

Speciation of inorganic arsenic and selenium in contaminated ground water samples collected from two areas (Alkermiah and Al-Sawani) in Tripoli-Libya

A. Etoriki , A. Elgahii and M.El Rais

Department of Chemistry, Faculty of Science, Tripoli University, Tripoli, Libya

Abstract

This work deals with the assessment of the arsenic and selenium concentration levels in ground water in two districts of Tripoli, Libya. The study conducted from March 2009 to January 2010 and 14 samples of ground water were collected and analyzed every two months using inductively coupled plasma optical emission spectroscopy (ICP-OES). A novel absorbent was prepared by 1,3-dimercapto propane sulphonic acid chemically modifying mesoporous titanium dioxide nanoparticles and was employed as micro column packing material for simultaneous speciation of inorganic arsenic and selenium species. As and Se species could be adsorbed quantitatively on 1,3-dimercapto propane sulphuric acid modified TiO₂ nanoparticles within a pH range of 3-7 and only As(III) could be quantitatively retained on the column within a pH of 10 while As(V) and Se(IV) were passed through the column without the retention. The results show that arsenic levels in ground water varied from 1.05 to 31.08 ng/ml with a mean value of 4.5 ± 0.34 , which is high than the recommended World Health Organization (WHO) guidelines of 10 ng/ml for drinking water in some ground water samples. The data generated in this study will provide base line values for monitoring arsenic concentrations in ground water in surveyed area.

Keywords: Speciation of arsenic, speciation of selenium, micro column packing, TiO₂ nanoparticles, 1,3-dimercapto propane sulphonic acid, ICP-OES

1 Introduction

Water pollution has become a serious problem nowadays. Both the environment and human beings are exposed to different pollutants (organic pollutants, metal ions, etc.) from waste and potable water. The enormous damage caused by water pollution have led to numerous investigations having as their objective the protection of the threatened environment and living systems through new methods. In recent years, arsenic has been extensively used in pharmaceutical products, alloys, glass fire retardants, pharmacy and semiconductors. They inevitably entered the environmental and caused environmental pollution [1]. The toxicological and physiological behavior of this element is known to depend on their oxidation state and chemical form. In natural waters, arsenic exists predominantly in inorganic form, as trivalent arsenite, As (III), and pentavalent arsenate, As (V), while organic forms of arsenic are rarely quantitatively important [2]. Actual valence states of arsenic depend on the redox environment in water systems. Pentavalent arsenic is more prevalent in surface water while trivalent arsenic is more likely to occur in anaerobic ground waters [3].

The stability and dominance of arsenic compounds depend directly on the pH of the solution. Pentavalent arsenic is stable at pH 0-2 as neutral H_3AsO_4 , while $\text{H}_2\text{AsO}_4^{2-}$, HAsO_4^- , AsO_4^{3-} exist as stable species in the pH intervals 3-6, 7-11 and 12-14, respectively. Selenium is an important trace element in biological systems by being both an essential nutrient at low concentrations and a toxic substance at higher levels. Recent evidence indicates that consumption of selenium in excess of the Recommended Dietary Allowance (RDA) may provide substantial cancer-protective benefits for humans [4]. In recent years, many modern instrumental techniques including electrochemical analysis [5], atomic absorption spectrometry (AAS) [6], atomic fluorescence spectrometry (AFS) [7], inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) [8] have been employed for the determination of As(III), As(V) and Se(V). Among these techniques, ICP-MS is the most widely employed because of its highest analytical sensitivity. However, direct determination of arsenic by ICP-MS is often difficult due to the complexity of sample matrix and the low concentrations of arsenic in water samples. Therefore, a number of simple, sensitive and low cost speciation methods have been used for arsenic and selenium speciation. These include solid phase extraction (SPE) [9], solvent extraction [10], coprecipitation [11], and voltammetry method, the aim of this work is to use a new absorbent of 1,3-dimercapto propane sulphuric acid chemically modified mesoporous TiO_2 for simultaneous preconcentration of inorganic As and Se species and to use micro column and ICP-OES detection for simultaneous speciation of inorganic As and Se at ng ml^{-1} levels in ground water samples collected from Two Areas (Alkermiah and Al-Sawani) in Tripoli-Libya by using the novel absorbent as micro column packing material.

2 Experimental

2.1 Apparatus

ICP-OES instrument model (5200 Perkin Elmer, USA) with a concentric model nebulizer and a cinnabar model spray chamber was used for the determination. A WTW digital pH/mV meter (model pH-340-A/SET2) with a combination glass electrode (WTW D82362 Weiheim) was used for all pH measurements. Self made poly tetrafluoro ethylene (PTFE) micro-column (20 mm × 4.0 mm i.d.) packed with 1,3-dimercapto propane sulphuric acid (DMPSA) modified mesoporous titanium dioxide was used in the on-line separation/preconcentration process.

2.2 Standard solution and reagents

All reagents used were analytical-reagent grade. The stock standard solutions (1000 mg L⁻¹) of As(III), As(V) and Se(IV) were prepared by dissolving appropriate amounts of NaAsO₂ (sigma, USA), NaAsO₃ (sigma, USA), NaSeO₃ (Merck, Germany) in high purity water, respectively. Working solutions were prepared daily by appropriate dilutions of stock solutions. High purity deionized water was used throughout. Mesoporous TiO₂ was prepared in our laboratory, and the details on its synthesis and characterization were described in [12]. To avoid contamination, all the containers before use were treated with 10% HNO₃ for 24 h, rinsed well with high purity deionized water, and dried at room temperature.

2.3 Synthesis of 1,3-dimercapto propane sulphuric acid modified TiO₂

Ten gram mesoporous TiO₂ was added to 100 ml 4.5 mol L⁻¹ HCl and refluxed for 10 h at 60°C with the stirring of a magnetic stirrer. Then, the mesoporous TiO₂ was filtrated with a 0.42 µm membrane, washed with high purity deionized water and ethanol for several times and dried in vacuum. 3.0 g of the activated mesoporous TiO₂ powder was immersed into 50 mL of toluene with 2 g of DMPSA, and reacted for 8 h at 60°C under the protection of N₂. After that, the mesoporous TiO₂ was filtrated with a 0.42 µm membrane again and the resulting powder was washed several times with water and ethanol and dried in vacuum for future use.

2.4 Micro column preparation

A total of 50 mg 1,3-dimercapto propane sulphuric acid modified mesoporous TiO₂ was filled into a PTFE micro-column (20 mm × 2.0 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, ethanol

and high purity deionized water were passed through the column in sequence in order to clean it.

2.5 Sample preparation

Ground water samples were collected in acid-leached polyethylene bottles. The ground water samples were filtered through the filters of 0.42 μm . The ground water samples and standard samples were adjusted to appropriate pH with 0.01 mol L⁻¹ HCl and NH₄OH and immediately analyzed.

2.6 General Procedures

The solution was passed through the column by using a peristaltic pump at the desired flow rate. Afterwards, eluent was passed to elute the analytes. Finally, the analytes in the effluents were determined by ICP-OES. The recoveries of the elements were calculated from the ratio of the concentration found by ICP-OES to that of the initial sample.

High purity deionized water was chosen as the blank solution. The determined values for inorganic arsenic and selenium species were obtained after subtracting the blank values.

3 Results and discussion

3.1 The effect of pH

pH value plays a key role in the SPE procedure. An appropriate pH value cannot only improve the adsorption efficiency, but also depress the interference of the matrix. The adsorption behavior of various species of inorganic As and Se on DMPSA modified titanium dioxide was studied according to the general procedure. Fig. 1 is effect of pH on the adsorption (R%) of inorganic As and Se species on DMPSA modified TiO₂. It can be seen that both trivalent and pentavalent of inorganic As and Se(IV) species are adsorbed quantitatively on DMPSA modified TiO₂ within a pH range of 4–7. When pH =7, the adsorption percentage of As(V) and Se(IV) decreased rapidly and almost no adsorption was observed after pH increased to pH 6 for As(V) and pH 4 for Se(IV), while a quantitative adsorption was kept unchanged for As(III) with the increase of pH to 11. This means that only As (III) can be quantitatively adsorbed by the DMPSA modified TiO₂ within a pH range of 10–11 while As(V) and Se(IV) cannot be retained on the column. Hence, simultaneous speciation of inorganic As and Se can be achieved. For further

experiments, pH 6.0 was chosen for preconcentration of As (V) and pH 4.0 for Se(IV) and pH 10 was selected for speciation of As(III).

3.2 The optimization of elution conditions

From Figure. 1, it was found that the adsorption of these target analytes was negligible at high pH value. For this reason, various concentrations of NaOH were tested to elute the adsorbed target analytes. It was found that 0.5 mol L^{-1} NaOH was sufficient for quantitative recovery of all the target species.

The elution volume and the elution flow rate could affect the elution efficiency remarkably. By keeping the eluent concentration of 0.5 mol L^{-1} NaOH, the influence of the elution volume on recovery for triplicate determination of the target analytes at concentration of $0.1 \mu\text{g mL}^{-1}$ was investigated. The result shows that 0.8 mL of 0.5 mol L^{-1} NaOH was sufficient for quantitative elution. Thus the eluent concentration of 0.5 mol L^{-1} NaOH, elution volume of 0.8 mL and the elution flow rate of 1 mL min^{-1} were used in all experiments.

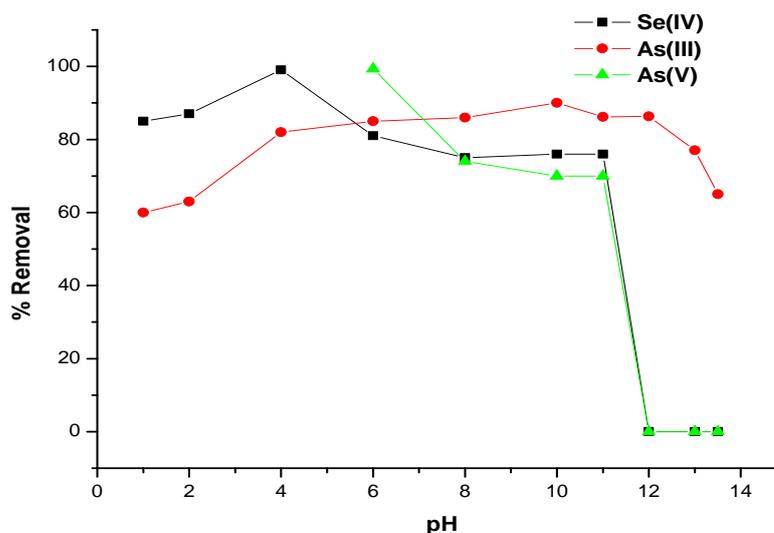


Figure 1 : The effect of pH on the adsorption (% Removal) for the As(III), As(V) and Se(IV) on DMPSA modified TiO_2 , the concentration of target analyte is $0.5 \mu\text{g mL}^{-1}$.

3.3 The effect of sample flow rate and sample volume

In order to obtain higher enrichment factor, a large volume of sample solution is required. It was found that quantitative recoveries for all target species were obtained when sample volumes were less than 60 ml. So an enrichment factor of 50 can be achieved by this method. A sample volume of 40 ml was used for gaining high enrichment factor.

3.4 Adsorption capacity and regeneration

Adsorption capacity is an important factor to evaluate the property of the adsorption material, because it determines how much DMPSA modified TiO₂ is required to quantitatively concentrate the analytes from a given solution. The method used for capacity study was adapted based on the method recommended by Maquieira et al. [13], and the maximal adsorption capacities for As(III), As(V) and Se(IV), are 2.4, 5.3 and 3.6 mg g⁻¹ respectively. The regeneration is one of the key factors in evaluating the performance of the adsorption material. It is imperative to investigate the change in the adsorption capacity of modified mesoporous TiO₂ after several adsorption/elution steps. In this work, it was found that the DMPSA modified TiO₂ is stable with long column lifetime, enabling more than 25 loading and elution cycles to be performed without the loss of analytical performance.

3.5 Analytical Performance

Under the optimized operating conditions, a preconcentration time of 4 min and elution time of 48 s with enrichment factor of 10 and sampling frequency of 10 h⁻¹ were obtained by using this method. The relative standard deviations (RSDs, n = 7, C = 20 ng ml⁻¹) of As(III, V) and Se(IV)) are 4.4%, 1.7% and 3.2%, respectively.

3.6 Sample analysis

In order to establish the validity of the proposed procedure, the method has been applied to the determination of the content of As(III, V) and Se(IV)) in standard water samples (GSBZ5004-88, GBW(F)08332, and the analytical results are listed in Table 1. As can be seen, a good agreement between determined values and the certified or reference values could be obtained. The method was also applied to the simultaneous speciation of dissolved inorganic arsenic and selenium in ground water samples and the analytical results are given in Table 2. As can be seen, the results for As(III) in ground water samples were found high in some samples than the recommended World Health

Organization (WHO) guidelines of 10 ng/ml for drinking water. For As(V) and Se(IV) is below the recommended World Health Organization (WHO) guidelines of 10 and 60 ng/ml, respectively for drinking water.

Table1: Determination of As and Se in certified reference materials (mean \pm SD, n =3)

Sample	species	Certified ($\mu\text{g/ml}$)	Found ($\mu\text{g/ml}$)
GSBZ-5004-88	As(III)	0.0479 \pm 0.0025	0.0452 \pm 0.0021
	As(V)	0.034 \pm 0.004	0.030 \pm 0.004
GBW(F)08332	Se(IV)	4.15 \pm 0.35	3.99 \pm 0.24

The low detection limit obtained in this method is 1.05 \pm 0.1 (ng/ml) for As(III), 0.92 \pm 0.05(ng/ml) for As(V) and 1.03 \pm 0.1(ng/ml) for Se(IV).For comparison, the LODs of some other methods reported in literatures [13] using solid phase extraction for inorganic arsenic and selenium. As can be seen, the LODs of this method were comparable with that obtained by other established methods. However, it should be noted that LODs reported in the literatures are all obtained for single element determination of As or Se, while the LODs in this work are obtained for simultaneous speciation of inorganic As and Se.

Table2: Analytical results for As(III), As(V) and Se(IV) in ground water samples in Alkermiah and (Al-Sawani) sites (mean \pm SD, n=4)

Ground water samples	As(III) ng/ml	As(V) ng/ml	Se(IV) ng/ml
Plastic factory (Alkermiah)	3.1 \pm 0.04	1.1 \pm 0.02	1.03 \pm 0.1
Farm next to the National Company for Flour Mills and Fodder (Alkermiah)	4.2 \pm 0.21	0.92 \pm 0.05	7.25 \pm 0.55
Iron and steel plant (Alkermiah)	12.33 \pm 0.76	1.33 \pm 0.18	4.12 \pm 0.22
Power Plant (Alkermiah)	1.53 \pm 0.08	1.1 \pm 0.08	1.11 \pm 0.41
Libyan Moroccan Company for soap and cleaning materials	24.10 \pm 1.03	2.05 \pm 0.32	9.05 \pm 2.43
Saraya for tile factory	5.10 \pm 0.36	1.09 \pm 0.22	50.10 \pm 3.09
Libyan Store for oil	3.67 \pm 0.16	1.80 \pm 0.07	2.65 \pm 0.14
Farm next to Plant Litter (Al-Sawani)	25.33 \pm 2.09	2.08 \pm 0.16	5.79 \pm 0.31
Concrete columns plant (Al-Sawani)	10.85 \pm 3.02	4.06 \pm 0.53	18.2 \pm 0.64
Farm next to furniture Factory (Al-Sawani)	31.08 \pm 4.11	6.55 \pm 1.11	57.03 \pm 6.04
Fodder Factory (Al-Sawani)	3.22 \pm 0.72	1.04 \pm 0.19	9.05 \pm 1.05
Marble Factory (Al-Sawani)	3.01 \pm 0.05	1.50 \pm 0.30	25.2 \pm 0.58
National Company for Mills and Fodder (Al-Sawani)	1.05 \pm 0.11	0.98 \pm 0.04	2.11 \pm 0.08

Conclusions

DMPSA modified TiO₂ was synthesized and used as the micro column packing material for simultaneous speciation of inorganic As and Se. Compared with most of the analytical methods for the speciation of As and Se, the advantages of this method can be summarized as follows:

- (1) DMPSA modified TiO₂ is an efficient adsorption material for simultaneous speciation of inorganic arsenic and selenium in ground water samples.
- (2) No chelating agent was added in the process of separation, preventing the potential transformation of speciation and reagent blank.
- (3) This method is applied to ground water samples collected from two areas Alkermiah and Al-Sawani in Tripoli-Libya and give very good results and very low concentrations of inorganic arsenic and selenium (ng/ml).

References

- [1] Gebel.T, Arsenic and antimony: comparative approach on mechanistic toxicology,. *Chem.Biol.interact.*, **107**, pp. 131-144, 1999.
- [2] Bissen M, Frimmel FH, Arsenic – a review.Part1.Occurance, toxicity, speciation, mobility.*Acta Hydrochim Hydrobiol* **31**:pp.9-17, 2003.
- [3] Satinder.A., *Arsenic Contamination of Ground Water*, Wiley,New York, pp-23-96,2008.
- [4] Merian.E, *Metals and their compounds in the environment/occurrence, Analysis and biological relevance*,VCH,New York, pp-22-78, 1991.
- [5] Song.Y,Swain.GM., Total inorganic arsenic detection in real water samples using anodic stripping voltammetry and a gold coated diamond thin film electrode, *Anal Chim Acta*,**593**,pp-7-16,2007.
- [6] Poole, C.F., New trends in solid phase extraction. *Trend Anal. Chem*, **22**, pp. 362-373, 2003.
- [7] Long.XP, Miro.M,Hansen.E.H, Estela.JM, Cerda.V,Hyphenating multisyringe flow injection lab on valve analysis with atomic fluorescence spectrometry for online bead injection preconcentration and determination of trace levels of hydride forming elements in environmental samples., *Anal.Chem*,**78**, pp.8290-8298, 2006.
- [8] Yu.CH,Cai. QT,GUO.ZX,Yang.ZG,Khoo.SB,Inductively coupled plasma mass spectrometry study of the relation behavior of arsenic species on various solid phase extraction cartridges and its application in arsenic Speciation. *Spectrochim Acta B*,**58**,pp.1335-1351,2003.
- [9] Vassileva.E,Hadjivanov., Solid phase extraction of heavy metal ions on a high surface area titanium dioxide (anatase), *Analyst*, **121**,pp.607-612, 1996.
- [10] Lang.P,Peng.LL,Yan.P., T, Speciation of As(III) and As(V) in water samples by dispersive liquid-liquid microextraction separation and determination by graphite furnace atomic absorption spectrometry, *Microchem Acta*, **166**, pp.47-55,2009.
- [11] Gil.A, Ferrua.N,Salonia JA, Olsina.RA,Martinez.LD, On-line arsenic Co-precipitation on ethyl vinyl acetate turning packed mini column followed by hydride generation-ICP-OES determination, *J.Hazard Mater*, **143**, pp.431-438,2007.

- [12] Huang.CZ,Hu.B,Jiang ZC,Simultaneous speciation of inorganic arsenic and antimony in natural waters by dimercaptosuccinic acid modified mesoporous titanium dioxide micro column on line separation and inductively coupled plasma optical emission spectrometry determination *Spectrochim Acta part B* ,**62**, pp.454-460,2007.
- [13] Maquieira.A, Elmahadi.H.A.M, Puchades.R, Immobilized cyanobacteria for Online trace metal enrichment by flow injection atomic absorption Spectrometry, *Anal.Chem*,**66** ,pp.3632-3638.