple sampling procedure without addition of any reagent for stabilization. Arsenic species in water were stable under neutral conditions for a period of four months if they are placed in polypropylene bottles in a refrigerator. Before all ICP–MS measurements, the samples were acidified with 5.0% HNO_3.

Concentration of As(III) was measured directly in the effluent of SBAE resin. Concentration of DMAs(V) was measured directly in the effluent of HY–Fe resin. Concentration of oAs [MMAs(V) and DMAs(V)] was measured directly in the effluent of HY–AgCl resin. The concentration of As(V) and MMAs(V) were calculated from:

$$C_{MMAs(V)} = C_{oAs} - C_{DMAs(V)} \quad (4.4)$$

$$C_{As(V)} = C_{As} - C_{As(III)} - C_{oAs} \quad (4.5)$$

Where: $C_{As(III)}$ is concentration of As(III) in µg/L, $C_{As(V)}$ is concentration of As(V) in µg/L, C_{oAs} is concentration of organic species of arsenic in µg/L, $C_{MMAs(V)}$ is concentration of MMAs(V) in µg/L, and $C_{DMAs(V)}$ is concentration of DMAs(V) in µg/L.

The developed method was applied for determination of iAs and oAs species in different water samples. In order to be concise the results of wide investigations by proposed procedures with standard solutions are presented in table 4.22.

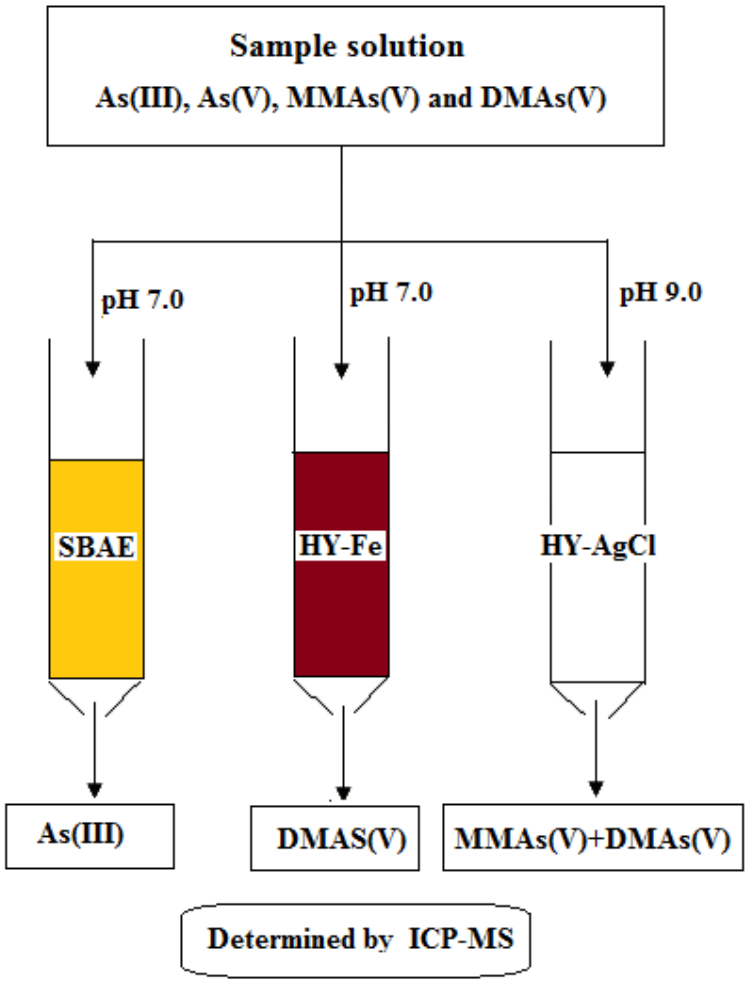

Fig. 4.12 Scheme for selective separation and determination of the arsenic species in water using SBAE, HY-Fe and HY-AgCl resins

Standard arsenic solutions were prepared by standard procedure. The concentrations investigated were very low, closed to MPC in drinking water (10 µg/L). Results presented in table 4.22 confirmed that As(III) as a nonionic species was not retained on the SBAE resin under proposed conditions, whereas As(V) and oAs, which are present as anionic species, are retained on resin. After separation by HY−Fe, only DMAs(V) species were present in the water, while after separation by HY−AgCl resin iAs species were not present in the water, only oAs was confirmed by ICP−MS measurements and calculations.

Good recoveries were found in the samples that contained traces and low concentrations of arsenic up to 5.0 µg/L of DMAs(V) and MMAs(V). The results showed that DMAs(V) and MMAs(V) exist after the separation process and they are not bonded with the HY−AgCl resin at pH less than 9.0, while As(V) and As(III) were bonded with HY−AgCl resin. The RSD for

organic arsenic for total concentration of 10, 15, 20, 25 μg/L was between 1.3–5.1%. The recovery and reproducibility of laboratory blank and spiked samples were good.

Table 4.22 Results of the proposed separation procedure by SBAE, HY-Fe and HY-AgCl resin applied for the standard arsenic solutions. Separation conditions: m_{resin}=6.0 g, temp.=20 ^{o}C, Q=1.25-1.66 mL/min, EBV=12.5 mL, τ=7.5 min, V_{sample}=100 mL, n=5

Sample	As concentration, μg/L						
	Standard solutions analyzed					Found in effluent	
	As(III)	As(V)	MMAs(V)	DMAs(V)	Total As	As±σ	%As
SBAE; pH=7.0							
1	**0.00**	5.0	5.00	5.00	15.0	<0.030	/
2	**5.00**	5.0	5.00	5.00	20.0	5.20±0.25	104
3	**5.00**	10.0	5.00	5.00	25.0	4.80±0.18	96.0
4	**10.0**	5.0	5.00	5.00	25.0	10.62±0.24	105
5	**10.0**	10.0	10,0	10.0	40.0	9.50±0.35	95.0
6	**5.00**	25.0	5.00	5.00	40.0	5.05±0.22	101.0
HY-Fe; pH=7.0							
1	5.00	5.00	5.00	**0.00**	15.0	<0.030	/
2	5.00	5.00	5.00	**5.00**	20.0	4.75±0.80	95.0
3	5.00	5.00	5.00	**10.0**	25.0	10.64±0.41	106
4	10.0	5.00	5.00	**5.00**	25.0	5.06±0.12	100.0
5	10.0	10.0	10,0	**10.0**	40.0	9.60±0.43	96.0
6	25.0	25.0	10.0	**5.00**	65.0	5.05±0.11	101.0
HY-AgCl, pH=9.0							
1	5.00	5.00	**0.0**	**0.00**	10.0	<0.030	/
2	5.00	5.00	**5.0**	**5.00**	20.0	9.77±0.27	97.7
3	5.00	5.00	**5.0**	**10.0**	25.0	15.60±0.54	104
4	10.0	5.00	**5.0**	**5.00**	25.0	10.53±0.44	105
5	10.0	10.0	**10,0**	**10.0**	40.0	18.75±0.95	93.7
6	1.00	1.00	**10.0**	**15.0**	27.0	23.00±2.00	92.0
7	5.00	5.00	**10.0**	**15.0**	35.0	25.0±1.21	100.0

4.7 ANALYTICAL PROPERTIES OF NEW PROCEDURES FOR PRECONCENTRATI--ON, SEPARATION AND DETERMINATION OF ARSENIC SPECIES IN REAL DRINKING WATER AND RIVER WATER

After evaluating the main features of the proposed speciation procedure, its application to the analysis of tap water and drinking water samples from the Vojvodina region, known as region in which underground waters have an appreciable arsenic content, was performed. The samples were analyzed without any previous stabilization or preservation. The method of standard addition was applied; each sample was analyzed twice, with and without spiking. Standard solutions of both arsenic species were added as presented in table 4.23, 4.24 and

4.25. The standard addition method is useful because some unknown variations of the matrix can be prevented, and it was suggested in some studies [146,158].

Table 4.23 Results of arsenic analysis of real water samples by the proposed separation method using SBAE resin, n = 3

Sample	As content [a] Standard addition (µg/L)		**Measured**			
			Result, (µg/L)		Recovery (%)	
	As(III)	**As(V)**	As(III)±σ	As(V)±σ	As(III)	As(V)
Tap water # 1	<0.02	0.55	1.03±0.06	1.59± 0.08	103.0	102.5
Added	1.00	1.00				
Tap water # 2	<0.02	0.55	5.20±0.36	5.45±0.2	104.0	98.0
Added	5.00	5.00				
Tap water # 3	<0.02	0.55	5.14±0.1	10.95 ± 0.09	102.8	103.7
Added	5.00	10.0				
Modified tap water # 1	<0.02	0.55	0.98±0.09	1.50± 0.02	98.0	97.0
Added	1.00	1.00				
Modified tap water # 2	<0.02	0.55	5.05±0.2	4.59± 0.05	101.0	92.0
Added	5.00	5.00				
Well #1, Zrenjanin	145.0	70.0	150.5±2.6	81.6± 1.09	97.1	102.0
added	10.0	10.0				
Well #2, Zrenjanin	15.0	100.0	25.25±2.0	105.65± 1.15	101.0	96.1
added	10.0	10.0				
Lake Palic	22.0	75.0	30.05±2.06	86.2± 1.09	94.0	101.4
added	10.0	10.0				
Well#1, Obrovac	14.2	70.0	23.08±2.30	82.0±1.10	95.4	102.5
added	10.0	10.0				

[a] The values were previously determined by HG-AAS

4.7.1 Application of proposed methods for determination of As(III) and As(V) in real drinking water and river water

All analyzed samples were from the Vojvodina region. The determination of the arsenic in the samples presented in table 4.23, showed different levels of arsenic; sample #1 had about 1.0 µg/L, but the other samples contained higher amounts. It is notable that the mass balance for the total arsenic was the sum of the two arsenic species found by the AAS-HG technique.

Good recoveries were found in the samples that contained traces and low concentration of arsenic species. Smaller recoveries for As(III) species in some samples could be due to the possible oxidization of As(III) to As(V). The recovery for As(V) was always higher than for As(III) species. The recovery and reproducibility of laboratory blank and spiked samples were good. No interference effects were observed in the studied natural water samples.

With this simple procedure, analysts obtain a good insight into status of arsenic species in water samples. This represents a great improvement compared with direct ICP-MS measurements, which gives only data of the total arsenic concentration. This method can be recommended for speciation analysis when appropriate equipment for highly sophisticated coupled techniques are not available. The proposed procedure can be adapted for on site collection or separation of As(III) and As(V) prior to their determination in laboratories.

4.7.2 Application of proposed method for determination of organic arsenic oAs species in real drinking water

The results of the arsenic species analysis of real water samples are presented in table 4.24. It is noticeable that the mass balance for the total arsenic was the sum of the four arsenic species. The results indicate different levels of arsenic; tap water had less than 0.52 µg/L, but other samples contained higher amounts of arsenic.

Good recoveries were found in the samples that contained traces and low concentration of arsenic up to 5.0µg/L. The presence of oAs compounds was observed only in one sample, it was wastewater sample, and the presence of oAs is the result of anthropogenic activities. oAs is very rarely present in natural waters [159].

The recovery and reproducibility of laboratory blank and spiked samples were good. No interference effects were observed in the water samples analysis. With this simple procedure, analysts obtain a good insight into status of organic arsenic species in water samples. This represents a great improvement compared with direct ICP–MS measurements, which gives only data of the total arsenic concentration. This method can be recommended for speciation analysis when appropriate equipment for highly sophisticated coupled technique is not available.

Table 4.24 Results of arsenic speciation analysis of real water samples by proposed separation method using SBAE, HY-Fe and HY-AgCl resins

Sample	Arsenic concentration, µg/L			
	Arsenic species			
	As(III)	**As(V)**	**MMAs(V)**	**DMAs(V)**
Tap water ±σ	<0.030	0.52±0.06	<0.030	<0.030
Added	5.00	5.00	5.00	5.00
Measured ±σ	4.55±0.15	5.34±0.25	4.63±0.28	4.42±0.20
Recovery %	91.0	96.0	92.4	88.4
Lake water	23.40±1.05	72.00±2.95	<0.030	<0.030
Added	10.00	10.00	5.00	5.00
Measured	33.90±1.12	80.10±3.16	4.80±0.50	4.62±0.83
Recovery	101.5	97.6	96.0	92.4
Well water ±σ	15.20±0.78	55.00±1.18	<0.030	<0.030
Added	10.00	10.00	5.00	5.00
Measured ±σ	25.60±2.03	65.80±2.98	4.80±0.05	4.58±0.09
Recovery	102.4	101.2	96.0	91.6
Wastewater ±σ	98.30±3.75	110.5±5.15	0.58±0.030	<0.030
Added	10.00	10.00	5.00	5.00
Measured ±σ	110.7±4.05	122.5±6.43	4.54±0.09	4.76±0.06
Recovery	102.2	101.6	90.8	95.2

4.7.3 Application of proposed method for determination of dimethylarsenate DMAs(V) in drinking water

The proposed method has been applied to drinking water samples in order to separate and determine DMAs(V). In table 4.25 are presented the results of DMAs(V) determination in drinking water samples spiked with different concentrations of arsenic species. The standard addition method is useful because some unknown variations of the matrix can be prevented and this was suggested in some studies [146,158] because no water samples with known concentrations of various arsenic species were available, the accuracy of the analytical results was evaluated by recovery studies. The table 4.25 illustrated that the recovery and

reproducibility of tap water samples and modified water were good, with RSD values of 3.9 to 5.4%.

Table 4.25 Analytical data of the determination of DMAs(V) species using HY-Fe and SBAE resins in tap water and Modified tap water containing MMAs(V), As(V) and As(III)

Standard solutions analyzed					**Measured**	
Sample	As content standard addition, µg/L				(µg/L)	Recovery (%)
	DMAs(V)	MMAs(V)	As(V)	As(III)	DMAs(V) ±σ	DMAs(V)
Tap water 1	5.00	5.00	5.00	5.00	4.55±0.05	91.0
Tap water 2	5.00	5.00	10.0	5.00	5.15±0.2	103
Tap water 3	10.0	10.0	100	10.0	9.95±1.1	99.5
Tap water 4	10.0	50.0	100	50.0	10.0±0.2	100.0
Tap water 5	50.0	50.0	100	50.0	48.1± 1.0	96.2
Modif. tap water # 1	50.0	50.0	100	50.0	53.3±2.8	106.6
Modif. tap water # 1	5.00	5.00	50.0	10.0	5.05 ±1.0	101.0
Modif. tap water # 3	10.0	10.0	50.0	10.0	10.11±0.9	101.1
Modif. tap water # 4	5.00	5.00	5.00	5.00	4.85±0.5	97.0

V CONCLUSION

V CONCLUSION

The aim of the thesis was the development and application of hybrid sorbents for determination of arsenic species and selective removal of arsenic from water. Water soluble arsenic species in natural water are inorganic (iAs) species as arsenite, As(III) and arsenate, As(V). As a result of anthropogenic pollution in water can be present organic (oAs) species as monomethilarsenic acid, MMAs(V) and dimethylarsenic acid, DMAs(V). Each method developed for iAs species should consider and solve oAs species as interferences for the iAs determinations.

In the frame of these tasks efficiency of three types of resins were investigated: a strong base anion exchange (SBAE) resin and two hybrid (HY) resins, HY-Fe which integrates sorption activity of hydrated iron oxides (HFO) with the anion exchange function and HY-AgCl which integrates effects of chemical reaction the anion exchange function. Two systems were employed: a batch and a fixed bed flow system. The selective bonding of arsenic species on three types of resins makes possible the development of the procedure for measuring, and calculation of all arsenic species in water. In order to determine capacity of resins the preliminary investigations were performed in batch system and fixed bed flow system. Resin capacities were calculated according to breakthrough points in a fixed bed flow system which is the first step in designing of solid phase extraction (SPE) module for arsenic speciation separation and determination.

The main achievement of thesis is that three methods for arsenic species determination were developed.

A method for preconcentration, separation and determination of iAs species in natural and drinking water is the first method. This method is based on the selectivity of two types of resins, the strong base anion exchange, SBAE, and the hybrid resin, HY. HY resins integrates the anion exchange function with sorption and chemisorption. The HY-Fe integrates the anion exchange function with sorption on hydrated iron oxides (HFO). The separation of As(III) and As(V) species on SBAE resin was accomplished by adjusting the acidity of water samples to a pH less than 8.00; ionic forms of As(III) were bonded while molecular forms of

As(V) were retained in water. The preconcentration of all iAs species was accomplished with HY-Fe resin.

A method for separation and determination of iAs and oAs species is a second method. This method is based on the application of three types of resins, an anion-exchange, SBAE and two hybrid resins: HY-Fe and HY-AgCl. The SBAE resin was convenient for the separation of As(III) from As(V) and oAs species. The concentration of As(III) can be measured directly in the effluent of the SBAE resin, while anionic forms of other arsenic species were retained on SBAE resin. The HY-Fe resin was convenient for the separation of DMAs(V) from all other arsenic species, which were retained on the HY-Fe resin that has a high sorption capacity for the arsenic species, 9000 µg/g. The concentration of DMAs(V) can be measured directly in the effluent of the HY-Fe. A new hybrid resin, the HY-AgCl resin, was synthesized in our lab and it was effective for iAs and oAs analytical separation. The concentration of oAs was measured directly in the effluent of the HY-AgCl. Concentrations of As(V) and MMAs(V) were calculated.

The third method is a simple and efficient method for separation and determination of dimethylarsenate DMAs(V). Two resins, SBAE and HY-Fe were tested. By simple adjusting pH value of water at 7.0, DMAs(V) passed through the HY-Fe column without any changes, while all other arsenic species (inorganic arsenic and monomethyl-arsenate, MMAs(V)) were quantitatively bonded on HY-Fe resin. The resin capacity was calculated according to the breakthrough points in a fixed bed flow system. At pH 7.00 the HY-Fe resins bonded more than 4150 µg/g of As(III), 3500 µg/g of As(V) and 1500 µg/g of MMAs(V). Arsenic adsorption behavior in the presence of impurities showed tolerance with the respect to potential interference of anions commonly found in natural water. DMAs(V) was determined in the effluent by ICP-MS. The detection limit was 0.03 µg/L and relative standard deviation (RSD) was between 1.1-7.5 %.

The separation and preconcentration procedures were well coordinated with the ICP-MS technique for a sensitive determination of the total As concentration and iAs and oAs species at low µg/L. Measurements with certified reference materials proved that the measurements of arsenic species concentrations in model solutions and real samples were in agreement with the certified values.

With the proposed separation and preconcentration procedures, satisfactory results of the analysis of As species in water were obtained. Methods could be applied routinely for monitoring arsenic levels in various water samples: fresh natural, drinking water and wastewater. The proposed procedures showed themselves to be accurate, precise and time efficient, as just a very simple sample treatment is required. Speciation analysis can be realized through implementation of adequate non-chromatographic separation procedures, standard methods and highly sophisticated equipment for detection.

FUTURE WORK

The work presented in the thesis provides a good foundation for many studies involving sorbents for selective bonding of arsenic species. Past works have shown that iAs species can be separated simply by acidification of water. It would be interesting for future studies to investigate selective sorbents for total removal of all arsenic species and some new sorbent for specific removal of only one arsenic species without preparing the pH value of water. It would be very interesting to develop the procedure for encapsulating the sorbent particles in order to reuse sorbent. Open question is how to dispose sorbent saturated by arsenic species. Arsenic studies would be an excellent way to investigate the question of integrated process for removal of arsenic. Furthermore, since aqueous arsenic concentrations are so low after reaction with sorbent, it is critical to establish a low method detection limit to obtain a high degree of certainty in experimental results for all arsenic species.

VI. REFERENCES

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BIOGRAPHY

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1. Analysis of " water, inorganic compound, soil, concrete, metals and alloys using different methods as classical and instrumentation
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3. Special study in pollution Caused by heavy metals in traffic, drinking water and sea water
4. Evaluation of natural silica in Abo-Gelan south of Tripoli and its uses
5. Nitrate analysis in drinking water (South of Tripoli)
6. Teaching courses program in "Analytical chemistry,

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8. N.B. Issa, Lj. Rajaković, Efficiency of ion exchange resins for arsenic removal from water, European Conference on Analytical Chemistry, Euroanalysis, Innsbruck, 2009, P079-B2

Прилог 1.

Изјава о ауторству

Потписани-а Mr NUREDDIN A. BEN ISSA

број индекса _____

Изјављујем

да је докторска дисертација под насловом

RAZVOJ I PRIMENA HIBRIDNIH SORBENATA ZA ODREĐIVANJE I SELEKTIVNO UKLANJANJE ARSENA(III) i ARSENA(V) IZ VODE

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- резултат сопственог истраживачког рада,
- да предложена дисертација у целини ни у деловима није била предложена за добијање било које дипломе према студијским програмима других високошколских установа,
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- да нисам кршио/ла ауторска права и користио интелектуалну својину других лица.

Потпис докторанда

У Београду, 03. 12. 2012

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Прилог 2.

Изјава о истоветности штампане и електронске верзије докторског рада

Име и презиме аутора _____**NUREDDIN A.A. BEN ISSA**

Број индекса _____

Студијски програм ANALITIČKA HEMIJA

Наслов рада _____**THE DEVELOPMENT AND APPLICATION OF HYBRID SORBENTS FOR DETERMINATION AND SELECTIVE REMOVAL OF ARSENIC(III) AND ARSENIC(V) FROM WATER**_____

Ментор _____**Ljubinka Rajaković, professor of TMF, Thesis Supervisor**_____

Потписани/а Rajaković Ljubinka

Изјављујем да је штампана верзија мог докторског рада истоветна електронској верзији коју сам предао/ла за објављивање на порталу **Дигиталног репозиторијума Универзитета у Београду.**

Дозвољавам да се објаве моји лични подаци везани за добијање академског звања доктора наука, као што су име и презиме, година и место рођења и датум одбране рада.

Ови лични подаци могу се објавити на мрежним страницама дигиталне библиотеке, у електронском каталогу и у публикацијама Универзитета у Београду.

Потпис докторанда

У Београду, 3.12.2012.

Прилог 3.

Изјава о коришћењу

Овлашћујем Универзитетску библиотеку „Светозар Марковић“ да у Дигитални репозиторијум Универзитета у Београду унесе моју докторску дисертацију под насловом:

RAZVOJ I PRIMENA HIBRIDNIH SORBENATA ZA ODREĐIVANJE I SELEKTIVNO UKLANJANJE ARSENA(III) i ARSENA(V) IZ VODE

која је моје ауторско дело.

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У Београду, 03. 12. 2012.