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Arsenic species analysis in porewaters and sediments using hydride generation atomic fluorescence spectrometry

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Abstract: It was observed that the atomic fluorescence emission due to As(V) could has a 10% to 40% of fluorescence emission signal during the determination of As(III) in the mixture of As(III) and As(V). Besides, interferes from heavy metals such as Pb(II), Cu(II) can cause severe increase of the signals as compared to the insignificant effects caused by Cd(II), Zn(II), Mn(II) and Fe(III). On the basis of further studies, the masking agent of 8-hydroxyquinoline was used as an efficient agent to eliminate interference of As(V) emission and the heavy metal of Cu^{2+} and Pb^{2-} in the measurements of arsenic species. After a series standard additions and CRM researches, a sensitive and interference-free analytical procedure was developed for the speciation of arsenic in samples of porewaters and sediments in Poyang Lake, China.

Keywords: arsenic speciation; 8-hydroxyquinoline; porewaters; sediments; Poyang Lake

Introduction

The toxicity of arsenic (As) is depended on the chemical species present. In the aquatic environment, arsenic can occur in several oxidation states (-III, 0, III , and V), but in natural waters it is mostly found in inorganic form as oxyanions of arsenite As (III), arsenate, As (V) (Smedley and Kinniburgh, 2002). Organic As associated with various inorganic and organic compounds or colloids forms could display different biological and geochemical behaviors in natural system. Inorganic arsenic compounds as arsenite, As(III), and arsenate, As(V), are more toxic than organic arsenic compounds and have been established as human carcinogens mainly with lung and skin cancer (Samanta *et al.*, 2000). In order to understand the distribution and the mobility of the various arsenic species, an analytical scheme supported by very sensitive and accurate measuring techniques is essential.

Many analytical methods that have been developed for the determination and speciation of arsenic are well reviewed (Gong *et al.*, 2002; Burguera and Burguer, 1997). A highly sensitive and practical analytical technique is required because of the relatively lower content even in total arsenic and particularly in its species. There are several techniques available for the determination of As species, including hydride generation-atomic absorption spectrometry (Shraim *et al.*, 1999), high performance liquid chromatography inductively coupled plasma mass spectrometry (Samanta *et al.*, 2000), ion chromatography-inductively coupled plasma mass spectrometry (Pantsar-Kallio and Manninen, 1997; Huang and Ilgen, 2004), combined gas chromatography and mass spectrometry (Pantsar-Kallio and Korpela, 2000), and neutron activation analysis (Sun and Yang, 1999). However, hydride generation (HG) combined to atomic fluorescence spectrometry (AFS) is the most common powerful tool for the speciation of metalloids, such as As, Se and Sb, particularly in environmental samples at low concentrations (Deng *et al.*, 2001; Cai, 2000). This technique involves the conversion of all arsenic species to As(III), which can then react with the reducing agent to form the hydride (Cai, 2000). The hydride generator can be coupled to cooling traps to dry and pre-concentrate the gas of hydride generation. The speciation of arsenic in porewaters requires a technique that is not only sensitive and reproducible but also capable of using a minimum volume of solution.

The purpose of this study was to establish a preparation and analytical scheme for the speciation of arsenic in lake porewaters and the partitioning of arsenic in lake sediments.

1 Experimental

1.1 Apparatus

An AFS-2202 equipped with a continuous flow injection hydride generation system and a boosted discharge hollow cathode lamp as the source of atomic fluorescence detector (Beijing Haiguang Analytical Instrument Co., China) was used for all the determinations. Hydride compounds were atomized in hydrogen flame produced during hydride formation. Instrument working conditions are given in Table 1.

1.2 Reagents

Stock solutions of 1000 mg/L As(III), As(V) were prepared from commercial salts: sodium arsenite ($NaAsO_2$, Sigma), sodium hydrogenarsenate heptahy-

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Table 1 Instrument working conditions

Parameter	Data	Parameter	Data
High voltage of PMT, V	270	Flow rate of carrier gas (Ar), ml/min	400
Atomizer temp., ℃	200	Flow rate of shield gas (Ar), ml/min	1000
Atomizer height, mm	8	Measure mode	Std. curve
Lamp current, mA	55	Signal type	Peak area

drate ($Na_2HAsO_4 \cdot 7H_2O$, Sigma) in 10% (v/v) HCl (G. R., Chengdu), respectively. A 2.5% potassium terahydroborate (99%, Sigma) stabilized in 0.5 % (w/v) KOH (G. R. Chengdu) was prepared. The solution was filtered through a 0.45-μm membrane. A stock solution of 50% (w/v) potassium iodide (A.R., Shanghai Chemical Co.) containing 10% (w/v) L-ascorbic acid (A.R., Shanghai Biochemistry Co., China) was prepared. To prepare 8-hydroxyquinoline stock solution 0.1 % (w/v), 0.10 g of 8-hydroxyquinoline (G.R., Sigma) was dissolved in a 1.0-ml of methanol (99.8%, A.R., Chengdu), then diluted with double deionized water to make 100.0 ml in 10% (v/v) HCl. All acids in G.R. grade (Chengdu Chemicals Co., China) and double deionized water were used. All stock solutions were stored at 277.15 K in the dark and used for daily preparation.

1.3 Sampling sites

Poyang Lake, which is the largest freshwater lake in China located in north of Jiangxi Province, China and in the south of mid-to-low of Yangtze River at 115°49'—116°46'E and 28°24'—29°46'N. The average depth is 8 m, and the maximum depth is 23 m. With eleven counties around the lake, it is connected with five main rivers named Ganjiang, Fuhe, Xinjiang, Raohe and Xiuhe. The water from these five rivers runs through the lake, empty into the Yangtze River through a 1-km long channel at Hukou. In this study, three places corresponding to Kangshan (the mainly input from external resources), Ruihong (almost in the center of the Lake) and Hukou (the only output from Poyang Lake to the Yangtze River) were chose, respectively.

Sediment and porewater samples were collected using diffusion sampling method (Xu *et al.*, 1997; Carignan *et al.*, 1985) in Kangshan (116°22'25.3"E, 28°49'27.6"N),Ruihong(116°20'41.1"E, 28°45'40.1"N) and Hukou (116°11'35.8"E, 29°43'50.7"N), respectively in Poyang Lake. With this sampling approach, a volume of deoxygenated demineralized water contained within a filtration membrane (0.22 μm membrane) was allowed to equilibrate the overlying and interstitial waters as the Plexiglas support was inserted in the sediments. After a 14-d equilibration period *in situ*, the peepers were retrieved from the sediment by diver and sampled immediately. The samples were stored in precleaned Teflon containers, kept in refrigerator at 193.15 K soon.

Sediment cores were collected by a diver close to the peepers using a Plexiglas tube. The cores were transported to the laboratory and extruded immediately in a glove-box bag with nitrogen gas around to prevent the oxidation. Sediment samples from each depth were collected and placed in precleaned polyethylene containers and kept frozen at 193.15 K until analysis.

1.4 Analytical procedures for porewater samples

1.4.1 Determination of As(Ⅲ)

The determination of As (III) by HG-AFS does not require any sample pretreatment. A 3.0-ml aliquot of the porewater sample, 195.0 μl of 0.1% 8-hydroxyquinoline solution and 700.0 μl HCl (50%, v/v) were added to a 5-ml polyethylene tube to obtain a 3.895-ml of final solution in 0.005% 8-hydroxyquinoline and 10% HCl matrix. The concentration of As(III) in the sample was determined directly by HG-AFS.

1.4.2 Determination of As(Ⅴ)

For the determination of As(V), a prereduction step is necessary. A separate aliquot of porewater 3.0 ml, 165.0 μl of 50% KI solution, 205.0 μl of 0.1% 8-hydroxyquinoline solutions and 741.0 μl of HCl (50%) were added to 5-ml polyethylene tube to obtained a 4.111-ml of final solution in 2.0% KI, 0.005% 8-hydroxyquinoline and 10% HCl. Then, left for 20 min at room temperature. The concentration of As(Ⅴ) was obtained by subtracting As (Ⅲ) from the total inorganic As (As(Ⅴ) + As(Ⅲ)).

1.4.3 Total arsenic analytical procedure of As(Ⅴ) + As(Ⅲ) + organic As

To determine the fraction of total dissolved As associated to organic matter (As-org), a third aliquot of porewater 3.0 ml was poured into a 10-ml Teflon bomb and 0.1 ml of nitric acid (con.) was added, and then the cap was tightened. The sample was subjected to microwave oven digestion at 720 W for 5 min. After digestion, the sample was allowed to cool at room temperature, then 165.0 μl of 50% KI and 205 μl of 0.1% 8-hydroxyquinoline solutions and 741 μl of HCl (50%) were added to obtained a 4.211-ml of final solution in 2.0% KI, 0.005% 8-hydroxyquinoline and 10% HCl, then determined. The concentration of organic As was obtained by subtracting the sum of (As(V) + As(III)) from the total As concentration.

1.5 Sequential extraction procedures for sediment samples

1.5.1 Arsenic bound to Fe and Mn oxyhdroxides (identified as As(ox))

The sequential method used in the partitioning of As for lake sediment samples in the experiments was a modified version described by Tessier *et al.* (1979,

1985) and has also been used to study the geochemistry of Se (Xu *et al.*, 1997; Belzile *et al.*, 2000) and Sb (Chen *et al.*, 2003). In briefly, a solution of 20 ml of 0.2 mol/L oxalic acid buffered to pH 2.0 with 0.2 mol/L ammonium oxalate was added to a portion of wet sediment sample (equivalent to 0.5 g dry weight). The sediment was extracted in a shaker (Model QYC-211 Rocking Incubator, Shanghai Fuma Test Equipment Co. Ltd) at room temperature for 8 h to remove trace As mainly bound to Fe and Mn oxyhydroxides. The dissolved phase and the residue were separated by vacuum filtration (0.22 μm membrane). The filtrate was analysed for As(ox).

1.5.2 Arsenic bound to organic matter (identified as As(red))

In the next step, a solution of 6.0 ml of 0.02 mol/L of nitric acid and 10.0 ml of pH=2 of commercial hydrogen peroxide adjusted with 0.02 mol/L nitric acid were added to the sediment residue, then extracted in a hot water bath (Model SHA-C, Jiangshu Southern River Instrument Factory) at (358.15 ±2) K for 5 h with occasional agitation to remove trace As bound to organic matter. After cooling, it is followed by a 5.0-ml of 3.2 mol/L of ammonium acetate in a 20% (v/v) nitric acid at room temperature for 30 min to prevent the adsorption of extracted As onto the oxidized sediments. Arsenic present in the second filtration (0.22 μm membrane) was analysed for As(red).

1.5.3 Total sedimentary arsenic (As(tot))

A portion of 0.2250 g of sediment sample which was dried in oven and a certified reference standard marine sediments PACS-1 (from the National Research Council of Canada) were digested for 20 min in Teflon bomb with a microwave at 720 W using 6.0 ml of HNO_3(con.), 2.0 ml of HCl (con.) and 1.0 ml of H_2O_2 (con.).

The arsenic species in the above extracts were then converted to As (III) by the procedure described above and analysed by HG-AFS.

2 Results and discussions

2.1 Atomic emission of As (V) and heavy metal interferences

Like Sb(V) (Deng *et al.*, 2001), As (V) has an atomic fluorescence emission in HCl matrix. It is found in the present study that the peak area signal varied from 10% to 40% when compared to the As(III) form (Table 2). This would introduce large errors when speciation of As is required, particularly when it needs to be done at sub μg/L level.

Since this procedure designed was to be used for As speciation in porewater and sediment samples, the interferences of transition metals were studied. In this series of tests, the 20.0 μg/L As(III) in 10% (v/v) HCl was used in all the experiments. Fig.1 shows the results of the study done with Zn^{2+}, Fe^{3+}, Cd^{2+}, Mn^{2+} and Pb^{2+}. It indicates that Cd^{2+}, Mn^{2+} and Fe^{3+} had no interference up to 50.0 mg/L respectively. Zn^{2+} had no significant signal depression when its concentrations was 50 mg/L, but the signal gradually dropped to about 93% when its concentration was decrease to 10 mg/L. Generally, this group of elements can be considered as non interfering elements. However, the studied Cu(II) and Pb(II) present a severe positive interference to arsenic signal. Cu^{2+} started showing a serious increase of signal at a concentration of 10.0 mg/L, whereas the signal increased by 50% at a Cu^{2+} concentration of 30.0 mg/L. This group of elements is usually present in relatively high concentrations in samples, particularly those with high level of metal contamination.

Table 2 Elimination of As(V) atomic fluorescence emission by 8-hydroxyq (n=5)

Condition	As(III) added, μg/L	As(V) added, μg/L	Result of As(III), μg/L	Recovery of As(III),%
10% HCl	40.0	0.0	41.00	102.5
	10.0	10.0	13.91	139.1
	40.0	10.0	45.53	113.8
0.005% 8-hydroxyq.+10% HCl	10.0	0.0	9.38	93.8
	20.0	0.0	19.63	98.2
	10.0	10.0	10.22	102.2
	40.0	10.0	39.62	99.1
0.005% 8-hydroxyq.	10.0	10.0	19.82	99.1
+2% KI + 10% HCl	40.0	10.0	50.22	100.4

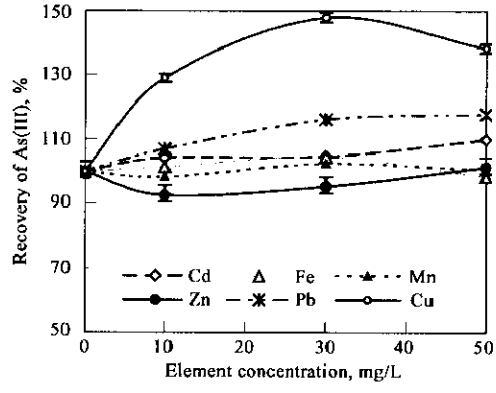

Fig.1 Interference study of As(III) at 20.0 μg/L in 10% HCl with heavy metals

2.2 Masking agents

After a series masking agents studies, we found that the presence of 0.005% of 8-hydroxyquinoline in 10% HCl matrix could prevent the atomic fluorescence emission of As(V) in a mixed As(III) and As(V) solution (Table 2). Without KI in the mixture of As (III) and As (V), the recovery of As (III) were between 93.8%—102.2%. Those results demonstrated

that the masking agent of 8-hydroxyquinoline can efficiently eliminate the fluorescence emission of As(V). In the presence of 2% prereductant KI in 0.005% of 8-hydroxyquinoline and 10% HCl matrix, it was found that 2% KI solution could quantitatively reduce As(V) to As(III), and the recovery of As(III) was almost 100%.

The most remarkably in the further study, it was found that the presence of 8-hydroxyquinoline could also efficiently mask the interference of Cu^{2+} and Pb^{2+}. The stability of 8-hydroxyquinoline in solution was tested with the mixed 10.0 μg/L of As(III) and 10.0 μg/L of As(V) in the interference solutions described in Fig.2. Under these two conditions, the recoveries were close to 100% and the solution was stable for at least 8 h (Fig. 2).

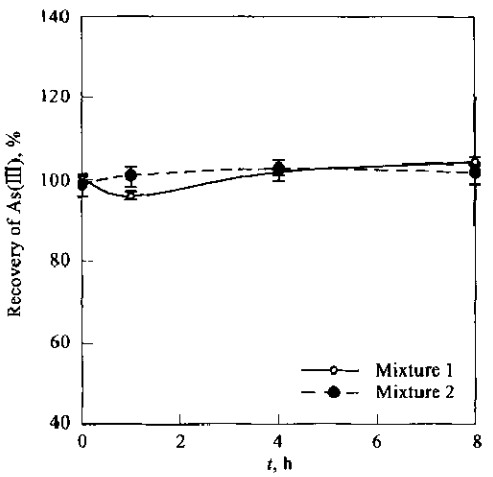

Fig.2 Stability of 0.005% 8-hydroxyquinoloine in 10.0 μg/L of As(III) and 10.0 μg/L of As(V) standard solutions containing 2% KI, 10% HCl and different concentrations of mixed interfering elements
Mixture 1 (mg/L): Pb^{2+} =30.0, Cu^{2+}=30.0; mixture 2 (mg/L): Zn^{2+} = 30.0, Fe^{3+}=30.0, Cd^{2+}=30.0, Mn^{2+} = 30.0, Pb^{2+}=30.0, Cu^{2+}=30.0

2.3 Recovery of arsenic from the samples of porewaters and sediments

The recovery for arsenic by standard addition from samples is given in Table 3. The recovery of As (III) varies from 96.4% to 104% . Those results demonstrated that the proposed procedure is valid for both porewater and sediment samples. Table 3 indicates that the presence of 8-hydroxyquinoloine did not induce any redox modification of As species. This found is of great significance for the speciation of arsenic in porewater and sediment samples, as the utilization of this agent is easy, inexpensive and characterized by a low background.

A comparison of standard calibration plots of As (III) and As (V) was done under the optimal conditions. For As (III), the calibration curve is described as:

$$y=19.886\ (\pm 0.212)\ x + 2.9096\ (\pm 0.321)$$
$$r^2 = 0.9999;\ n = 4 \qquad (1)$$

where y represents the peak area signal and x is the As concentration expressed in μg/L.

For As(V), the calibration curve is given as:

$$y=20.508\ (\pm 0.133)\ x + 0.6765\ (\pm 0.011)$$
$$r^2 = 0.9998;\ n = 4 \qquad (2)$$

Standards deviations of th e slopes are not significantly different. Under such conditions, As(V) could be completely reduced to As(III) and quantitatively measured. The detection limit was of 0.014 μg/L for As(III) on the basis of 3σ criterion for 11 replicate measurements of the blank signal, and the linear range was up to 100.0 μg/L.

Table 3 Recovery of As from porewater and sediment samples by standard addition

Samples ID	As(III) added, μg/L	As(V) added, μg/L	As(tot) determined, μg /L	Recovery, %
Porewater sample (n=3)	0.00	0.00	4.62	
	2.50	0.00	7.22	104.0
	5.00	2.50	11.86	96.5
Samples ID	As(III) added, mg/kg	As(V) added, mg/kg	Determined, mg/kg	Recovery, %
Sediment sample (n=3)	0.00	0.00	20.03	
	2.50	0.00	22.44	96.4
	2.50	2.50	24.96	98.6

2.4 Applications

According to the speciation procedures for porewater and sediments established in Section 1.4 and 1.5, we conducted some work with samples of porewaters and sediments in the three regions of Poyang Lake, one marine sediment reference materials (PACS-1). The results are given in Tables 4 and 5, respectively. Table 4 shows that the concentrations of As(III), As(V) and As(org) in porewaters at two difference depths in the three places of Poyang Lake, and the relative standard deviation (RSD) for all the measurements were usually less than 5.8%.

Table 4 Concentrations of arsenic species in the three regions of Poyang Lake porwater samples (μg/L, n=6)*

Lake	Depth, cm	As(III)	As(V)	As(org)
Kangshan	0	1.74(1.6)	0.61(0.5)	2.27(0.4)
	-10	2.73(3.3)	0.85(1.8)	1.72(2.2)
Ruihong	0	2.89(1.0)	0.17(0.5)	0.47(0.4)
	-10	4.41(0.4)	0.020(0.4)	0.29(1.2)
Hukou	0	1.40(0.5)	1.38(5.8)	0.74(1.7)
	-10	1.68(1.2)	1.08(4.2)	0.87(2.1)

Note: * Values in parentheses are the relative standard deviations

Arsenic bounded to Fe and Mn oxyhydroxides, which are present mainly in the surficial oxic layer of the sediment, is called reducible arsenic, As (red). Three replicate extractions and analyses were preformed from each of two depths in the three regions (Table 5). The second fraction of arsenic is

Talbe 5 Concentrations of arsenic species (mg/kg) in sediments at the three places of Poyang Lake (n=3)* and comparison of the result obtained by this work for certified reference material (PACS-1)

Lake	Depth, cm	As (red)	As (ox)	As (tot)
Kangshan	0	11.08(1.8)	0.20(4.0)	21.94(0.1)
	-10	7.33(5.9)	0.18(3.8)	16.41(1.1)
Ruihong	0	8.48(2.9)	0.12(2.5)	17.39(0.3)
	-10	7.99(3.1)	0.14(3.3)	14.64(1.0)
Hukou	0	17.22(1.1)	0.62(1.4)	26.74(0.3)
	-10	13.83(0.9)	0.67(2.3)	24.53(0.2)
PACS-1	Certified value, mg/kg		This work, mg/kg (n=6)**	
	211 ± 11		210 ± 4.6	

Notes: * Values in parentheses are the relative standard deviations; ** the uncertainties represent 95% confidence limit

called oxidizable arsenic, As(ox), and identified as arsenic associated with various inorganic and organic compounds or colloids. Table 5 shows that concentrations of As(ox) were low, and As bounded to Fe and Mn oxyhydroxides represents a high percentage of the total As in sediments. The relative standard deviations in parentheses for all the measurements were also less than 6%. Table 5 also demonstrated that the proposed procedure is valid for sediment sample after a comparison of the results obtained by this work for certified marine sediment reference material (PACS-1).

3 Conclusions

In this study, it was clearly demonstrated that the presence of As (V) has a 10% to 40% of fluorescence emission signal during the determination of As(III). Fe (III), Mn(II), Cd(II) and Zn(II) do not cause any interference in As determination, whereas Cu(II) and Pb(II) interfere seriously at a concentration as low as 10 mg/L with arsenic species determinations. All the interferences could be efficiently eliminated by 8-hydroxyquinoline in 10% HCl solutions including the unwanted As(V) atomic fluorescence emission during the determination of As(III), which greatly simplifies the process and improves the quality of As speciation. After a series standard addition and CRM studies, a reliable, sensitive and interference-free procedure was then developed and applied to the speciation of arsenic in porewater and sediments from Poyang Lake, China.

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