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ASSESSING OF AS(III) AND TOTAL INORGANIC ARSENIC (IAS) IN WATER SAMPLES COLLECTED FROM MUĞLA(TURKEY) PROVINCE USING HYDRIDE GENERATION-ATOMIC ABSORPTION SPECTROMETRY

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Abstract

In this study, simple and robust procedure was improved to directly assessing and speciation of trace inorganic As(III) and As(V) using hydride generation-atomic absorption spectrometry (HG-AAS). The determination of total arsenic was obtained by reduction of As(V) to As(III) using 0.30 % (w/v) ascorbic acid and 1.0 % (w/v) KI. The most appropriate values of HCl, NaBH$_4$ and NaOH concentrations and flow rate of argon gas were experimentally determined. The detection limit(3s) was 0,62 µg L^{-1} and relative standard deviation (RSD) was 2.9 % (n=11). The accuracy of the proposed method was evaluated by analyzing the certified reference material (NIST CRM 1643e) sample. The method was applied for arsenic speciation in different water samples. This can be suggested to be a pioneer study carried out on tracing inorganic arsenic in water samples collected from Muğla province.

Keywords: Arsenic determination, HG-AAS, speciation, water toxicity

MUĞLA İLİNDEN TOPLANAN BAZI SU ÖRNEKLERİNDE HİDRÜR OLUŞTURMALI-ATOMİK ABSORPSİYON SPEKTROMETRİ YÖNTEMİ İLE AS(III) VE TOPLAM ARSENİK TAYİNİ

Özet

Bu çalışmada, hidrür oluşturmalı-atomik absorpsiyon spektrofotometrisi kullanılarak eser miktardaki inorganik As(III) ve As(V)'in direk olarak değerlendirilmesi ve türlemesi için kolay ve güçlü bir prosedür geliştirilmiştir. Toplam arsenik miktarı, 0.30 % (w/v) askorbik asit ve 1.0 % (w/v) KI kullanılarak, örneklerdeki As(V)'in As(III)'e indirgenmesi ile bulunmuştur. En uygun HCl, NaBH$_4$ ve NaOH konsantrasyonları ile argon gazı akış hızı deneysel olarak belirlenmiştir. Gözlenebilme sınırı : (3s) 0,62 µg L^{-1} ve bağıl standart sapma (RSD): 2.9 % (n=11) olarak bulunmuştur. Önerilen metodun doğruluğu, standart referans madde (NIST CRM 1643e) analizi ile değerlendirilmiştir. Metot değişik su örneklerinde arsenik türlemesi için uygulanmıştır. Bu araştırma, Muğla ilinde sularda inorganik arsenik belirlenmesi için öncü bir çalışma olarak kabul edilebilir.

Anahtar kelimeler: Arsenik tayini, HG-AAS, türleme, su toksisitesi

1 Introduction

Speciation and quantification of the different chemical forms of As in waters is important in assessing overall health risk, due to their various toxicological effects related to their speciation [1]. Out of about 25 different As species were identified in waters, arsenate (As(V)), arsenite (As(III)), monomethylarsonic acid (MMAA) and dimethylarsenic acid (DMAA) have been reported to be dominant forms occuring mainly in water environment. The rest of forms occur maily in water organisms [2,3]. Inorganic arsenic (iAs) is a potential human carcinogen and toxicant [1]. Epidemiological studies have been well correlated with arsenic in drinking water and different forms of cancer, skin lesions, vascular diseases and diabetes mellitus [4]. People take arsenic into their bodies mainly via drinking water and food. Millions of people exposing to arsenic in drinking water in many parts of the world has been reported in guideline of EPA (Environmental Protection Agency) [5].

EPA has declared the arsenic standard for drinking water at 0.010 parts per million (10 parts per billion) to protect consumers through public water systems from the effects of long-term, chronic exposure to arsenic. Inorganic compunds of arsenic are far more toxic than organic forms and As(III) and As(V). They are the most important species released in the environment from mineral deterioration. Because of different toxicity of the inorganic arsenic species (arsenite > arsenate), their determination in the environment has generated considerable interest.

Hydride generation-atomic absorption spectrometry (HG-AAS) is currently most popular technique for routine determination of trace amounts of arsenic [6] , selenium [7], cadmium [8], lead [9], etc. which generate volatile hydrides. In this technique, the signal response obtained from As(V) is about 40% lower than that obtained from As(III), thus a pre-reduction of As(V) to As(III) is recommended before the formation of arsine gase [3,6]. The reduction agents typically applied to convert As(V) to As(III) are potassium iodide and L-cysteine. Although potassium iodide has been the more widely used reductor, it entails various problems [10]. KI demands relatively strong acidic conditions for both the sample and the reduction

medium. High concentrations applied can lead to generation of considerable levels of iodine, which are especially disadvantageous if the quantification of the analyte is effected via hydride generation (HG) and atomic absorption spectrometry (AAS). In addition, use of L-cysteine as pre-reductant is advantageous, because it allows the reduction to proceed under mild acidic conditions [6,10]. In order to eliminate the potential oxidation of iodide to free iodine by the oxygen present in the aqueous streams, ascorbic acid is also added.

Hydride generation method for arsenic and other hydride forming elements has two basic advantages. First, the analyte is separate from the matrix so that possible interferences are eliminated. And secondly, scientists can achieved detection limits are $\mu g\ l^{-1}$ levels with a simple, robust and economical method [11,12], These ppb ($\mu g\ l^{-1}$) levels for very toxic elements like arsenic, lead, cadmium are enough for investigations about toxicity level. Because these elements are not dangerous for health under these ppb levels.

The main reason for the interest in the determination of arsenic species is its highly toxic effects of this species. It would be possible to intake 3.0 mg of arsenic per day with daily use if drinking water contained 0.8 mg of arsenic per liter. Once this situation has been continued up to 2-3 weeks, due to the toxicity of arsenic, poisoning condition will be inevitable [13] .

In literature, Schaumlöffel and Neidhard [14] have been used flow injection system to As (III) / As (V) detection. In total arsenic determination, As (V) has been suggested to reduce As (III) using KI or L-cysteine at 368,15 K. The As (III) and total inorganic arsenic linear calibration range has been reported within 5.0-50.0 $\mu g/L$ with the limit of detection for 0.4 $\mu g/L$ As (III) .In another study [6] the total arsenic using HG-AAS technique has been detected. For this purpose, all the species in the medium have been determined by conversion to $AsH_3(g)$ using $NaBH_4$, NaOH and HCl. For determination only As (III) , citric acid buffer have been used instead of HCl. In this way, As (III) species were selectively reduced to AsH_3 and detected. As (V) concentration could be calculated between total As and As (III). Arsenic speciation in water at ng / L level by flow injection hydride generation electrothermal atomic absorption spectrometry (HGETA- AAS) were investigated [15]. Apart from the other studies tetrahydroborate and As (V) was successfully kept on anion exchange resin. The strongly basic anion exchange resin Amberlite IRA-410 have been used in this study.

Yu et al. [16], investigated using solid phase extraction - Inductively coupled mass spectrometry (SPE-ICP-MS) hyphenated technique for arsenic speciation. At the end of the study, retention of arsenic species depending on the type of sorbent material was found. Different arsenic species in the solution were eluted in order of the column and were determined by ICP-MS. Limit of detection in water samples were found to be 8.0 ng / L As and method were found to be applicable successfully in the various water samples for As speciation.

Another method used for speciation was the hydride generation atomic fluorescence spectrometry (HG-AFS) technique. AFS detection system was very sensitive. A coupling between column liquid chromatography (LC) and atomic fluorescence spectrometry was developed for arsenic. After separation, the compounds were oxidised on-line by UV irradiation, volatilised by hydride-generation and carried to the detector by astream of argon. Limits of detection were 4.0–22.0 pg [17] .

The aim of this study was the devolopment of a technique for the direct determination of trace amounts of As(III) and As(V) in water samples using hyride generation-atomic absorbtion spectrometry (HG-AAS) with pre-reduction step of As (V). The accuracy of the method was demonstrated analyzing a standard reference material. The water samples were tap water, well water and spring water. Two water samples were taken from a district that near a Thermal Power Plant. We aimed to investigate any contamination in water resulting from thermal power plant wastes. To the best of our knowledge, this is the first study on investigation of arsenic speciation in Muğla province.

2 Materials and Methods

An Agilent Technologies 200 Series AA atomic absorbtion spectrometer was used in combination with a hydride generation accessories. An arsenic hollow cathode lamp was used at 193.7 nm with a spectral bandpass of 0.5 nm and lamp current was 10.0 mA. The air flow was 13.5 L/min. and acetylene flow was 2.1 L/min. Agilent VGA 77 peristaltic pump was used to controlled transportation of solutions. Atomization of arsenic hyride (AsH_3) to As was provided by air-acetylene flame. The operating parameters for arsenic are given in Table 1.

Table 1. Working conditions for determination of Arsenic by using AAS

Parameters	Working Conditions
Wavelength	193.7 nm
Lamp current	10.0 mA
Slith width	0.5 nm
Radiation source	As hallow cathode lamp
Fuel	Air-acetylene
Air /Fuel ratio (L/min)	13.5/ 2.1

All reagents used were of analytical grade and deionised water (resistivity 18.0 mohm cm) was used for preparation of solutions. Standard stock solution of 1000 mg L^{-1} As (III) was made dissolving 1.3203 g of As_2O_3 (Merck, Germany) in 25 mL of 20.0% (w/v) KOH solution, followed by neutralisation with 20.0 % (v/v) sulphuric acid and diluting to 1000 ml with 1.0 % (v/v) sulphuric acid. The As(V) Standard stock solution of 1000 mgL^{-1} was obtained dissolving 4.1511 g of $Na_2HAsO_4.7H_2O$ (Merck, germany) in deionised water. Working standard solutions were prepared daily by dilution of appropriate volumes of 1000 mgL^{-1} solutions in deionised water. Analytical grade chemicals; NaOH (pellets) , HCl (37%), HNO_3 (65%) , KI, $NaBH_4$ and ascorbic acid were purchased from Merck (Darmstad, Germany). All glassware was soaked for at least 24 h in 10.0% HNO_3 solution, finally rinsed in distilled water before use.

The experiments were carried out in CF mode in HGAAS. The HCl, NaOH and $NaBH_4$ concentrations and Argon gas flow rate were optimized in conventional HGAAS studies by using a 5.0 $\mu g\ l^{-1}$ Arsenic solution containing 0.25 mol l^{-1} HCl. The blank was 0.25 mol l^{-1} HCl solution. The reductant and analyte solutions were pumped at the flow rates of 1. 55 ml min^{-1} and 4.32 ml min^{-1}, respectively. The generated Arsin gas (AsH_3) was separated from the liquid phase by the GLS and was transferred to quartz-T-tube atomizer through a Tygon tubing using a carrier gas of Ar . The experimental set-up is illustrated in Fig. 1.
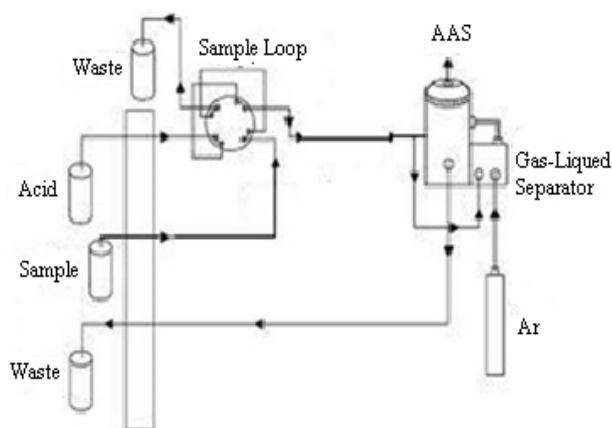
Figure 1. Schematic diagram of system used for determination of arsenic species

As (V) species do not give signal in HG-AAS method because they do not react with sodium borohydride to give hydrides directly. That's why all As(V) must be convert into As(III). For this reduction, KI (% 1.0 w/v) and ascorbic acid (% 0.3 w/v) were used (15). Ascorbic acid was used to remove I_2, otherwise I_2 can oxidize As(III). By this procedure, firstly total arsenic concentration was determined. After that from the difference between total arsenic and As(III) concentration, As(V) concentration can be determined.

3 Results and Discussion

The experimental conditions for determination of As(III) and As (V) were established employing the manifold described in Fig. 1. The fallowing hydride generation parameters were evaluated: HCl, $NaBH_4$ and NaOH concentrations, carrier gas (Ar) flow rate. 5.0 µg L^{-1} As (III) solution was used in each optimization study.

3.1 Optimization of Concentration of Carrier Solution

In this study, HCl was used as carrier solution. In order to find the optimum HCl concentration, HCl concentration in the analyte solution (5.0 µg L^{-1} Arsenic) was varied between 0.125 and 1.50 mol l^{-1}. The optimum value for HCl was found as 0.250 mol l^{-1} (Fig.2.). Higher and lower values resulted in a relatively sharp decrease in the peak height of the analytical signal. In these experiments; $NaBH_4$ and NaOH concentrations were % 1.50 and % 0.5 respectively and Ar flow rate was 19.5 mL/min.
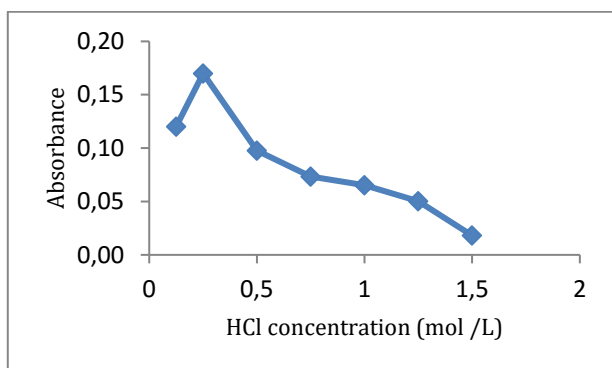

Figure 2. Effect of HCl concentration on the absorbance of As(III)

3.2 Optimization of Concentration of Reductant Solution

For the production of arsenic hydride species, $NaBH_4$ was used as a reductant solution. The effect of $NaBH_4$ concentration on AsH_3 production was investigated by using continuous flow. In order to find the optimum $NaBH_4$ concentration in the reductant solution, concentration was varied between 0.25 and 1.75% (w/v); 1.0% (w/v) $NaBH_4$ was found as the optimum reductant solution using the changes in the analytical signal. In this optimization, it was observed that the signal increased up to a concentration of 1.0 % (w/v), somewhat in the middle of the plateau and decreased for higher values. The decrease can be explained by the dilution effect, since more H_2 was generated at higher concentrations of reductant. In this optimization; HCl and NaOH concentrations were 0.250 mol l^{-1} and % 0.5 respectively and Ar flow rate was 19.5 ml/min. The results were illustrated in Fig.3.
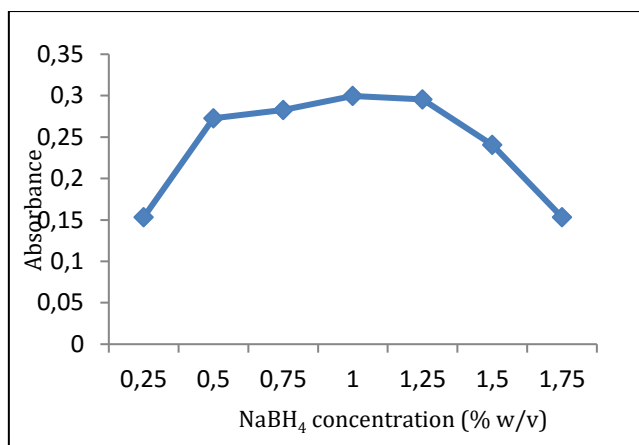

Figure 3. Effect of $NaBH_4$ concentration on the absorbance of As(III)

3.3 Optimization of Concentration of NaOH Solution

In addition, NaOH was used for the stabilization of $NaBH_4$. Concentration of NaOH was varied between 0.125 and 1.50 % (w/v). It was found that concentration of NaOH has a significant effect on the analytical signal of arsenic. The highest signal for arsenic was obtained using the reductant solution containing 0.5% (w/v) of NaOH while the other parameters were kept at their optimum found values.

3.4 Optimization of Carrier Gas Flow Rate and Optimization of Flow Rates of Carrier and Reductant Solution

Ar gas was used as a carrier gas. Ar gas flow rate important because of transportation of arsenic species to the atomizer and residence time of atoms on the radiation source. More residence time means higher sensitivity, on the other hand Ar gas flow dilutes the hydride production, so carrier gas flow needs to be as low as possible. The carrier gas flow rate was assessed over the range 17.0-20.0 ml min^{-1}. It was found that a higher flow rate of carrier gas resulted in signal instability and a decrease in sensitivity. The best argon gas flow rate was found 18.0 ml min^{-1} (Fig.4.)
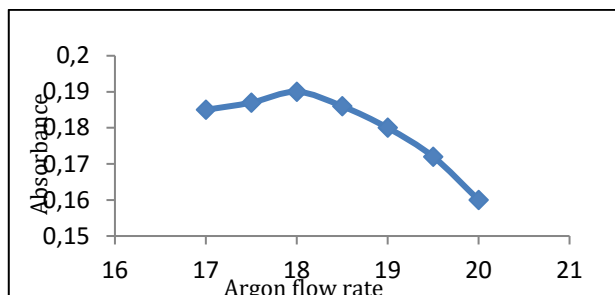
Figure 4. Effect of Ar flow rate on the absorbance of As(III)

The efficiency of the production of arsenic hydride species is directly related with the flow rates of carrier and reductant solutions. In this study, the flow rate of HCl that was used as the carrier solution was varied between 2.0 mL min^{-1} and 12.0 mL min^{-1} and the optimum value was found to be 7.0 mL min^{-1}. The signal increased as the flow rate was increased until the value of 7.0 mL min^{-1} is reached and stayed constant afterwards. The flow rate of NaBH$_4$ solution was varied between 1.0 mL min^{-1} and 15.0 mL min^{-1}; the optimum result was found as 9.0 mL min$^{-1.}$ Optimization of concentrations and flow rates for HCl and reductant solutions were carried out by keeping all parameters constant while only the test parameter was varied.

In this study, also the suction rate of the waste rate optimization was carried. The suction rate of the waste affected the As signal. If the suction rate of the waste was increased, As signal was decreased. In this study, suction rate of the waste was selected as 5.0 mL min^{-1}, the waste rate must be suitable. If the suction rate is very low, waste could have gone to the atomizer.

3.5   Analytical Performance of the Proposed Method

Under optimized conditions, the calibration curve in Fig. 5 was constructed. Dedection (L.O.D.) and quantitation limits (L.O.Q.) were calculated as the concentrarions that gave signals equal to 3 times and 10 times the standard deviations of the blanks respectively. 11 times blank readings were taken for this aim. The detection limit(3s) was 0.62 µg L^{-1} and quantitation limit

was 1.55 µg L^{-1}. Precision expressed as % relative standard deviation (RSD) is 2.9 % (n=11). The calibration curve was linear from 1.00 µg L^{-1} up to 20.0 µg L^{-1} The linear range was adequate for the determination of arsenic species in water samples.
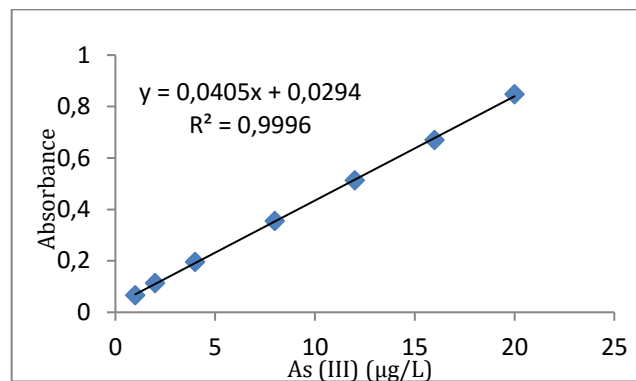

Figure 5. Standard calibration curve of As(III) under

optimized conditions

3.6   Analysis of Water Samples

Water samples were collected from Muğla city (tap water), campus of Muğla Sıtkı Koçman University, Muğla TOKİ street, Muğla Kötekli street, Muğla Yayla region. In addition to these samples, for investigation the possible effect of Yatağan Thermal Power plant by means of arsenic contamination to the water sources, two type water samples were taken from Yatağan. Yatağan is a district of Muğla city and twenty five km far from Muğla. All samples were collected in acid-washed polypropylene containers. Samples were filtered through filter paper (Whatman No:1) and sub-boiled concentrated HCl was added to water samples to obtain the concentration of 3.0 mol l^{-1}. The water samples were stored at 4.0 °C until analysis. The obtained results are presented in Table 2.

Table 2. Determination of arsenic in different water samples

Water Samples	As (III) [a] (µg l^{-1})	As(V)[a] (µg l^{-1})
Sample 1. (Muğla City Center)	2,23 ± 0,12	1,56 ± 0,07
Sample 2. (Muğla University)	2,96 ± 0,08	1,81 ± 0,03
Sample 3. (Muğla Toki)	2,18 ± 0,15	1,75 ± 0,09
Sample 4. (Muğla Kötekli)	1,87 ± 0,11	N.D.
Sample 5. (Muğla Plateau well water)	6,78 ± 0,22	3,26 ± 0,14
Sample 6. (Yatağan District City Center)	4,90± 0,20	2,22 ± 0,20
Sample 7. (Yatağan District Plateau well water)	11,34± 0,18	3,57 ± 0,15

N.D.: not detectable

[a] Results are means of 11 measurements

It can be seen the from the Table 2. that all arsenic species concentrations of water samples except sample 7. are lower than limit value (10.0 µg L^{-1}). Sample 7 is belongs to Yatağan District Plateau well water. It is important for evaluation of the effect of waste disposal site of the Yatağan Thermal Power Plant on groundwater. Toxic trace elements such as arsenic (As), cadmium (Cd), lead (Pb), antimony (Sb), selenium (Se), tin (Sn) and zinc (Zn), which are produced by burning coal, have the potential to cause environmental pollution.

These elements, waste with rainwater washing and possible underground conveyed as a result ground cover, surface waters

and groundwater waters are involved in various environmental and health problems creating [18].

3.7   Accuracy of the Method

The accuracy was evaluated by determinig the arsenic concentration of a certified reference material NIST CRM 1643e (drinking water) by using proposed method. Certified value is 60.45 ± 0.45 µg L^{-1} and faund value is 58.95 ± 0.73 µgL^{-1} (n=5) with % 96 recovery. The result was in good agreement with the certified value and the calculated recovery was satisfactory. Altough no interference study was undertaken, it is obvious

from the data that there are no systematic errors due to the presence of the matrices. In addition, it can be said that proposed method as sensitive as ICP-MS [19] and better than ICP-OES [20].

4 Conclusion

Inorganic arsenic (iAs) detection and speciation in different water samples collected from Muğla Province and Yatağan District were performed using HG-AAS method. With Flame

Atomic Absorbtion Spectrophotometer, only total arsenic can be determined. Altough, ICP-MS is a very sensitive tecnique, ICP-MS can be also determined only total arsenic concentration. The simplicity, easy handling, low cost and good sensitivity of the HG-AAS method has been proved for routine determination of the two main species of arsenic As(III) and As(V) in water samples. In the literature the methods for the determination of arsenic in various samples are presented in Table 3.

Table 3. Analytical methods for the determination of arsenic in various environmental and biological samples.

Method	Sample	Arsenic species	Detection limit	Reference
Hydride generation-atomic fluorescence spectrometry (HG-AFS)	Chards	As(III)	3.1 ng/g	[21]
Inductively coupled plasma–mass spectrometry (ICP–MS)	Water	Total arsenic	0.069 µg/L	[22]
Electrothermal – atomic absorption spectrometry (ET–AAS)	Water	Total arsenic	1.0 µg/L	[23]
This study (HG-AAS)	Water	Total arsenic	0.62 µg/L	

The world health organization (WHO) has set a recommended limit of 10 µg/L for arsenic in drinking water [24]. Of seven water samples, only 7th. sample contains higher arsenic concentation. This result can be associated with the place of well water which is near thermal power plant, that is expected to be ordinary situation. Waste of thermal power plant should be disposed more in a safely than present situation. In further studies, assessing arsenic residues in expanded samples should be followed considering the production seasons in plants.

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