Determination of nano and sub-nanogram amount of Arsenic in natural waters by hydride generation atomic absorption Spectrometry (HGAAS)

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Abstract

A method is described for the determination of sub-nano gram levels of arsenic in natural waters by hydride generation atomic absorption technique. Arsenic is reduced from its sample in reduction vessel (without associated collection vessels), the reduction products were continuously swept into a heated silica tube using nitrogen as carrier gas, and the absorbance is measured with atomic absorption spectrometry. There is no interference were observed from other ions which were found in natural water. With this simple, rapid and accurate technique, determinations of arsenic have been made on a large number of natural water samples.

تقدير عنصر الزرنيخ في المياه الطبيعية بواسطة تقنية الهيدرايد لاستخدام مطياف الامتصاص الذري

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الخلاصة

اهتم البحث الحالي بتقدير عنصر الزرنيخ في المياه الطبيعية بوساطة تقنية الامتصاص الذري – توليد الهيدريد باستخدام أنبوبة من السليكا كخلية تذرية تسخن على لهب الهواء أستـتلين (2250 م). تميزت الطريقة بسهولتها وسرعتها ودقتها العالية حيث بلغت نسبة الاسترجاع المئوية (97-100%) لكميات معلومة التركيز من عنصر الزرنيخ مضافة إلـى نمـاذج مـن الميـاه الطبيعية . تم تحليل نماذج من مياه الأنهار ومياه البرك والمياه الجوفية لأماكن مختلفة من مدينـة البصرة بلغ مستوى الزرنيخ منها لمستوى تركيز نـانوغرام/مللتـر . وجـد أن حـد الكشـف والأنحراف العياري القياسي للطريقة (0.95ng) (1.9-4.8%)على التوالي مما يـدل علـى أن الطريقة ملائمة جداً لتحليل المناشئ التي تحتوي على تراكيز نزرة من الزرنيخ و اعتمادها فـي التحليل وبثقة عالية .

Introduction

The levels of arsenic in environment were of considerable interest because of its potential toxicity and carcinogenic properties. A need is seen for sensitive methods for the determination of arsenic. The sensitive

methods require extensive sample pretreatment e.g.,neutron activation analysis (Gohda 1975); others do not adequate sensitivity, e.g.,calorimetric method (Kopp 1973), dc-discharge emission technique (Braman and Foreback 1973).

A method proposed by (Talmi and Bostick 1975) using gas chromatography with microwave emission spectrometric detection system requires equipment not usually available in analytical laboratories. A review on the determination of arsenic has been published by (Talmi and Bostick 1975).

Hydride generation (HG) is the most widely used method for the selective determination of arsenic in water samples (Goulden and Brooksbank 1974 , Andreae 1977) , geochemical samples (Kuldvere 1989) (Branch and Hutchison 1985), food stuffs (Evans etal 1979) ,and low – alloy steels (Welz and Melcher 1981) .

In this paper, concerned with monitoring of natural waters across Basrah . The poor sensitivities of arsenic when determined by flame atomic absorption spectrometry induced us to try direct analysis of natural water using hydride generation atomic absorption technique.

Experimental

Apparatus:

A shimadzu atomic absorption spectrophotometer model (AA-630-12) equipped with a hallow cathode lamp for arsenic; The silica tube (17 × 0.8 cm) is placed in an air – acetylene flame (2250 C°), about 5mm above the slot burner head.

Nitrogen gas was used for sweep arsine in to heated absorption cell. The hydride generation system used has been described in detail elsewhere (Awad and Abdulsahib 2002) (Awad and Abdulsahib 2004) .

Reagents:

Arsenic (III) stock standard solutions, (1000 µg / ml) was prepared by dissolving 1.320g of arsenic (III) oxide (As_2O_3) in 20 ml of 1M NaOH , 10ml of 10% V/V HCl were added and the pH adjusted to 1.5 and dilute to

1000 ml with de-ionized water. Aliquots were diluted with 0.5 M HCl to obtain appropriate working reference solutions.

Sodium tetrahydroborote (III) solution, 3% (w/v).was Prepared by dissolving appropriate wt. of sodium tetrahydroborate (III) powder in de – ionized, water and stabilizing with 1% (w/v) sodium hydroxide solution. The solution was filtered before use and could be stored for a few days only.

Potassium Iodide Solution, 10% w/v. was prepared by dissolving appropriate wt. of potassium iodide powder (BDH) in de- ionized, water.

Analytical – reagent grade hydrochloric acid used was further purified by sub-boiling distillation. The metals salts used for interference studies were of analytical – reagent grade.

Sample Treatment and Storage: -

Samples were collected from different parts of Basrah (Fig 1) either by hand with plastic bottles from the bow of a boat or by oceanographic samplers (GO-FLO sampler, made from Teflon–Coated PVC) . The samples were stored in LPE (linear polyethylene bottles) for a few days . The free arsine's are stable in solution for up to 4 days if stored in above containers. They are slowly oxidized arsenite to arsenate by traces of air for corresponding acids. Acidification of the sample increases the oxidation rate , arsenite loss can be detected after one day. From untreated samples, tests did not show any measurable change of arsenite concentration over 4 days if the samples were stored in the dark at room temperature .For longer storage the samples freezing down rapidly and storing at a temperature of less than –20 C°.

Procedure:

Arsenic was determined as arsenic (III) .,by the reduction of As (V) to As (III) is carried out in 5M HCl medium. 1-ml volume of 10% w/v potassium iodide solution is added to 10ml of sample solution and left at ambient temperature for at least 15 min. After this time the reduction is complete and solution is transferred into the hydride system.

An appropriate volume of the final sample solution (10ml) was transferred into the reaction vessel. 3 ml aliquot of 1.5%(v/v) HCl was then

added and the flask was purged of air using nitrogen, 2 ml of reductant is added with stirring, the arsenic hydride was swept into the heated silica tube using nitrogen as carrier gas. The absorbance is measured of the evolved arsine at 193.7nm , the concentrations of arsenic determined by interpolation on standard graphs in the ranges (0.1-100)using the optimum conditions listed in table (1).

Results and Dissuasion

Influences of pH and hydride concentration:

The criteria for the optimization of the hydride generation process are species selectivity, maximal yield, minimal blank, speed and convenience of manipulation .Arsenic (III) can be separated from inorganic metals on basis of their atomic absorption spectrometric behavior .The efficiency of the hydride generation process depends strongly on the reaction pH, the reduction yield normally decreases sharply above the pH corresponding to the pKa of As (III)(arsenous acid ,pKa:9.2). Acidification to (pH:1-2) releases further amounts of metals which found in waters,thus;arsenic (III) was separated from other species by reducing with sodiumborohydride at(pH :1.5). The reduction is effected as follow:

$$BH_4^- + 3H_2O + H^+ \longrightarrow H_3BO_3 + 8H^+$$

$$3H + As^{3+} \longrightarrow AsH_3 .$$

The concentration of the borohydride reagent was chosen at (3%) to the convenient volumes (1-3ml) for injection into the sample solution .We have not observed changes in yield with different borohydride reagent concentrations. The amounts of borohydride solution injected have been chosen about 50%above the amount at which a plateau in the solution as a function of the borohydride addition is reached .Injection rate was critical at the pH of the As(III) reduction because the borohydride ion hydrolyzes

rapidly in acid solution, it is necessary to inject the reagent slowly(45-60s) into the acid solution for the As(III) determination.

Interference studies: -

A number of ions, especially transition metal cations, interfered with borohydride reductions. The metal concentrations at which interference occurs are however, far above those usually found in natural waters. It was observed no interferences from 0.05 ppm concentrations of the following elements: mercury, tin , copper , iron , lead , zinc, and cadmium . Nitrite are also found in natural waters at concentration of (more than 3 μM), there was no interference from nitrite are noted at this levels . This may be due either to low acidity used in the methods, or the stability of arsine relative to other elements hydride (Cutter 1983).

Accuracy and Precision: -

The Precision of the method were evaluated from the results of ten replicates of a typical natural water sample. Relative standard deviation (RSD%) was found to be (1.90-4.96%).

The accuracy of the method was assessed by spiked natural water samples with arsenic at 2.0, 4.0 and 6.0 ng/ml As levels resulted in complete recovery of the added arsenic . The percentage recovery were ranged from (97%--100%) as shown in table (2).These results indicate that the method is , accurate and gives reproducible results .

Absolute Sensitivity, Detection limit and Linearity :-

The sensitivity, defined as the concentration which gives a mean net absorbance > 0.0044 was determined to be 0.63 ng/ml Arsenic for injected aliquots of 2 ng/ml arsenic solution .

The detection limit (2S) was 0.95 ng/ml , calculated for injected aliquots of 2ng/ml arsenic solution (10 replicates) by analytical procedure . Limit of linearity ranged between 0.1 ng/ml up to 40 ng/ml Arsenic solution (Fig 2) .

Analysis of samples

One hundred fifty natural water samples have been analyzed for the determination of arsenic, the samples containing levels of arsenic ranging

from 1ng/ml to 10 ng/ml were analyzed using standard addition method and direct method (Fig.3). From the results in table (3) it is clear that there was no significant difference observation between the two methods. Results obtained ranged from 0.25 ng/ml in some ground waters and 6.83 ng/ml found in lake water to 10 ng/ml in some river waters .

At most the arsenic levels are much higher for river waters than lake waters and ground waters, by a factor of at least one to thirty times .The observed variations of arsenic levels are probably a reflection of the geographical influences and geochemical environment which were thought to be the main source of variability.

For river waters, typically; the level of arsenic (III) in the river region was (<6.0 ng/ml).The concentration tended to be highest near the surface (9.0 ng/ml) and declined to low levels (9.0 ng/ml) at depths greater than 15 m (Fig.4).

Maaqal Port is quite shallow (generally<10 m) and well mixed , so samples were collected from the surface only . The results found are generally (8.0 ng /ml),which is more than an order of magnitude greater than those found in open river waters .The levels were highest close to shore areas where river inputs and sewage and industrial outfalls were most significant, and the lowest values were obtained close to the mouth of the Port .

Summaries of the literature values for the concentrations of arsenic in various types of waters using hydride generation technique are listed in table (4), comparison of the values from previous work with ours show certain clear differences. The samples of ground water from Colorado and river water samples from Canada gave somewhat higher arsenic values than those of other workers. A possible explanation is that the concentration of this element in the waters supplies varies with the different regions. Most of our values are somewhat lower than those obtained in earlier studies .This may be partially due to the lower risk of contamination with arsenic which was normally contaminants from industrial waste.

Conclusion

The method described provides a simple sensitive analysis of arsenic in the nanogram   range . The procedure have been applied in the analysis of a variety of samples .The advantage of this method is the significantly lowering the interference of hydride forming elements and transition metals , no complexing agents are required , decreasing the risk of contamination .With direct method it is possible to determined nanogram

quantities of arsenic with the convenience and rapidity of analysis .

For natural waters samples ,the described method is equivalent to the method of standard additions ,however , the results obtained by the direct method shows that the river waters contains arsenic concentration higher than the ground and lake waters which were contains low concentration of arsenic .
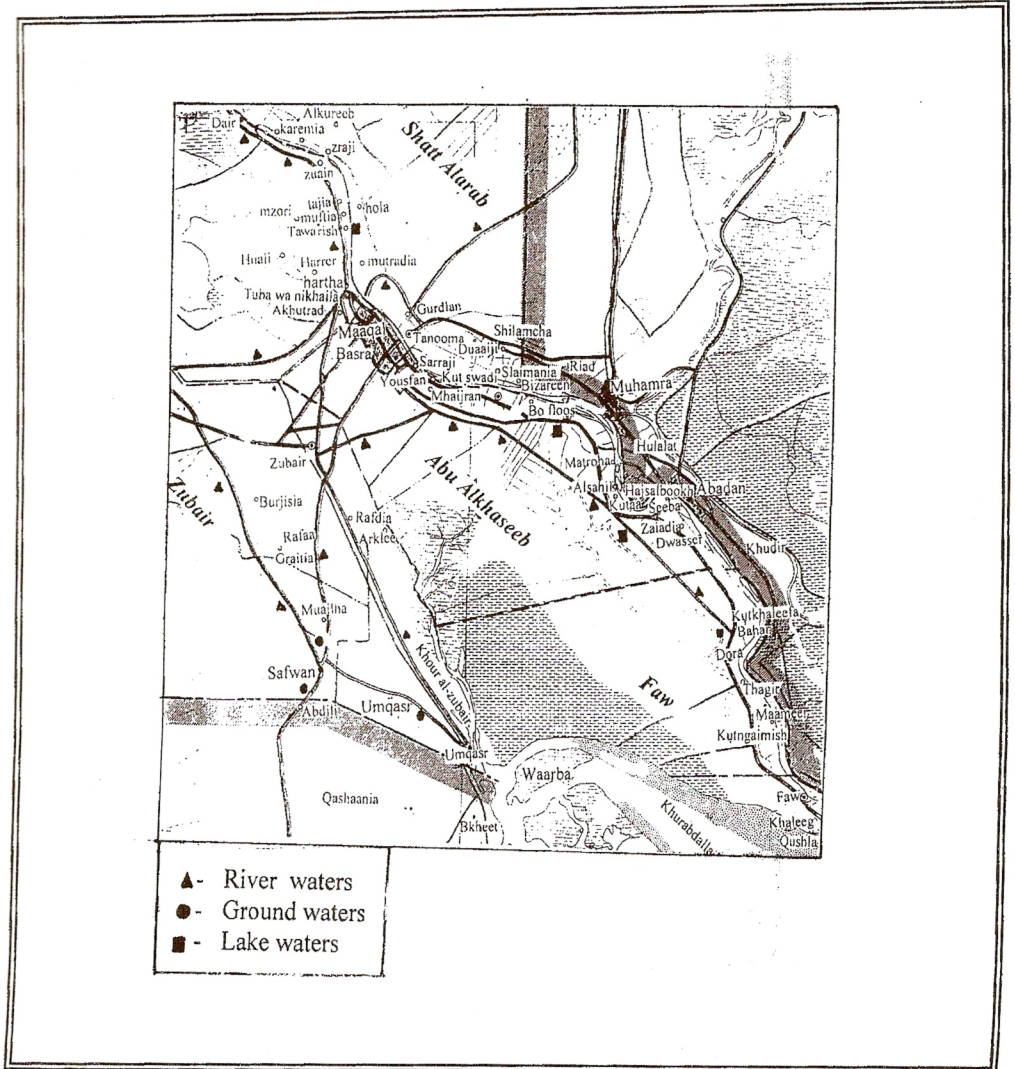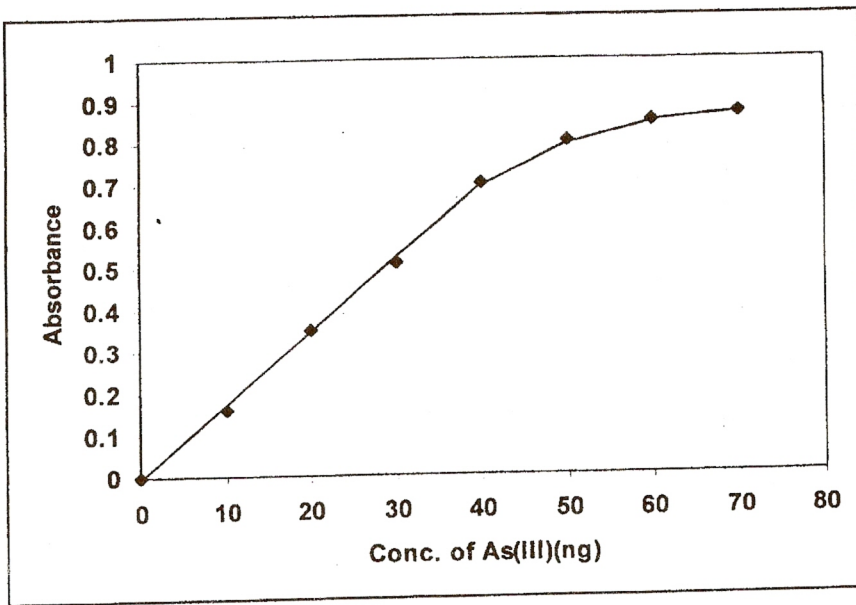

Fig. (1) : Basrah City

Fig.(2): Calibration   Curves (conditions as described in table 1) for the
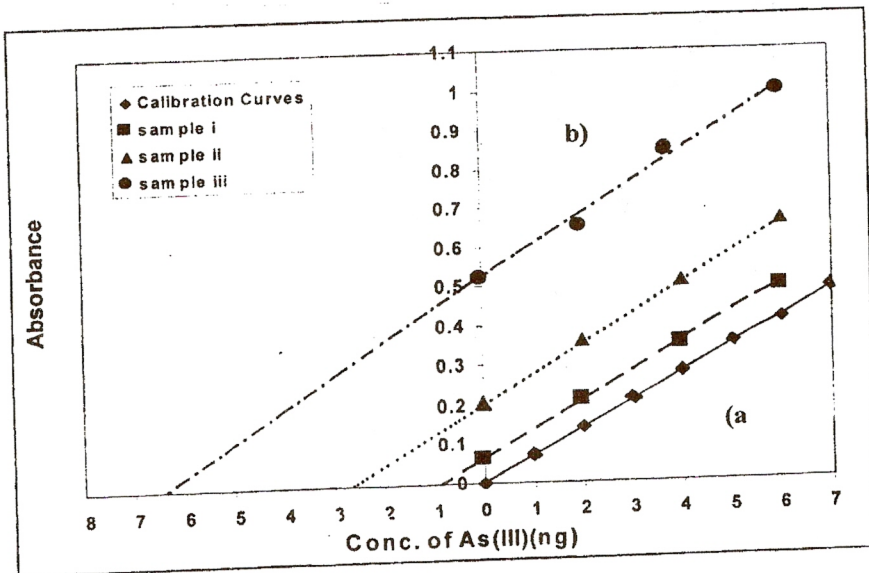determination of As(III).

Fig.(3):Determination of As(III) in water samples by Calibration Curves of
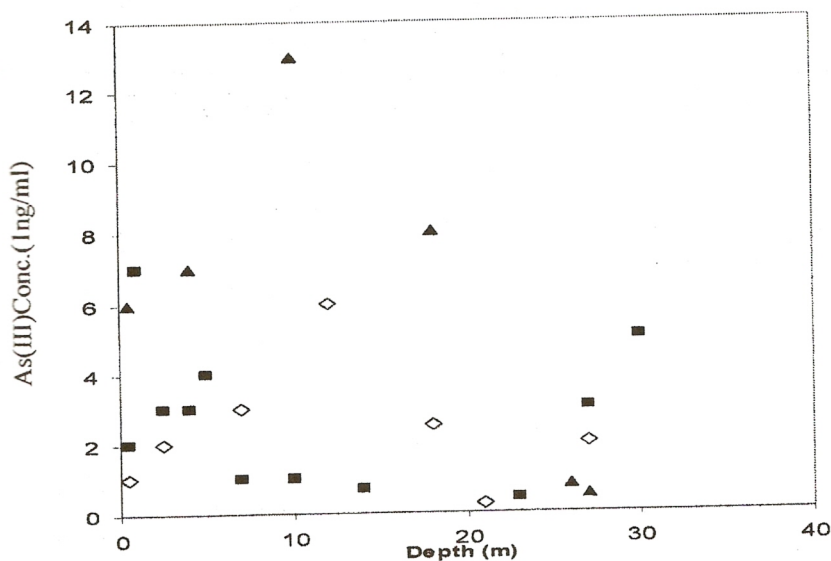a)Direct method   b)Standard addition method

Fig (4).Depth profile of As(III) in the Shatt AL-arab river, Geographical positions:(▲)34.4 S,151.5 E;(■)33 S,154.5 E; (◇)33.5 S ,152.5 E

Table (1) Instrumental Parameters

Light source	Hallow cathode lamp
Wave length (nm)	193.7
Band width (nm)	1.9
Lamp current (mA)	6
Mode	Absorbence
Back ground correction	None
Flow rates (L/min)	Air 11.5
	Acetylene 2.5
Time of mixing (sec)	20
Flow rate of carrier gas (L/min)	1.2
Conc. of $NaBH_2$ (%)	3.0
Conc. of HCl (M)	1.5
Temperature of reduction	25 (room temp.)

Table (2): Recovery percentage of the direct method of natural Water samples.

Sample No.	As levels (ng)	As Added (ng)	As found (ng)	Recovery (%)
1	0.63	2	2.58	98.2
		4	4.49	97.0
		6	6.56	99.0
2	4.75	2	6.58	97.5
		4	8.63	98.6
		6	10.75	100.0
3	7.27	2	9.21	99.4
		4	11.17	99.1
		6	12.99	97.9

Table (3): Arsenic concentrations (ng) of natural water samples and relative standard deviation (10 replicates)

Sample	Direct method As concentration		Std. Addition method As concentration	
	ng	RSD %	ng	RSD %
i	1.05	2.60	0.98	4.58
ii	2.97	2.44	2.88	4.96
Iii	6.43	4.80	6.41	6.11
iv	9.26	1.90	9.32	1.62
v	9.95	3.66	10.02	1.73

Table (4) :Concentrations of Arsenic (ng/ml) in various types waters

Samples	As conc. (ng/ml)	Position	Method	Reference
Ground water	23.3	Colorado USA	HGAAS	W. H. Ficklin [1983]
Sea water	0.71	Pisa, Italy	HGAFS	A. D'ulivo, etal [1985]
River water	1.23			
Tap water	0.18			
Sea water	15.0	Kingston, USA	HGAAS	S. A. Amankah and J.L. Fasching [1985]
Ground water	0.5	Canada	HGAAS	O.Goulden and p. brooksbank [1974]
River water	15.0			
Sea water	3.0	Iran	HGICP	M. Thompson, etal . [1978]
Ground water	0.25	Basrah, Iraq	HGAAS	Present study
River water	10.0			
Lake water	6.83			

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