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Article

Selective Reduction of Arsenic Species by Hydride Generation - Atomic Absorption Spectrometry Part 1 - Reduction Media

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A determinação seletiva de As(III), As(V) e ácido dimetilarsínico (DMA) foi estudada pela técnica da geração de hidretos - espectrometria de absorção atômica. Os meios de redução selecionados permitiram a determinação de As(III) na presença de tampão citrato (0,4 mol/L, pH4,4), As(III) + As(V) no meio HCl 6 mol/L, após uma pré-redução com iodeto de potássio, e As(III) + DMA em CH_3COOH 0,12 mol/L. O teor de arsênio total pode ser determinado no meio HCl 6 mol/L, após ser efetuada a pré-redução das formas As(V) e DMA com iodeto de potássio e cloreto estanoso. Os efeitos de interferência causados por diferentes íons metálicos foram, também, avaliados.

Hydride generation - atomic absorption spectrometry, using sodium tetrahydroborate(III) as a reductant, was used to form arsines selectively from inorganic arsenic(III) and arsenic(V), and dimethylarsinic acid (DMA). The selected reaction media allowed the rapid determination of arsenic(III) alone (citrate buffer 0.4 mol/L, pH 4.4), arsenic(III) + arsenic(V) (HCl 6 mol/L, after pre-reduction with potassium iodide) and arsenic(III) + DMA (acetic acid 0.12 mol/L). Total arsenic could be measured in HCl 6 mol/L, after arsenic(V) and DMA pre-reduction with a potassium iodide and stannous chloride mixture. Interference effects produced by heavy metal ions were also evaluated.

Keywords: *arsenic speciation, hydride generation, selective reduction, atomic absorption spectrometry*

Introduction

The environmental chemistry of arsenic is complicated by the widely differing properties of naturally ocurring and anthropogenic arsenic compounds. Arsenic can be present in nature mainly as inorganic species, arsenite and arsenate, and as methylated species, including methylarsonate and dimethylarsinate. The most widely observed biochemical fate of arsenic in the environment is methylation[1,2] . Even where methylated arsenic compounds have not been used agriculturally, inorganic arsenic can be converted into methylated forms in the environment; these organoarsenic compounds are released into the aqueous environment, thereby becoming available to higher levels of the food chain [3,4].

The bioavailability and the physiological / toxicological effects of arsenic depend on its chemical form[5] and, thereby, knowing the arsenic speciation and transformations in the environment becomes very important, needing accurate methods for separation and determination of arsenic species.

Numerous analytical techniques have been applied to arsenic determination in environmental samples; the most widely accepted procedure for total arsenic analysis uses the reduction of arsenic compounds to gaseous arsine. This gas can be decomposed to give elemental arsenic for atomic absorption spectrometry or undergo a colorimetric reaction. In differentiation studies, various chromatographic techniques have been used, which are often coupled with element-specific detection methods (graphite furnace ato-

mic absorption spectrometry or inductively coupled plasma atomic emission spectrometry)[6-14].

The literature shows that the reduction of arsenic compounds with sodium tetrahydroborate is pH dependent and related to the dissociation constants of the individual arsenic acids[15]; each acid must be totally protonated in order to allow arsine formation.

This paper describes the use of pH, reaction matrix and redox agent for the selective determination of arsenate (As(V)), arsenite (As(III)) and dimethylarsinic acid (DMA), using hydride generation with sodium tetrahydroborate as reductant and atomic absorption spectrometry for detection.

Experimental

Apparatus

A Varian Techtron AA-175 atomic absorption spectrophotometer, set to 193.7 nm, and equipped with a hydrogen hollow cathode lamp (Varian Techtron) background corrector and an arsenic hollow cathode lamp (CG Instrumentos Científicos), operating at 6 mA, was employed; the slit width on the spectrophotometer was set to 1 nm.

The hydride generation apparatus consisted of a 100 mL flask with a hole half-way down the side which served for the addition of reagents. At the top of the flask a syringe was adapted to permit the addition of the reductant solution. A nitrogen stream was used to sweep the arsines into a quartz tube (11.5 cm x 1.5 cm i.d.) atomizer aligned in the optical path of the spectrophotometer, and heated by an air/acetylene flame.

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

Reagents

Arsenic oxide 99.5%, for inorganic As(III), Riedel-De Haenag

Arsenic pentoxide 99.3%, for inorganic As(V), Baker Analyses

Dimethylarsinic acid, sodium salt, 98%, Sigma

Sodium tetrahydroborate 95%, Merck

All other reagents were of analytical - reagent grade.

Aqueous stock 1000 μg/mL solutions of arsenic species were standardized [16] ; arsenic(V) and DMA solutions were standardized against arsenic(III), using flame atomic absorption spectrometry technique.

Procedure

Sodium tetrahydroborate solution, stabilized with 0.5% sodium hydroxide, was injected into the generator flask containning the arsenic solution, with stirring; the nitrogen flow was directed so as to bypass the solution. After 60 s, the flow of nitrogen was quickly directed through the hydride generating solution, allowing the analytical signal to be measured. The solution was drained and the flask rinsed with distilled water. The absorbance peak height measurements for each solution were corrected for reagent blank signals.

Effect of acid medium on arsine generation

Species response *vs.* reaction media constituents profiles were monitored by analysing solutions containning a constant concentration of the arsenic species - 5.0 ng As/mL, but varying the nature and the concentrations of the reaction matrix.

The responses generated from As(III) in hydrochloric acid, acetic acid, sulphuric acid and orthophosphoric acid were investigated. Hydrochloric acid, acetic acid and citrate buffer media were studied as reaction matrix for the selective determination of As(III), As(V) and DMA.

Interference Effects

Interference effects from Fe(III), Ni(II), Zn(II), Cu(II), Cr(III), Cr(VI), Mn(II), Se(IV), Sb(III), Hg(II) and Bi(III) were evaluated in the established media which were suitable for the selective reduction of arsenic. The concentration of each arsenic species used in this study was 5.0 ng/mL; the potentially interfering ion was added up to 2.0 μg/mL (except for zinc ion), *i.e.*, up to 400 - fold excess. Calibrators were run at regular intervals, and blanks solutions were analysed for each matrix and matrix plus interfering ion.

Pre-reduction of As(V) and DMA

The As(V) pre-reduction step was achieved by adding potassium iodide 10% m/v solution (1 mL) to the sample, in the selected medium, HCl 6 mol/L. The addition of 250 L of stannous chloride 0.5 mol/L solution and 1 mL of potassium iodide 10% m/v solution to a 100.0 mL portion of sample in HCl 6 mol/L allowed the DMA and As(V) pre-reduction.

Results and Discussion

Hydrochloric acid was shown to give the best sensitivity in the determination of As(III), in a large concentration range, with similar profiles being obtained with sulphuric acid up to 1.2 mol/L. Nevertheless, when using sulphuric acid, the reproductibility was low. The signals in sulphuric acid decayed considerably for concentrations above 1.2 mol/L, but with hydrochloric acid the response increased above this acid concentration, thus permitting investigation of this matrix for the selective reduction of arsenic species. In the orthophosphoric acid matrix, a very narrow concentration range was shown to give the highest analytical signal but acid concentrations above or below 0.2 mol/L resulted in smaller responses.

The signals generated from As(III), As(V) and DMA in hydrochloric acid are shown as a function of acid concentration in Fig. 1. For the studied acid concentrations, the responses of As(III) were higher than DMA or As(V) signals. The responses for DMA were shown to fall after 0.1 mol/L, with the absorbance approaching zero at 5 mol/L acid concentration. The response for As(V) was low, although increasing up to 5.0 mol/L acid concentration. These results were similar to there same obtained by other authors[17,18].

Figure 2 shows the signals obtained with acetic acid. This matrix allowed the generation of arsines from both As(III) and DMA to almost identical extents over the entire concentration range studied. As(V) response was low, showing a broad plateau for an acetic acid concentration greater than 0.2 mol/L. Good separation between the responses of As(III) + DMA and As(V) can be seen at 0.1-0.2 mol/L acetic acid concentration.

The responses produced by using citrate buffer, as can be seen in Fig. 3, showed the maximum signals for DMA at approximately 0.1 mol/L citrate concentration. At higher citrate concentrations the DMA signal decayed steadily. The response from As(V) was much lower than that of As(III), which showed a plateau for the studied citrate concentrations. The maximum separation between the responses of As(III) and DMA or As(V) was achieved above the 0.4 mol/L concentration in the citrate buffer solution. This suggested that this matrix should be further studied for determining As(III) in the presence of DMA or As(V). Figure 4 shows the absorbance for As(III) and DMA as a function

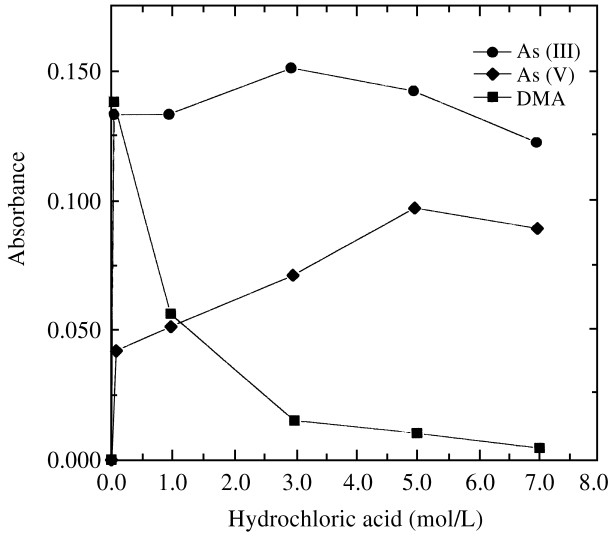

Figure 1. Effect of hydrochloric acid concentration on the response of As(III), As(V) and DMA during reduction by $NaBH_4$.

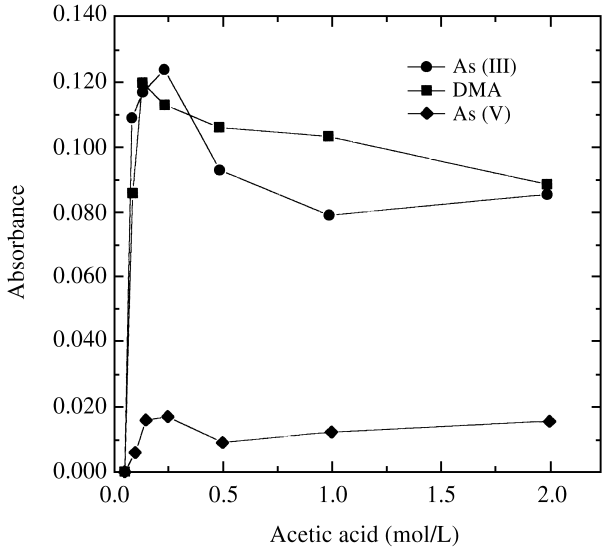

Figure 2. Effect of acetic acid concentration on the response of As(III), As(V) and DMA during reduction by $NaBH_4$.

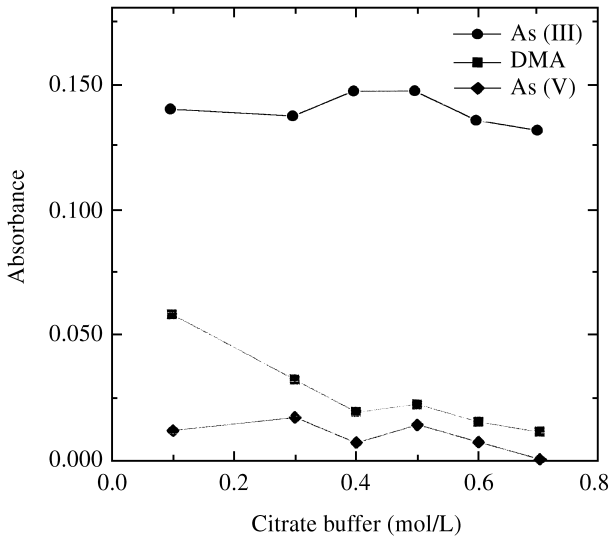

Figure 3. Effect of citrate buffer concentration on the response of As(III), As(V) and DMA during reduction by $NaBH_4$.

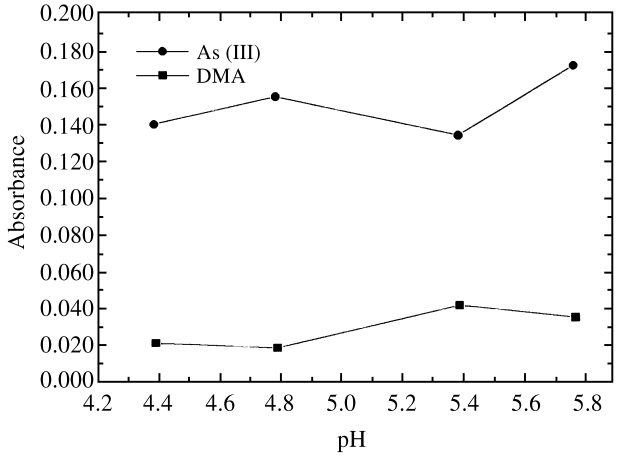

Figure 4. Effect of pH on the response of As(III) and DMA during reduction by $NaBH_4$. Reduction matrix: 0.4 mol/L citrate buffer soluti-

of initial pH values in citrate buffer solution (0.4 mol/L); as As(V) responses were negligible they were excluded from the diagram. This figure shows that for pH values above 4.8 the DMA contribution to the arsine generation becomes greater, so limiting the optimum pH range for the speciation studies.

As the reaction product is a gaseous compound, the arsine dissolution equilibrium is very important and like gas liberation is also affected by the volumes ratio in the flask (solution volume to free volume). The effect of the volume of the solution on the analytical signal was studied to achieve the best precision and sensivity, without lost of easiness in the procedure.

The influence of the sample volume on the efficiency of arsine evolution was assessed over the range 10-40 mL (Fig. 5). Up to 30 mL the sample volume had no effect on the absorbance of the arsenic in acetic acid medium, but for sample sizes above 30 mL lower signals were obtained. In hydrochloric acid, the absorbance was higher for the largest sample volume; nevertheless, volumes above 20 mL were problematic due to the gas pressure in the flask. In citrate buffer solutions, the greatest absorbances were found for sample volumes from 20 to 30 mL. This study allowed the choice of the sample volumes in the generator flask suited for each reaction matrix: 20 mL for hydrochloric acid and citrate buffer, and 10 mL for acetic acid; the total volume of the generator flask used was 300 mL.

An important parameter in the hydride generation technique involves the reductant concentration in the reaction media. When injecting the same volume of solutions of different reductant concentrations, in the range 1-2%, into the reaction flask containning a constant concentration of As(III), it was verified that the absorbance is higher for the greatest reductant concentration; the more concentrated sodium tetrahydroborate solutions produced a premature release of arsenic hydrides, and also increased the inner pressure in the flask, making difficult the measurements. In Fig. 6 the behavior of As(III) in each reaction medium with different reductant concentrations can be seen; the obtained curves were very similar, thus allowing to fix the 1.5% sodium tetrahydroborate concentration for all the media studied.

The effect of altering the carrier gas flow-rate on the arsine liberation and transport to the absorption cell can be seen in Fig. 7. This effect is influenced by the instrument response time and by the arsenic concentration in the atomizer. The analytical signals obtained, when varying the nitrogen flow rate from 0.1 L/min to 1.7 L/min, were greatest for the higher flow rate. Above 1.7 L/min it was impossible to measure the signal due to the smaller hydride residence time in the quartz cell. The 0.9 L/min nitrogen flow rate was selected for the laboratory system.

Potassium iodide was shown to cause the rapid reduction of As(V) in high concentrations of hydrochloric acid,

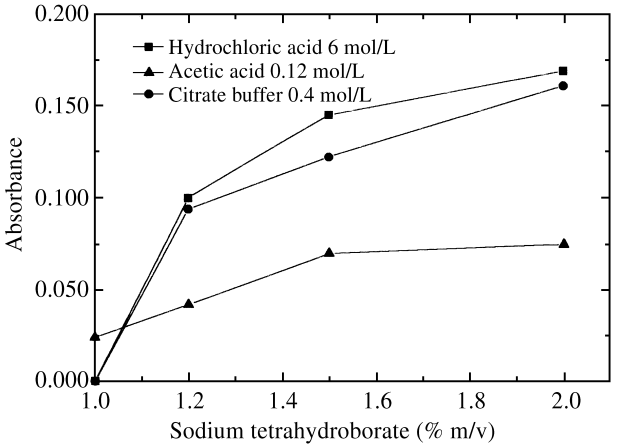

Figure 6. Effect of sodium tetrahydroborate (III) concentration on the response of As(III) in the selected reduction media.

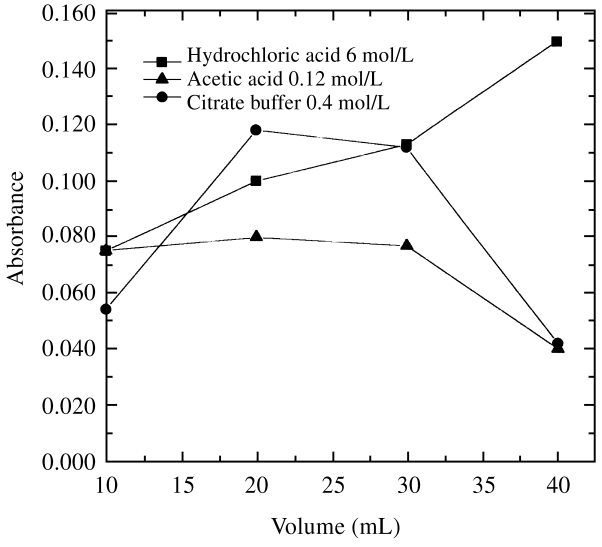

Figure 5. Influence of sample volume on the response of As(III).

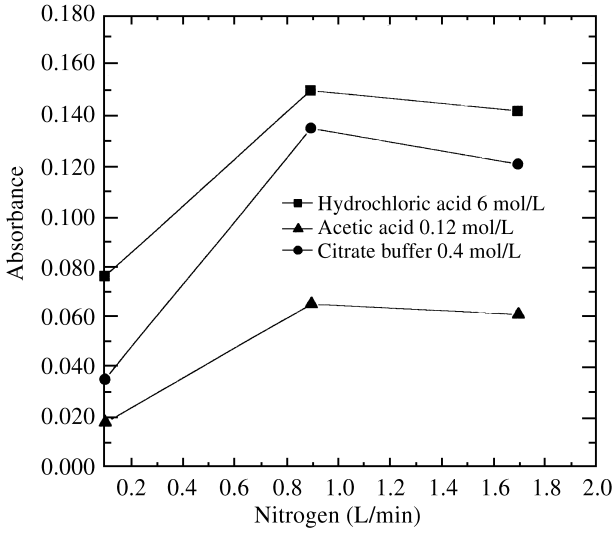

Figure 7. Influence of carrier gas flow rate on the response of As(III).

thus allowing the selective determination of As(III) + As(V) with negligible interference from DMA. In Fig. 8 an analytical curve for As(III) and As(V), after pre-reduction with potassium iodide, is shown; both species gave identical analytical signal, indicating that the As(V) reduction was complete. However, potassium iodide alone failed to reduce DMA, even in 6 mol/L hydrochloric acid concentration. Potassium iodide and stannous chloride were shown to reduce As(V) and DMA rapidly, thereby providing a way for the determination of total arsenic. After this pre-reduction, As(V) and DMA gave the same response as As(III), as can be seen in Fig. 9. The detection limit (located at 3σ above the blank signal, with σ as the standard deviation of 20 blank measurements) achieved in this acid matrix was 0.43 ng As/mL.

The analytical curves in acetic acid reaction medium for As(III) and DMA is shown in Fig. 10. Both species exhibited the same response in this medium, thus permitting their determination with only one analytical curve for As(III), with a detection limit equal to 1.04 ng As/mL.

In citrate buffer matrix, the presence of arsenic as DMA in the same quantity as As (III), had no effect on the signal of As(III), but when DMA concentration increased, the absorbance increased too, as could be expected from Fig. 3; when the ratio of As (III) to arsenic as DMA becomes equal to 0.1, the signals became almost 40% greater (Fig. 11). As(V) in this same matrix showed a similar behavior (Fig. 12), and the absorbance was 50% greater when As(III)/As(V) was 0.1. As in general both As(V) and DMA levels in natural waters are smaller than As(III) concentration, those arsenic species cause no problems when using analytical curves for As(III) alone, in citrate buffer and acetic acid reaction media. In this buffer matrix the detection limit achieved was 0.53 ng As/mL.

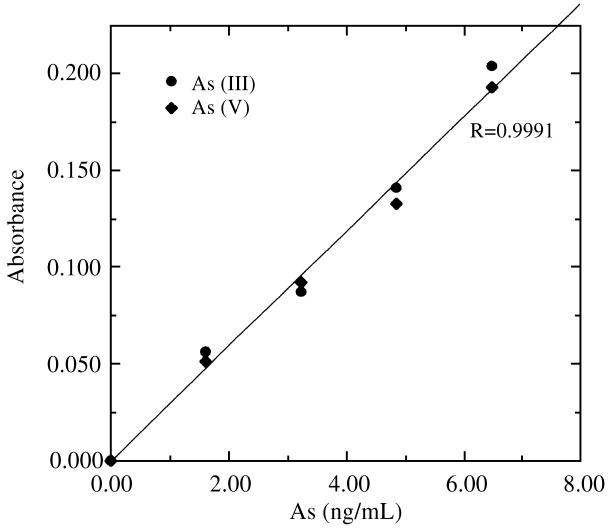

Figure 8. Analytical curves for arsenic in hydrochloric acid 6 mol/L, after pre-reduction of As(V) with potassium iodide.

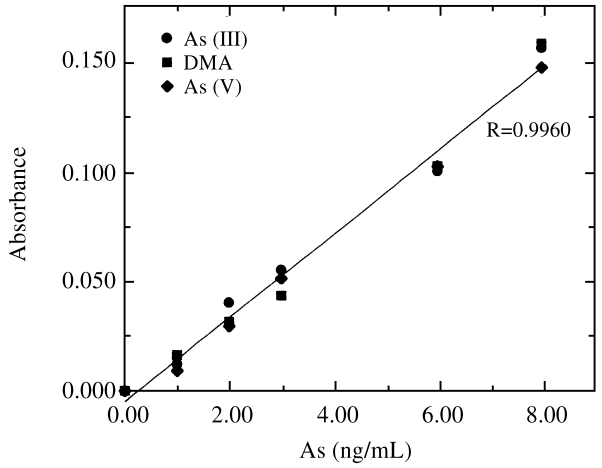

Figure 9. Analytical curves for arsenic in HCl 6 mol / L, after pre -reduction of As(V) and DMA with potassium iodide and stannous chloride.

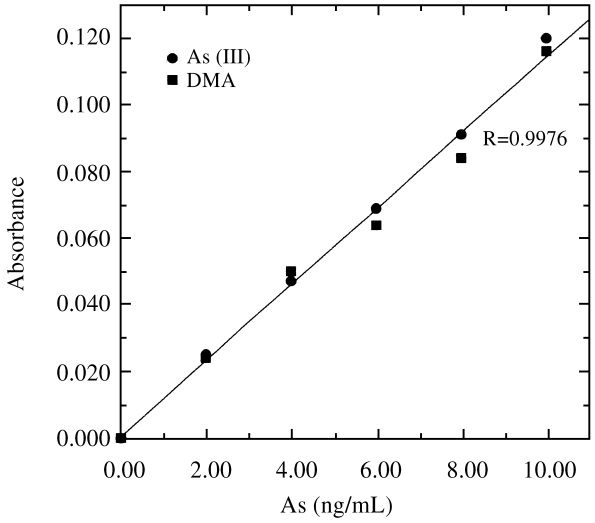

Figure 10. Analytical curves for arsenic in acetic acid 0.12 mol/L.

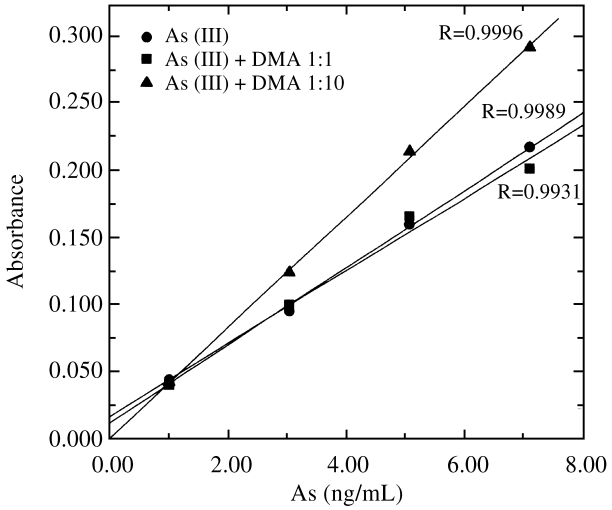

Figure 11. Analytical curves for As(III) in the presence of DMA. Reduction matrix: 0.4 mol/L citrate buffer solution.

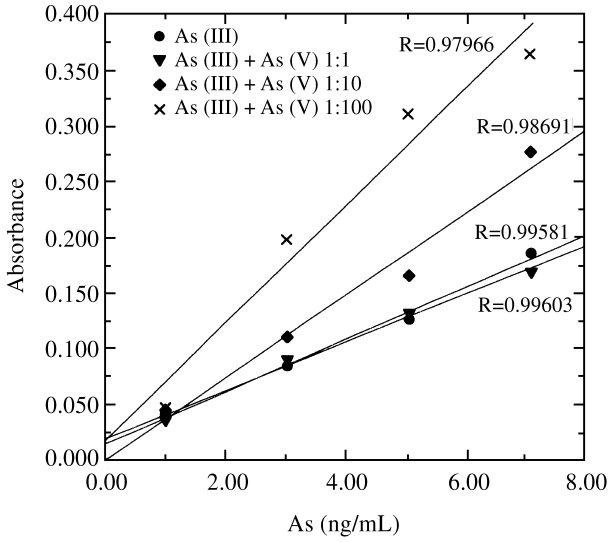

Figure 12. Analytical curves for As(III) in the presence of As(V). Reduction matrix: 0.4 mol/L citrate buffer solution.

Interference Effects

Interferences can be derived from two distinct sources, the formation of competing hydrides and inhibition of arsine generation. Tables 1-3 show the effect of various concentrations of elements on the recovery of arsenic species in the different reaction media. The effects are expressed as percentage deviation from the interference-free response; differences greater than 10% were considered to be a result of interference effects.

Interferences were most severe in the determination of As(III) in hydrochloric acid medium, with significant effects from excess of Mn(II), Cr(III), Cr(VI), Sb(III), Bi(III), and Hg(II). In acetic acid medium, Zn(II), Fe(III), Cu(II), and Ni(II) caused the greatest effects on the response of As(III); in the determination of DMA, in this same matrix, high interference effects from Zn(II), Cu(II), and Ni(II) were observed. Interferences due to Cr(III), Cr(VI), Se(IV), Cu(II), Zn(II), and Fe(III) were evident in the determination of As(III) in the presence of citrate buffer matrix.

Elements which give rise to volatile hydrides were shown to depress the response of arsenic in hydrochloric acid medium. The depression in the presence of Cu(II), Fe(III), Zn(II), and Ni(II) is believed to be due to inhibition of arsine generation.

Final Discussion

The use of different acid media allowed speciation studies of arsenic. Hydrochloric acid provided a means of minimising the hydride contribution from the methylated arsenic compounds, as the relative hydride response for methylated arsenic species decreased with increasing acidity of the hydride generating solution. Similarly, in acetic acid the As(V) response could be reduced, permiting a good separation between As(III) + DMA and As(V) responses.

Aiming to find a chemically inert buffer that would allow the selective reduction of arsenic species, particular consideration was given to buffers whose working ranges covered the pH range 4-9 (in consequence of the pK of the individual arsenic acids), mantaining a reasonably constant pH during mixing with the reductant solution stabilised by sodium hydroxide. Great difficulties were mentioned in the

Table 1. Effect of metal ions on the recovery of As(III) in the hydrochloric acid matrix.

interfering ion	concentration, μg/mL	deviation, %
Fe(III)	0.56	-5
	1.0	-8
	2.0	+8
Cu(II)	0.5	0
	1.0	+4
	2.0	+16
Zn(II)	5.0	-7
	10	+29
Ni(II)	0.5	+2
	1.0	+9
	2.0	-29
Mn(II)	0.5	-13
	1.0	-41
	2.0	-50
Cr(III)	0.5	-47
	1.0	-58
	2.0	-63
Cr(VI)	0.5	-66
	1.0	-45
	2.0	-53
Sb(III)	0.001	-44
	0.01	-49
	0.1	-23
Bi(III)	0.001	-47
	0.01	-55
	0.1	-47
Se(IV)	0.001	-24
	0.01	-5
	0.1	-40
Hg(II)	0.001	-35
	0.01	-38
	0.1	-37

literature in finding such buffer systems[18]. Hydrogen evolution and, consequently, degassing rates in media whose initial pH values were greater than 6.0-6.3 were slow, as the rate of decomposition of the reductant is strongly pH dependent. Therefore, hydride generation was not feasible at pHs approaching neutrality. In the different media investigated, only citric acid matrix led to As(III) determination in the presence of DMA or As(V).

In order to change the oxidation state of inorganic arsenic species, several redox systems have been used in a wide range of analytical procedures [18]; some of these redox systems require heating or long reaction times. In this work emphasis was towards speed and efficiency in analysis; appropriate reagents were therefore chosen for use with the reaction matrix previously selected. The employed low stannous chloride concentration allowed its use as a reductant, although the stannous ion reduces the arsenic signal.

Hydrochloric acid reaction medium can be considered interference free with respect to the determination of arse-

Table 2. Effect of metal ions on the recovery of As(III) in the citrate buffer matrix.

interfering ion	concentration, μg/mL	deviation, %
Fe(III)	0.56	-64
	1.0	-64
	2.0	-64
Cu(II)	0.5	-57
	1.0	-57
	2.0	-57
Zn(II)	5.0	-58
	10	-62
Ni(II)	0.5	-6
	1.0	-1
	2.0	-6
Mn(II)	0.5	-5
	1.0	+8
	2.0	+3
Cr(III)	0.5	-41
	1.0	-62
	2.0	-67
Cr(VI)	0.5	-28
	1.0	-56
	2.0	-71
Sb(III)	0.001	-3
	0.01	+1
	0.1	-7
Bi(III)	0.001	+14
	0.01	+10
	0.1	-10
Se(IV)	0.001	-2
	0.01	-19
	0.1	-50
Hg(II)	0.001	+3
	0.01	+3
	0.1	-2

Table 3. Effect of metal ions on the recovery of As(III) and DMA in the acetic acid matrix.

interfering ion	concentration, μg/mL	deviation, %	
		As(III)	DMA
Fe(III)	1.12	-18	-3
	11.2	-49	-5
	50.5	-51	-18
Cu(II)	0.44	-14	-27
	1.0	-29	-57
	5.0	-100	-95
Zn(II)	10	-70	-25
	100	-70	-82
Ni(II)	0.5	-62	-51
	1.0	-78	-65
	2.0	-99	-76
Mn(II)	0.5	-10	+8
	1.0	+3	+18
	2.0	-4	+18
Cr(III)	0.5	+6	+7
	1.0	+29	+15
	2.0	-31	-18
Cr(VI)	0.5	+14	+7
	1.0	+22	+3
	2.0	+7	+15
Sb(III)	0.001	+10	-17
	0.01	-7	-6
	0.1	-35	+14
Bi(III)	0.001	+6	0
	0.01	-8	+18
	0.1	-3	-6
Se(IV)	0.001	-8	+28
	0.01	0	+38
	0.1	+25	-19
Hg(II)	0.001	-1	+32
	0.01	-1	+14
	0.1	+32	+28

nic species in natural waters, as the concentrations of Ni(II), Mn(II), Cr(III), Cr(VI), Sb(III), Bi(III), Se(IV), and Hg(II) are low. In citrate buffer and acetic acid media several elements produce interference problems.

Conclusion

There were distinct differences between the responses of the arsenic species in each of the acid reaction media investigated. The use of 6 mol/L hydrochloric acid provided a means of minimising the hydride contribution from the methylated arsenic compounds as part of a speciation investigation.

Dimethylarsinic acid, expected to be the most abundant methylated arsenic compound in freshwater, could be determined together with As(III) in acetic acid matrix, thus permiting a speciation study.

The proposed method for the arsenic species determination in natural waters is simple, rapid and selective, dispensing any extraction or sample digestion procedure; due to its easy operation, it can be regarded as a very effective tool in the arsenic speciation studies.

Acknowledgments

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References

1. Lederer, W.H.; Fensterheim, R.J. In *Arsenic: Industrial, Biomedical, Environmental Perspectives*; Van Nostrand, New York, 1983.
2. Anderson, L.C.D.; Bruland, K.W. *Environ. Sci. Technol.* **1991**, *25*, 420.
3. Jitoh, F. *Anal. Chim. Acta* **1990**, *228*, 85.
4. Manahan, S.E. In *Environmental Chemistry*; Lewis, New York, 1991.
5. Greenwood, N.N.; Earnshaw, A. In *Chemistry of the Elements*; Pergamon Press, New York, 1984, p.637-644.
6. Chappell, J. *Talanta* **1995**, *42*, 323.
7. Hasegawa, H. *Anal. Chem.* **1994**, *66*, 3247.
8. Li, Z. *Anal. Chim. Acta* **1995**, *307*, 79.
9. Hwang, C.; Jiang, S. *Anal. Chim. Acta* **1994**, *289*, 205.
10. Ruede, T.; Puchelt, H. *Frenesiu's J. Anal. Chem. Sep.* **1994**, *350*, 44.
11. Santosa, S.J. *Anal. Chim. Acta* **1990**, *237*, 189.
12. Sanz, J. *Anal. Chim. Acta* **1991**, *255*, 113.
13. Haraguchi, H.; Takatsu, A. *Spectrochim Acta Part B* **1987**, *42*, 235.
14. Yan, Xiu-Ping; Ni, Zhe-Ming *Anal. Chim. Acta* **1994**, *291*, 889.
15. Agterdenbos, J. *Anal. Chim. Acta* **1987**, *197*, 315.
16. Meites, L. In *Handbook of Analytical Chemistry*; McGraw-Hill, New York, 1963, p.3(61).
17. Narasaki, H.; Ikeda, M. *Anal. Chem.* **1984**, *56*, 2059.
18. Anderson, R.K.; Thompson, M.; Culbard, E. *Analyst* **1986**, *111*, 1143.