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Article

Selective Reduction of Arsenic Species by Hydride Generation – Atomic Absorption Spectrometry. Part 2 – Sample Storage and Arsenic Determination in Natural Waters

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Arsênio total, As(III), As(V) e ácido dimetilarsínico (DMA) foram determinados seletivamente em águas naturais pela técnica da geração de hidretos – espectrometria de absorção atômica, em diferentes meios de redução. Para as amostras de água de rio investigadas os resultados mostraram ser arsenato a forma arsenical predominante. Os limites de detecção encontrados para As(III) (tampão citrato), As(III) + DMA (ácido acético) e As(III) + As(V) (ácido clorídrico) foram, respectivamente, 0.6, 1.1 e 0.5 mg As L^{-1}. O estudo da estabilidade das formas arsenicais em amostras de águas naturais revelou serem os próprios meios reacionais convenientes para uma preservação adequada das amostras.

Total arsenic, arsenite, arsinate and dimethylarsinic acid (DMA) were selectively determined in natural waters by hydride generation – atomic absorption spectrometry, using sodium tetrahydroborate(III) as reductant but in different reduction media. River water samples from the north region of Paraná State, Brazil, were analysed and showed arsenate as the principal arsenical form. Detection limits found for As(III) (citrate buffer), As(III) + DMA (acetic acid) and As(III) + As(V) (hydrochloric acid) were 0.6, 1.1 and 0.5 mg As L^{-1}, respectively. Sample storage on the proper reaction media revealed to be a useful way to preserve the water sample.

Keywords: natural waters, arsenic speciation, atomic absorption spectrometry, sample storage

Introduction

Arsenic biogeochemical cycle occurs mostly in the aquatic environment and its bioaccumulation is an important ecotoxicological aspect[1,2]. Besides this, arsenic contamination in natural waters has been related to different diseases in some countries; changes in the skin pigmentation, keratoses and carcinomas have been associated to the intake of contaminated waters for long time, once the accumulation by the organisms is more rapid than its excretion[3,4,5].

Arsenic can be found in natural waters as dissolved organic and inorganic forms. Many species with different toxicological and chemical characteristics can be formed depending on to the pH, alkalinity or some other variables. From geological sources arsenic is found in two valency states: salts of the arsenic acid (As(V)) and of the arsenous acid (As(III)); the ratio between these forms depends on the pH values and oxidising or reducing local conditions. In the environment, the presence of methylated arsenic compounds such as monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) is often caused by human industrial activities and agriculture. However, organic species may also be produced by bacterial biotransformation of inorganic arsenic forms[6]. Biotic transformations in aquatic systems depend on the kind of organisms present, and several organoarsenical compounds can be formed[1,7]. In natural freshwaters arsenite, arsenate, dimethylarsinate and methylarsonate species have been detected, but in general arsenite, arsenate and dimethylarsinate are the main arsenical forms[8].

Monitoring methods for determining the different chemical forms of arsenic in the environment are becoming increasingly important due to their different toxicity and chemical behaviour, such as solubility in water and adsorption at sediments[9]. Consequently, various speciation procedures have been proposed and reviewed[10]. Despite the variety of sensitive analytical techniques for trace element determination, atomic absorption spectrometry is still the method of choice for routine determination of a large number of elements. Atomic absorption spectrometry with hydride generation allows easy and sensitive determination of total arsenic, usually after complete reduction of the different forms to arsenite; several possibilities have been proposed for the arsenic speciation in different samples[11-17].

In a previous work the analytical conditions for the selective reduction of arsenic species by hydride generation – atomic absorption spectrometry were studied[18]. Briefly, arsenite alone

was measured in 0.4 mol L^{-1} citrate buffer (pH = 4.4); arsenite plus arsenate were determined together in 6.0 mol L^{-1} hydrochloric acid after a pre-reduction with potassium iodide, and arsenite plus dimethylarsinate species were determined in 0.12 mol L^{-1} acetic acid. Total arsenic could be determined in 6.0 mol L^{-1} hydrochloric acid following a pre-reduction step of the arsenate and dimethylarsinate species with a potassium iodide - stannous chloride mixture. This paper describes the determination of arsenic dissolved species in freshwaters using the reaction media previously proposed and a simple sample storage procedure.

Experimental

Apparatus

A Varian Techtron AA-175 atomic absorption spectrophotometer, equipped with a hydrogen hollow cathode lamp background corrector and an arsenic hollow cathode lamp was employed; the slit width on the spectrophotometer and the wavelength were set to 1 and 193.7 nm, respectively. The home-made hydride generation apparatus used was as previously described[18].

Reagents

Arsenic oxide 99.5%, for inorganic As(III) (Riedel – De Haen), arsenic pentoxide 99.3%, for inorganic As(V) (Baker Analyses), dimethylarsinic acid, sodium salt, 98% (Sigma) and sodium tetrahydroborate 95% (Merck). All other reagents used were of analytical – reagent grade:

The 1000 mg L^{-1} aqueous stock solutions of arsenate and dimethylarsinate species were standardized against arsenite, using flame atomic absorption spectrometry.

Procedure

Glassware cleaning. All glassware was soaked overnight in 1% v/v nitric acid and rinsed with distilled water before use.

Sample preservation. In order to evaluate the sample preservation known quantities (3.0 μg/L^{-1}) of each arsenic species were added to natural water samples previously adjusted to the selected reaction media and maintained in glass flasks at 4ºC. The different arsenic forms were determined over a period of nine days.

Arsenic determination in river water samples. The surface river water samples were collected in polyethylene flasks, filtered, adjusted as soon as possible to the appropriate reaction condition and maintained under refrigeration in glass flasks until the analyses. Figure 1 summarises the procedure for the selective determination of arsenite, arsenate and dimethylarsinate in natural water samples[18].

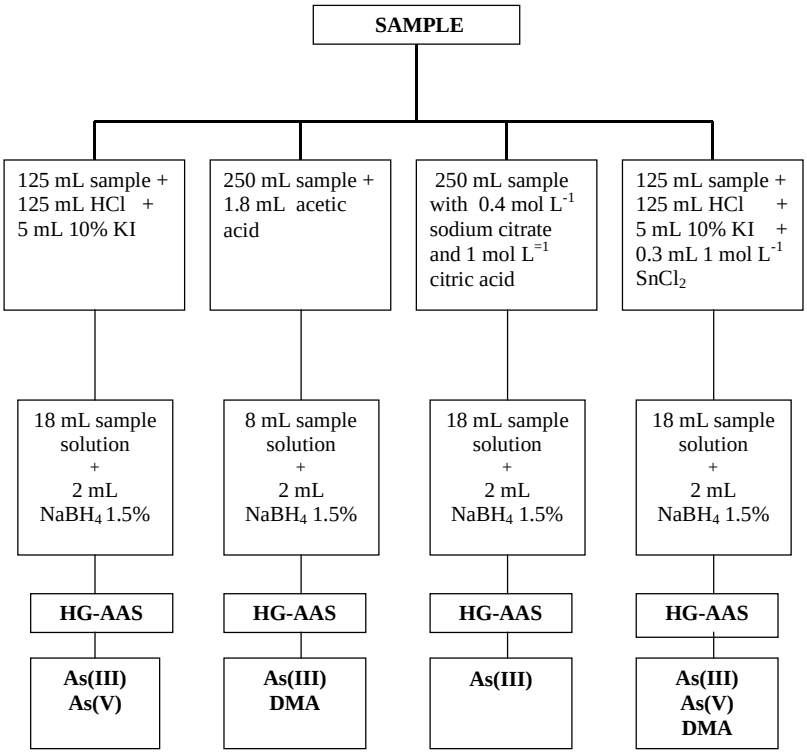

Figure 1. Procedure for As(III), As(V) and DMA selective determination in natural water samples

Results and Discussion

In a previous study[18] involving several ions, inter-ference effects in the arsenic determination were noted in hydrochloric acid medium, mostly due to manganese, chromium, antimony, mercury and bismuth. Interferences were also observed in citrate buffer and acetic acid media, due to iron, zinc, copper, nickel, chromium and selenium, when the ion was individually added to simple aqueous solutions; however, natural waters show much lower levels of such ions than their interference threshold, excluding Fe(III). As previously observed As(V) or DMA pre-reduction is rapid and complete, and these species give the same response as As(III) in the selected media[18]. Thus interfering effects in the analysis of real samples were evaluated adding known quantities of arsenite to a filtered water sample, adjusted to the selected reduction media. Once the slopes of these analyte addition curves were similar to those of the respective aqueous solutions, no interference was detected. So, a single curve could be established for each reduction medium, with very good correlation (Figures 2-4). Recovery tests adding arsenite to river water samples exhibited good mean values, always very close to 100% (Table 1). So, in spite of some interference effects of individual ions detected in simple aqueous solutions, the overall matrix contribution did not seem to cause errors when determining arsenic in real water samples.

Table 1. Recovery of Arsenic in Natural River Water (n=3).

Reaction media	Arsenic added, μg L^{-1}	Arsenic recovered, μg L^{-1}	Recovery, %
Hydrochloric acid			
6 mol L^{-1}	2.00	1.97±0.04	99
	3.00	2.99±0.06	99
	4.00	4.08±0.04	102
Citrate buffer			
0.4 mol L^{-1}	2.00	1.85±0.03	92
	3.00	3.11±0.04	104
	4.00	3.97±0.04	99
Acetic acid			
0.12 mol L^{-1}	2.00	2.03±0.20	101
	3.00	3.13±0.11	104
	4.00	3.85±0.07	97

An important aspect for speciation is the study of the conditions for sample preservation once the physico-chemical characteristics of the system must remain unaltered. The various equilibria occurring in natural waters involving metal ions make the sample preservation critical, as changes between arsenate and arsenite can be caused by bacterial activity, as well as by oxidising or reducing components in the natural water[19]. In general, the addition of acids has been recommended for natural water

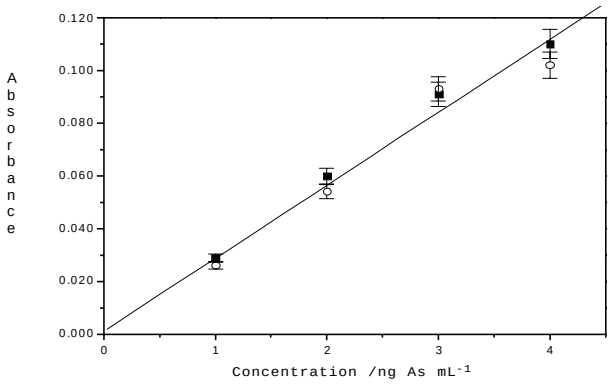

Figure 2. Analytical curve for As(III) in 6 mol L^{-1} HCl + 0.2% KI ○ aqueous solution ● analyte addition to the water sample. Average curve: A = 0.001 + 0.0276C (r^2 = 1); aqueous solutions curve: A = 0.0016 + 0.0282C (r^2 = 0.9969); analyte addition curve: A = 0.001 + 0.0271C (r^2 = 0.9882).

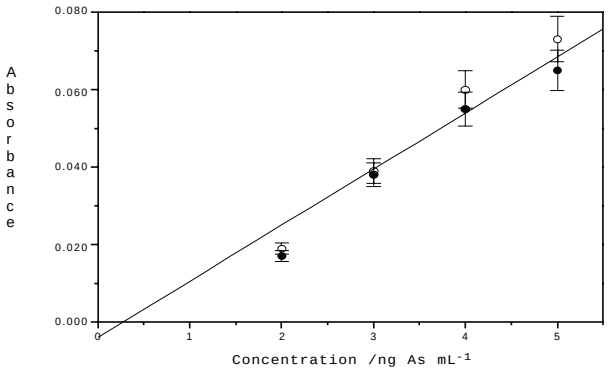

Figure 3. Analytical curve for As(III) in 0.12 mol L^{-1} acetic acid ○ aqueous solution ● analyte addition to the water sample. Average curve: A = -0.004 + 0.0144C (r^2 = 0.9944); aqueous solutions curve: A = -0.0044 + 0.0152C (r^2 = 0.9874); analyte addition curve: A = -0.003 + 0.0140C (r^2 = 0.9870).

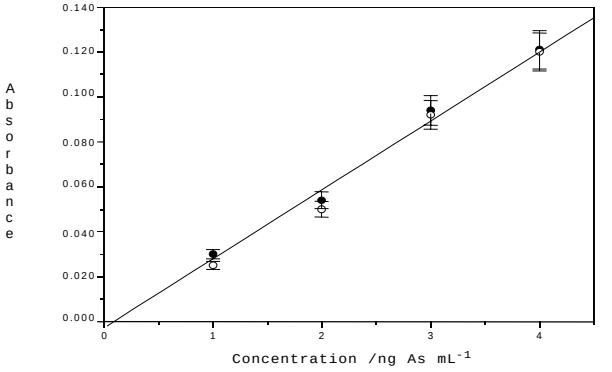

Figure 4. Analytical curve for As(III) in 0.4 mol L^{-1} citrate buffer solution ○ aqueous solution ● analyte addition to the water sample. Average curve: A = -0.003 + 0.0306C (r^2 = 1); aqueous solutions curve: A = -0.001 + 0.0306C (r^2 = 0.9974); analyte addition curve: A = -0.004 + 0.0307C (r^2 = 0.90).

preservation[7] but this procedure can not be used for arsenic speciation, as it would affect the arsenic forms present. On the other hand stored samples without any stabilisation resulted in arsenate reduction to arsenite within a few days[20]. Sample storage at the reduction media here proposed for speciation showed to be appropriate to preserve the water samples for arsenic speciation, according to Figures 5-7. Arsenic species concentrations in all the reduction media studied did not show significant changes over a period of three days, indicating sample stability for at least this period of time.

Arsenic species in eight water samples from different rivers (north and north-west region of the Paraná State, and south region of the São Paulo State, Brazil) were determined using the selective determination procedure proposed; all but two samples showed arsenic levels below the limit of detection. The samples, once collected and filtered, were subdivided and defined aliquots were adjusted to the proper reaction media (Figure 1). Triplicate analyses, for each particular system, were performed. The arsenic species – arsenite, arsenate and dimethylarsinate – were quantified both using aqueous analytical curves and the analyte addition calibration method and Table 2 shows the results obtained for the two samples. Total arsenic or arsenite plus arsenate concentrations were identical, whatever the calibration method considered, as pointed out by the statistical "t test" (p=0.95). These results confirm that speciation studies in 6.0 mol L^{-1} hydrochloric acid, after an appropriate pre-reduction, can be based on simple analytical curves from arsenite standards; for this medium, the detection limit was 0.47 μg As L^{-1} [18]. For these particular river water samples no analytical signal was detected in acetic acid or citrate buffer media, but this agrees with the detection limit found for these reduction media – 1.05 μg As L^{-1} and 0.6 μg As L^{-1}, respectively – and with the difference among total arsenic and the sum arsenite plus arsenate. The results indicate that arsenate was the predominant arsenical dissolved form for both samples analysed.

Once the sample was adjusted to the proper reaction media, all the speciation study can be carried out within less than thirty minutes, including triplicate measurements for each reduction system.

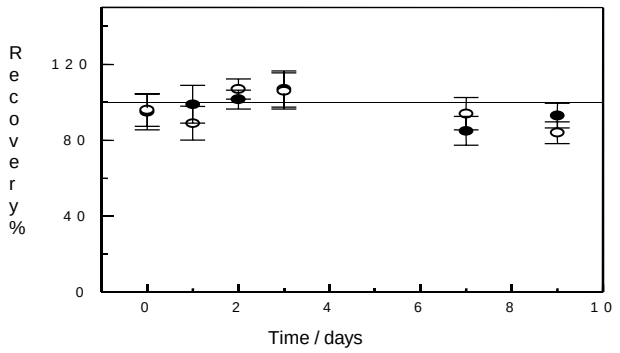

Figure 5. Sample stability in 6 mol L^{-1} hydrochioric acid (3.0 mg As/L) ○ As(III) ● As(V)

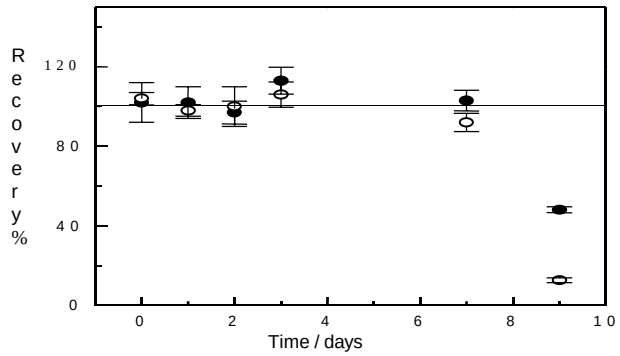

Figure 6. Sample stability in 0.12 mol L^{-1} acetic acid (3.0 mg As L^{-1}) ○ As(III) ● DMA

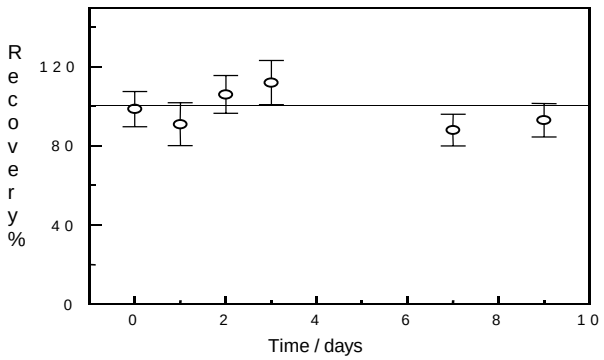

Figure 7. Sample stability in 0.4 mol L^{-1} citrate buffer (3.0 mg As L^{-1}) ○As(III)

Table 2. Arsenic Speciation in River Water Samples, ng mL^{-1}

	Analyte addition (n=3)			Analytical curve (n=2)		
Sample	(a)	(b)	(b) – (a)	(a)	(b)	(b) – (a)
Tibagi River	1.05±0.11	1.47±0.02	0.42±0.11	0.76±0.24	1.58±0.07	0.82±0.25
Cinzas River	0.87±0.04	1.55±0.03	0.58±0.03	0.95±0.03	1.81±0.09	0.86±0.10

(a) As(III) plus As(V) (b) As total

Conclusions

Selective reduction at different acid media allowed the speciation study of arsenic in natural waters, using arsenite aqueous analytical curves for calibration. No interference effect was observed in the studied natural water samples, certainly because the interfering metallic ions levels were below the interference threshold and also because they probably were present as complexed species; thus, the use of simple aqueous analytical curves without any previous separation or masking step was possible.

The sample storage at the reduction media proposed for the selective reduction speciation enabled a storage period of up to seven days for the different species studied.

The proposed procedure showed to be accurate, precise and low time consuming as just a very simple sample treatment is required.

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