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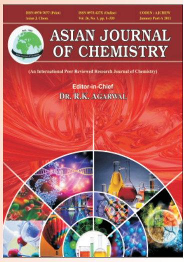

Determination of Arsenic Species in Underground Water by Capillary Electrophoresis-Inductively Coupled Plasma Mass Spectrometry

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A method for the detection of trace As(III), As(V), monomethylarsonic acid, dimethylarsinic acid in underground water by capillary electrophoresis-inductively coupled plasma mass spectrometry (CE-ICP-MS) was developed. The optimized conditions of capillary electrophoresis including pH and concentration of the buffer, separation voltage and injection time were studied. The results showed that the above four species of arsenic were baseline separated within 9 min under the optimized conditions. The detection limits (S/N = 3)of As(III), As(V), dimethylarsinic acid, monomethylarsonic acid were 0.25-0.53 µg/L and the RSD (n = 10) of the peak areas were smaller than 5 %. The method has been successfully applied to the determination of the species of arsenic in groundwater samples. The recoveries were 91-107 %. The method can be used for the speciation analysis of arsenic in real groundwater samples. The result indicated that As(III) and As(V) as the main arsenic speciations existed in groundwater of Nei Mongolia.

Keywords: Capillary electrophoresis, Inductively coupled plasma mass spectrometry (ICP-MS), Speciation analysis, Arsenic.

INTRODUCTION

Arsenic is a ubiquitous toxic metalloid element in the lithosphere, hydrosphere and biosphere[1,2]. In recent years, overexploitation of underground water has led to severe arsenic contamination of drinking water in India, Bangladesh, the United States, Argentina, China Taiwan and some other areas. About 36 million people has been threatened by arsenic contamination drinking in lives and health and it becomes a global problem[3]. IARC, the U.S. Environmental protection agency (EPA) and the National Toxicology Program have put arsenic into human carcinogen list[4].

Arsenic and arsenic compounds are extremely dangerous toxic and carcinogenic substances, however, the concentration of total arsenic is not an equitable way to show the impact of arsenic exposure levels, the environment and ecology. In general, inorganic arsenic is more toxic than organic arsenic, toxicity order: $AsH_3 > As(III) > As(V) >$ monomethylarsenic acid > dimethyl arsenic acid[5,7]. Therefore, it was important to proceeding the quantitative and qualitative analysis of arsenic existing speciation.

Compared to LC and GC, capillary electrophoresis has higher separation efficiency and a relatively rapid separation[8] and ICP-MS has the advantage in element detection and low detection limit[9-11]. Therefore, combined using of capillary electrophoresis and ICP-MS becomes a powerful analytical instrument for elements speciation analysis including arsenic. Since the first report of capillary electrophoresis and ICP-MS combined using by Olesik *et al.*[12], this hyphenated technique has gained widely attention.

In this paper, we separate various forms of arsenic and arsenic compounds with the high sensitive inductively coupled plasma mass spectrometry to achieve the determination of arsenic species in water samples. This method offers a realatively rapid separation, high sensitivity, requires much smaller volume of sample and simple operating procedure, *etc*.[13]. The speciation characteristics of arsenic in waters,collected form undergroud water of Nei Morgolia in North China, has been studied by using capillary electrophoresis coupled with ICP-MS (CE-ICP-MS). And get satisfactory spike results with standard substance.

EXPERIMENTAL

The standards of four species of arsenic including AsO_3^{3-}, AsO_4^{3-}, dimethylarsinic acid and monomethylarsonic acid were purchased from Narional Institute of Metrology China. All the stock standard solutions were stored at 4 °C and the running standard solutions were prepared by diluted stook standard solutions to the desired concentration with running buffer solution. The running buffer solution of 40 mmol/L H_3BO_3-

10 mmol/L $Na_2B_4O_7$ (pH = 9.10) was prepared by dissolving analytical grade boric acid (H_3BO_3) and sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$), which were purchased from TianJin BoHua Chemical Co. Lid., (TianJin, China), in Milli-Q water. In this experiment, water used is Milli-Q water (18.2 MΩ) prepared by a Milli-Q equipment (Millipore, Bedford, USA) and the purity of argon gass is not less than 99.999 %.

Capillary electrophoresis-inductively coupled plasma mass spectrometry (CE-ICP-MS): The CE-ICP-MS system consists of an capillary electrophoresis system (Reeko instrument Co., Ltd.) and an Bruker 820-MS (Bruker Technologies, USA) which is equipped with a microconcentric nebulizer. The capillary electrophoresis system was fabricated with a 60 cm length × 75 µm i.d × 375 µm o.d., fused silica capillary and a high-voltage power supply which provided -14KV voltage.

RESULTS AND DISCUSSION

Optimization of capillary electrophoresis conditions: Buffer solution including its chemical components, pH and concentration greatly affects the sepration of analytes by affecting the migration time of each analytes[14,16]. In order to obtain a better electrophoretic resolution, we optimized buffer solution under continuous sample-introduction mode with the similar manner reported earlier[17,18]. The experimental results showed that the mixture of boric acid and borate gave the most acceptable separation efficiency and reproducibility, therefore the mixed solution of boric acid and sodium tetraborate (4:1, mole concentration) was chosen as running buffer solution, which was used to seprated four species of arsenic [As(III), dimethylarsinic acid, monomethylarsonic acid, As(V)].

The pH of the running buffer solution strongly affects the electrophoretic resolution and sensitivity. The relationship between migration times/resolution and pH was studied with a 40 mM H_3BO_3-10 mM $Na_2B_4O_7$ buffer solution in the pH range of 8.80-9.20. The results revealed in Fig. 1 that dimethylarsinic acid and monomethylarsonic acid could not be baseline separated when pH was lower than 9.05. However, when pH was higher than 9.20, the migration time of each peak was prolonged and finally resulted in increased noise and poor reproducibility. When the pH was about 9.10, all four arsenic compounds were baseline separated with symmetrical peak shape. In this study, pH = 9.10 was selected as the optinum pH for the separation of As(III), dimethylarsinic acid, monomethylarsonic acid and As(V).

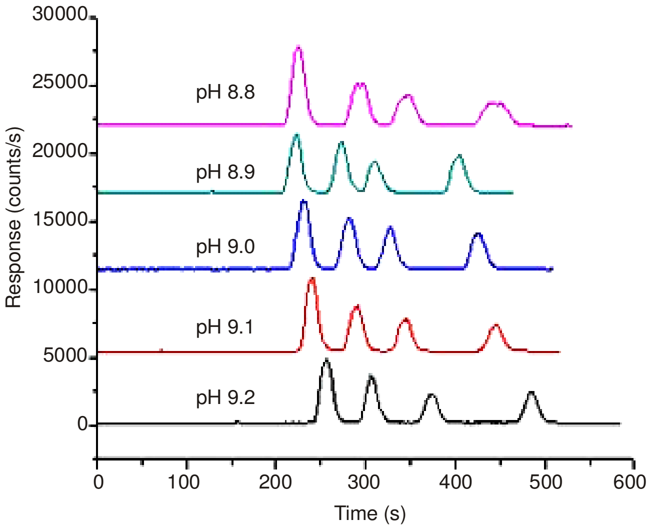

Fig. 1. Separation effect of different pH

The effect of concentration of running buffer solution on the separation was also studied by using different concentrations of boric acid-borate buffer solution (boric acid: borate = 20:5, 30:7.5, 40:10.0, 50:12.5 and 60:15.0 mM) at pH 9.10. The results showed in Fig. 2 that the peak shapes and sensitivities of all four species of arsenic were improved and the migration times became longer with an increase in the concentration of running buffer solution. Considering both the analytical time and electrophoretic resolution, 40 mM of H_3BO_3-10 mM of $Na_2B_4O_7$ (pH = 9.10) was selected as the running buffer solution.

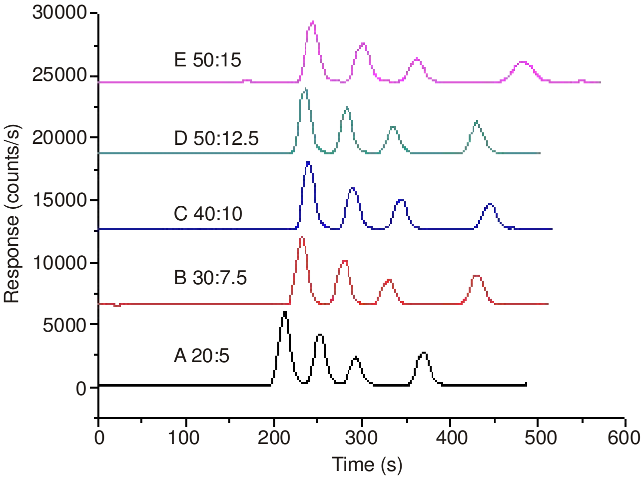

Fig. 2. Separation effect of different buffer concentration

Separation voltage optimization: The effect of the separation voltage on the migration time and electrophoretic resolution was investigated in the range of +10 to +18 kV. The results showed that higher voltage was favourable to shorten migration time,that was obviously revealed in Fig. 3. However, high voltage led to the broadening of peak due to Joule heating effect. Considering the reproducibility and peak shapes, +14 kV was selected as the separation voltage. Different injection

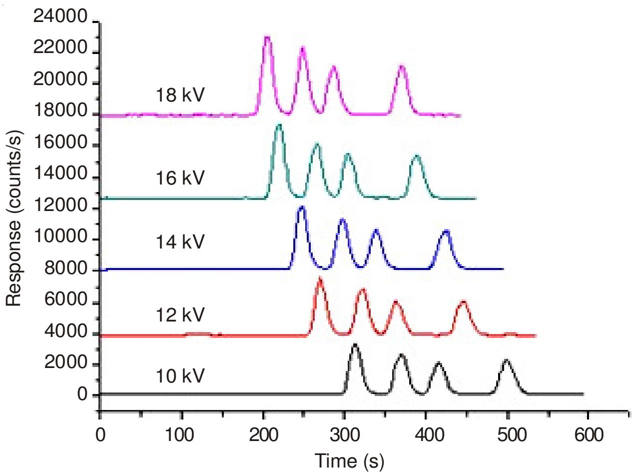

Fig. 3. Separation effect of different separation voltage

times (5s-25 s) were tested in this experiment and results showed that the ICP-MS signal becomes higher with increasing injection time. However, longer injection time will reduce electrophoretic resolution. The results show that In the case of injector time is 15 s, the pump speed is 14 µL/min, achieved good separation effect, good peak shape, high sensitivity for four forms of arsenic compounds.

The optimum CE-ICP-MS conditions are shown in Table-1. Under the conditions of Table-1, all arsenical species in underground water were completely separated and determined by CE-ICP-MS. The electropherogram shown in Fig. 4.

TABLE-1
OPERATING CONDITIONS OF CE-ICP-MS

Parameter	Value
CE voltage	14 kV
Injection time	15s
Buffer solution	40 mM of H_3BO_3–10 mM of $Na_2B_4O_7$ (pH = 9.10)
Plasma flow	18.0 L/min
Auxiliary flow	1.80 L/min
Sheath gas	0.18 L/min
Nebulizer flow	1.00 L/min
Sampling depth	6.5 mm
RF power	1.4 KW
First extraction lens	-1 V
Second extraction lens	-160 V
Third extraction lens	-208 V
Corner lens	-206 V
Skimmer gas source	H_2
Skimmer flow	30 mL/min

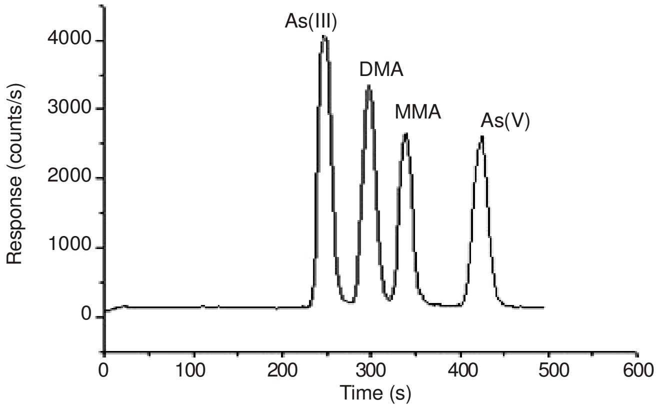

Fig. 4. CE-ICP-MS electropherogram of a mixed solution of As(III), As (V), dimethylarsinic acid and monomethylarsonic acid standards (10 µg/L)

Parameter studies of CE-ICP-MS method: At above optimum conditions, four species of arsenic were baseline separated with in 9 min, under continuous sample-introduction mode. The same experiment was repeated for ten times and the RSD (relative standard deviation, n = 10) of peak areas was calculated to be a range of 1.96-4.85 % for As(III) dimethylarsinic acid, monomethylarsonic acid and As(V) (Table-2). The detection limit (3s/s, the concentration necessary to yield a net signal equal to three times the standard deviation of the background) calculated with counts was 0.25,0.42,0.53 and 0.46 µg/L for As(III) dimethylarsinic acid, monomethylarsonic acid and As(V), respectively.

TABLE-2
PRECISION OF THE METHOD (n = 10)

Comp.	Low mass concentration		Middle mass concentration		High mass concentration	
	Detected (µg/L)	RSD (%)	Detected (µg/L)	RSD (%)	Detected (µg/L)	RSD (%)
As(III)	10.0	2.72	20.0	1.87	50.0	2.09
DMA	10.0	3.41	20.0	2.61	50.0	1.97
MMA	10.0	4.05	20.0	2.03	50.0	2.35
As(V)	10.0	4.85	20.0	2.12	50.0	1.96

Adding three mixed standard solutions of low, medium and high mass concentration of arsenic compounds into a same sample, determine the three samples by the method we established and the recovery rates were shown in Table-3. By the results, in the case of different concentrations the recovery rates of As(III), dimethylarsinic acid, monomethylarsonic acid, As(V) are 97-102, 91-107, 93-103 and 96-102 %, respectively.

TABLE-3
RECOVERIES OF FOUR ARSENIC SPECIATIONS FROM GROUNDWATER SAMPLE AT THREE SPIKED LEVELS

Comp.	Original (µg/L)	Added (µg/L)	Found (µg/L)	R (%)
As(III)	13.5	10, 30, 50	23.3, 42.6, 64.5	97-102
DMA	——	10, 30, 50	9.1, 29.6, 53.5	91-107
MMA	——	10, 30, 50	9.3, 28.2, 51.7	93-103
As(V)	2.9	10, 30, 50	13.1, 31.5, 51.6	96-102

Determination of sample: Determine groundwater samples from Hohhot and Baotou for four forms of arsenic, the determine results are shown in Table-4. The results showed that the arsenic in groundwater in these regions are mainly As(III) and As(V). The sum of various forms of arsenic is almost equivalent to total arsenic compounds result, so the established method is reliable.

TABLE-4
CONTENTS OF ARSENICS IN GROUNDWATER OF NEI MONGOLIA

Samples	As(III) µg/L	DMA µg/L	MMA µg/L	As(V) µg/L
1	14.7	———	———	3.6
2	235.1	———	———	52.6
3	4.5	———	———	2.7
4	1.2	———	———	0.2
5	98.9	———	———	45.1
6	78.4	———	———	26.8
7	105.6	———	———	36.4
8	23.2	———	———	12.7
9	13.5	———	———	2.9
10	1.6	———	———	56.3
11	142.3	———	———	———

Conclusion

A method used to couple capillary electrophoresis with ICP-MS for determinated four arsenic species from underground water were developed in this study. Four forms of arsenic compounds [As(III), dimethylarsinic acid, monomethylarsonic acid and As(V)] are fully separated within 9 mins, the correlation coefficients are all above 0.9996. The detection limit is 0.25-0.53 µg/L and RSD are less than 5 %. The recovery rates are 91-106 %. The results show that the method has advantages in good accuracy, high sensitivity, low sample consumption and short analysis time, it is suitable for determination of arsenic speciation in underground water. The predominant species of arsenic in water is inorganic arsenic such as As(III) and As(V), accounting for about 100 % of total arsenic. The most toxic As(III) was detected in water samples, suggesting that water in few part was not safe for consumption.

ACKNOWLEDGEMENTS

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