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Interface of on line coupling capillary electrophoresis with hydride generation electrothermal atomic absorption spectrometry and its application to arsenic speciation in sediment

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ABSTRACT

A novel interface for on line coupling capillary electrophoresis with hydride generation electrothermal atomic absorption spectrometry (CE–HG–ETAAS) has been developed. The interface performance was examined in detail. The technique could be used to convert arsenic compounds from CE separation to corresponding volatile hydrides determined by HG–ETAAS. This paper aims to explore the best condition in the speciation analysis of inorganic arsenic by using CE–HG–ETAAS. The application of the developed CE–HG–ETAAS to inorganic arsenic speciation in sediment was investigated. The detection limits of As(III) and As(V) were 135 ng/g and 160 ng/g, respectively. Relative standard deviations of arsenic speciation were better than 2%. The recoveries of As(III) and As(V) in the sample with spiking concentration of 2500 ng/g As(III) and 5000 ng/g As(V) were 97.6% and 96.7%, respectively.

1. Introduction

Speciation analysis of trace elements may lead to better understanding of the chemical/biochemical processes, environmental availability and toxicological risks associated with different species [1,2]. Arsenic and its compounds are highly toxic and carcinogenic. Different changes of the forms of arsenic in the human body determine the different mechanisms of toxicity and detoxification [3,4]. Although a series of analytical techniques have been used to analyze arsenic speciation, there are no standard procedures for such purposes [5]. Therefore, it is vitally necessary to develop a new and reliable method for arsenic speciation. Capillary electrophoresis (CE) is a combination of classic electrophoresis and modern micro-column separation. It has many advantages, such as simple operation, rapid analysis, little reagent consumption, easy automation, less environmental pollution and higher resolution [6]. With the utilization of the hydride generation (HG) technology in arsenic and other hydride-forming elements, the detection limits of hydride-forming elements can be improved by 1–3 orders of magnitude [7]. Capillary electrophoresis coupling hydride generation with atomic absorption spectrometry can realize the efficient separation and alternative determination of elements. Currently, the effective analytical techniques for arsenic speciation are hyphenated by coupling different separation procedures with various detection methods [8,9]. These techniques include hydride generation atomic absorption spectrometry (HG–AAS) and electrothermal atomic absorption spectrometry (ET–AAS) [10–20]. In addition, it is also linked with other techniques, including the hydride generation atomic fluorescence spectrometry [21–23], inductively coupled plasma mass spectrometry [24–36], inductively coupled plasma optical emission spectrometry [37] and cathodic stripping voltammetry [38]. However, those ICP-based methodologies require expensive instruments and high operational costs, which limits their wide acceptance for routine speciation analysis in general laboratories [39]. Compared with HPLC, CE offers unique characteristics that make it particularly attractive for elemental speciation analysis, such as high resolving power, minimal reagent consumption, rapid analysis and low cost and the possibility of separations with only minor disturbances of the existing equilibrium between the different species [36–45]. Compared to ICP, atomic absorption spectrometry offers certain advantages in terms of simple structure, easy operation, penny-a-line equipment and operation cost, good selectivity and good precision, so it is still widely employed in the field of chemical, medicine, clinic investigation, food hygiene, etc.

In this paper, a novel interface of capillary electrophoresis coupling hydride generation with electrothermal atomic absorption spectrometry was developed. This novel interface has presented the

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advantages of good stability, good gas–liquid separation efficiency, less dead volume, good reproducibility and easy operation. The device will combine the efficient separation function of CE with the high detection sensitivity of ETAAS to realize both the trace samples hydride generation and the online connection of CE and ETAAS. As(III) and As(V) were used as the research objects to explore the best condition in the speciation analysis of arsenic by using capillary electrophoresis and hydride generation coupled with electrothermal atomic absorption spectrometry.

2. Materials and methods

2.1. CE–HG–ETAAS interface

The interface of CE–HG–ETAAS is made of both interfaces of CE–HG and HG–ETAAS. And the interface of CE–HG is similar to that of previous report [42]. As shown in Fig. 1a, the self-designed CE–HG interface was made by two juxtaposed PTFE tubes: The lower one was connected with $NaBH_4$ solution; the upper one was inner set with a capillary; the HCl solution passed through between the PTFE tube and CE capillary tube. In order to escape too much gas caused by hydride generation, which would increase pressure inside the transmitting pipeline, generate back-pressure and cause interruption in the electrophoresis process, the distance between exits of two PTFE tubes was demanded to be set properly 2 mm. Moreover, in order to reduce the dead volume and escape the expansion of chromatography peak caused by convection, the following two measures we took were to (1) get rid of the surface coating around the exit end of capillary; (2) mix the HCl solution and effluent liquid of CE capillary at 2 mm distance from the exit end of PTFE tube. The electrical circuit at the interface was implemented by the 2 M HCl solution and Pt electrode in the exit end of capillary. The assistant HCl solution was either the carrier of CE effluent solution or an important medium of subsequent hydride generation. The HCl solution was mixed with effluent solution of CE, and then was mixed with $NaBH_4$ solution. The mixture solution entered into the hard glass tube together to keep on reaction and produces gaseous hydride. The waste solution was collected by waste liquid cell.

As shown in Fig. 1b, a ceramic tube (length of 10 cm, outer diameter of 2.2 mm, and inner diameter of 1.8 mm) was used. This new device might significantly enhance sensitivity due to long retention time and good stability. It was connected with improved graphite tube through the graphite furnace side hole while the other end of ceramic tube was connected with the export side of hydride generator, thus gaseous hydride was carried by argon into graphite furnace for testing directly. Because the ceramic tube can endure high temperature of more than 2000 °C, the interface does not require cooling system. Therefore, the interface is very convenient in real sample analysis.

The scrapped graphite tube was used to make a T-pattern graphite plug (Fig. 1b), which was used to block the top hole of graphite tube. Two concentric circular holes were drilled at front side of graphite tube. The inner diameter of the larger hole was 2.2 mm and the inner diameter of the smaller hole was 1.8 mm. The depth of the two holes shared the wall thickness of the graphite tube. During the experiment, ceramic tube was closely inserted into the graphite tube by the side hole, so gaseous hydride was carried by argon into graphite tube for testing directly, and then emission from the two exit ends of the graphite furnace was exhausted by ventilating system (Fig. 1b).

From the elaboration above, it is quite obvious that the interface is easy to use and is reproducible as well. The main performance of this device is that it is of good stability, good gas–liquid separation efficiency, low dead volume, good electrical conductivity, long lifetime and high sensitivity. Besides, the positive and negative electrode at the exit side of capillary can be adjusted in accordance with the difficulties of separation. Therefore, this interface is very convenient to separation of different charging analytes.

2.2. Reagents

All reagents used were of analytical reagent grade and double distilled water was used throughout the whole process of the

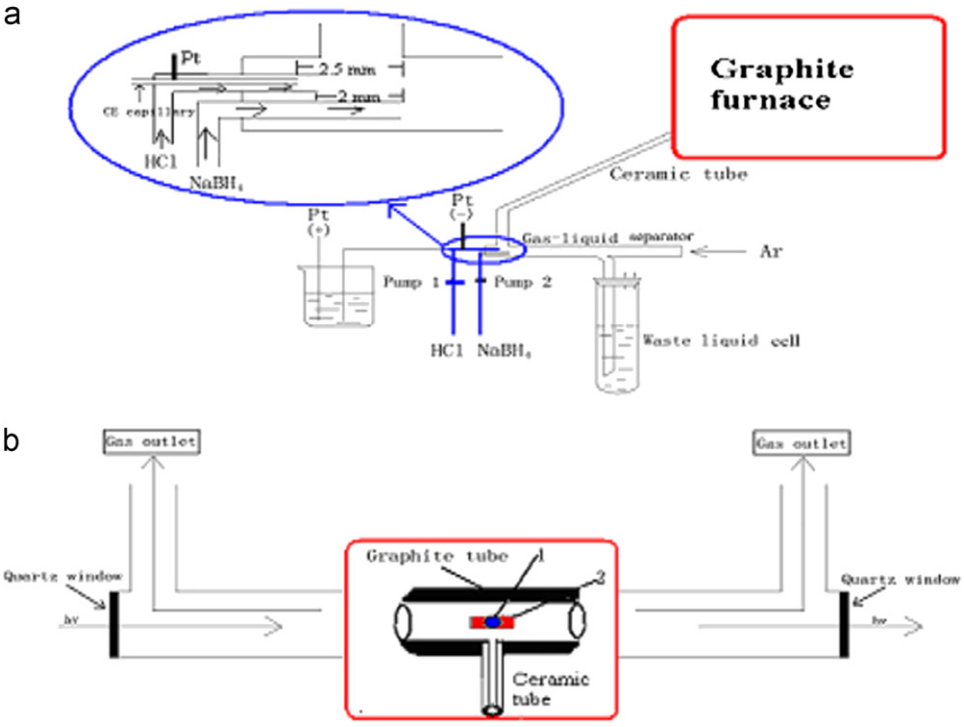

Fig. 1. Interface of CE–HG–ETAAS. Interface of CE–HG (a); interface of HG–ETAAS (b). In Fig. 1b, 1 for graphite furnace injection hole, 2 for T-pattern graphite plug.

experiment for solution preparation. Arsenic stock solutions of 1000 mg/L of each species were prepared by dissolving appropriate amount of sodium arsenite and disodium hydrogen arsenate heptahydrate (Sinopharm Chemical Reagent Co., Ltd, China). Standards of the desired concentration were prepared daily from the stock solutions. 10% (m/v) ascorbic acid 6.0% (m/v) thiourea and 2% (m/v) $NaBH_4$ were prepared in 0.1% (m/v) NaOH. The concentration of NaH_2PO_4–Na_2HPO_4 (Hunan Chemical Company) buffer solution is 25 mM (pH=6.5). All solutions were filtered through a 0.45 μm filter prior to use.

2.3. Instruments and operating conditions

Atomic absorption spectrophotometer (TAS-986, Beijing Purkinje General Instrument Co., Ltd, Beijing, China) was used in this study. The AAS operating parameters and CE separation conditions were summarized in Table 1. In order to increase graphite furnace lifetime, according to migration time and peak width of As(III) and As(V), the atomization temperature and hold time were controlled. In terms of the instrument requirements and preliminary experimental results, the temperature change process of graphite furnace was shown in Table 2. The working temperature of graphite furnace in Table 2 was inconstant during electrophoresis separation process due to ETAAS characteristics (a commercially available ETAAS operating temperature is not also fixed) and the interface lifetime was prolonged because of the use of lower temperature during no atomization stage. A high voltage power supply (ACS2000, Beijing Cailu Company, China) providing the CE voltage. Fused-silica capillary (Yongnian Optical Fiber Co., Hebei, China) with inner diameter of 100 μm, outer diameter of 365 μm and length of 60 cm was used for CE separation.

Table 1
CE–HG–GFAAS operating condition.

Capillary electrophoresis operating condition	
Fused-silica capillary	60 cm length × 100 μm i.d.
Buffer solution	NaH_2PO_4–Na_2HPO_4 (25 mM, pH6.5)
Applied voltage	25 kV
Sample injection	0.04 MPa × 10 s
Hydride generation operating condition	
HCl concentration	2 M
$NaBH_4$ concentration	2% (m/v)
Flow rate of HCl	12 mL/h
Flow rate of $NaBH_4$	10 mL/h
AAS operating condition	
Arsenic hollow cathode lamp current	6 mA
Spectrum bandwidth	0.4 nm
Detection mode	Peak height
Flow rate of carrier gas	0.2 L/min
Analytical line	193.70 nm

Table 2
Working condition of graphite furnace.

Temperature (°C)	Heating time (s)	Holding time (s)
80	10	100
200	3	5
900	3	5
1700	4	60
900	4	5
80	3	200
900	3	5
1700	5	90
2300	2	3

2.4. Sample preparation

With a stainless steel shovel, the sediment sample was took from Taohua river of Guilin of China and collected from 0 cm to 10 cm depth from the bottom of the river. The sediment was dried to constant weight at room temperature (30 °C), and then it was grounded to pass through a 0.15-mm sieve. Dry sediment sample used in the experiment was 1 g by weight. The sample was prepared by microwave extraction with 10 mL H_3PO_4 (0.10 mol/L). Extraction procedures were introduced as follows: 200 W powers, warming to 80 °C within 9 min, extraction time of 3 min. The extract was centrifuged for 15 min at 6000 r/min. The supernatant was filtered through 0.45 μm membrane filter. The extraction procedure was repeated twice under the same condition and the extract was combined into a 50 mL flask bottle.

2.5. Sample introduction

Sample solution was introduced into the CE capillary by hydrodynamic injection, with the nitrogen gas pressure of sample injection 0.04 MPa. The sample volume injected was determined by the injection pressure, injection time, capillary length and the nature of the sample solution. The sample injection time was 10 s in this experiment. The atomization process temperature was illustrated in Table 2. With the use of argon as its carrier gas, hydride, through gas–liquid separator and ceramic tube, was introduced to graphite furnace for testing which has been preheated to a certain temperature.

3. Results and discussion

3.1. Optimization of parameters of capillary electrophoresis

The pH value of separation buffer solution and electrophoretic voltage play an important role on the capillary electrophoresis separation of As(III) and As(V). With the increasing pH of separation buffer from 5.5 to 8.5, the absorbance of As speciation increased and then decreased. The maximum absorbance occurred at pH 6.5. The absorbance in the present work also changed as a function of the buffer concentration. With the increase of buffer concentration, the absorbance ascended first and then descended with a turning point of 25 mM. The influence of separation voltage on the absorbance of As speciation was carried out from 20 kV to 30 kV. The absorbance increased with separation voltage increased up to 25 kV, and then it dropped as the voltage was further increased. The peak bottom width decreased rapidly when the separation voltage changed from 20 kV to 25 kV, but decreased slowly when the voltage was higher than 25 kV. Considering both of absorbance and peak bottom width, the buffer solution of NaH_2PO_4–Na_2HPO_4 (25 mM, pH6.5) and 25 kV electrophoretic voltages were selected as the working conditions of capillary electrophoresis.

3.2. Optimization of atomization temperature

Atomization temperature will affect the service lifetime of the graphite tube if it lasts too long, and it will also result in failure detection if it lasts too short. Therefore, temperature control mode was selected in the atomization process. The optimum atomization temperature was determined by the best absorbance of a standard solution. As shown in Fig. 2, when the atomic temperature was more than 1700 °C, the arsenic absorbance was almost constant. In this case, in order to extend the service

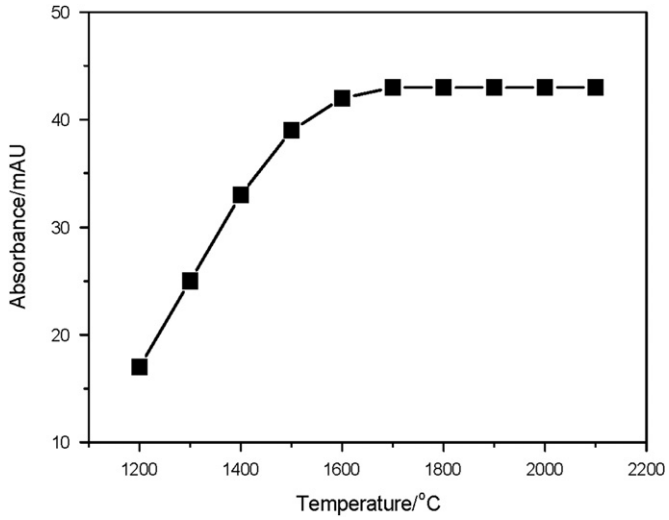

Fig. 2. Effect of atomization temperature on the signal intensity. Detection conditions: 100 ng/mL As(III), other condition as in Tables 1 and 2 except atomization temperature.

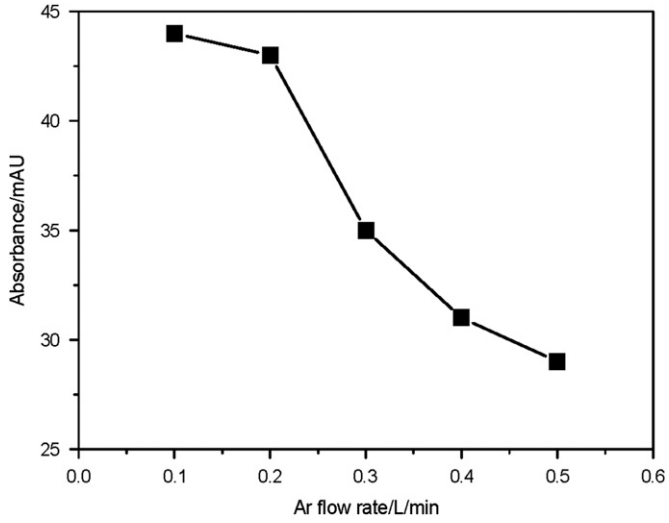

Fig. 3. Effect of carrier gas flow on the As signal intensity. Detection conditions: 100 ng/mL As(III), other condition as in Tables 1 and 2 except carrier gas flow.

lifetime of graphite furnace, we should use the lowest atomic temperature as possible as we can. Therefore, the 1700 °C was used as atomization temperature of arsenic.

3.3. Effect of argon flow rate

Argon is used as the carrier gas to carry the formed gaseous AsH_3 into the atomizer. As shown in Fig. 3, 0.1–0.5 L/min flow rates were studied. With the increasing of the carrier gas flow rate, the absorbance values of arsenic decrease due to the dilution of the concentration of arsenic hydride and shortness of residence time in graphite furnace, but too low flow rate could not retrain the hydride into the graphite furnace quickly, which led to a lower derivative absorbance. An analytical flow rate of 0.2 L/min was chosen for all further work.

3.4. Effect of acidity and $NaBH_4$ concentration

The effect of hydrochloride concentration from 0.5 M to 4 M was studied. When hydrochloride concentration was 2 M (containing 10% (m/v) ascorbic acid and 6.0% (m/v) thiourea), As(III) and As(V) quantitatively generated AsH_3, so the 2 mol/L hydrochloric acid medium was chosen. The effect of $NaBH_4$ concentration on the ETAAS signals was studied with the range from 0.5% to 4.0%. The results obtained have been plotted in Fig. 4. As can be seen from Fig. 4, the maximum of analytical signal was observed at a concentration of 2.0% $NaBH_4$. At high concentration, it appeared that the high amount of generated H_2 could diminish the residence time of the analyte in the graphite furnace with the corresponding signal decrease.

3.5. Speciation analysis of As(III) and As(V)

All separation and detection conditions for arsenic speciation were summarized in Tables 1 and 2. The electropherogram of arsenic speciation was shown in Fig. 5. The standard mixture of As(III) and As(V) could be completely separated in Fig. 5; therefore, the CE–HG–ETAAS was feasible for arsenic speciation. Comparing Fig. 5a and b, the peak height in Fig. 5b at migration time 140 s was increased substantially whereas another peak in

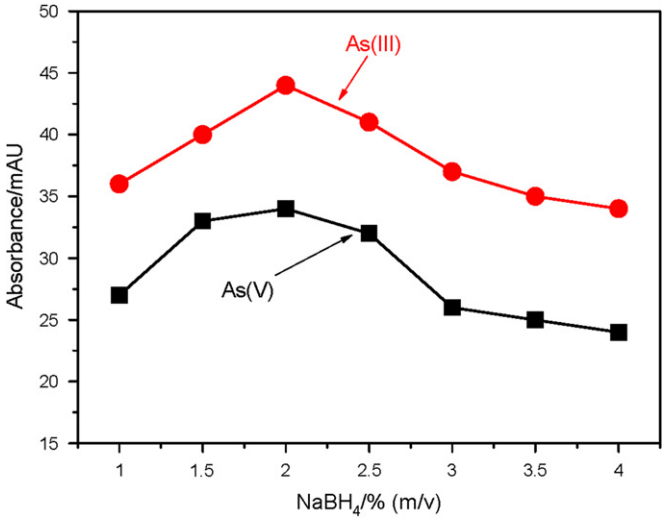

Fig. 4. Effect of $NaBH_4$ concentration on As signal intensity. Detection conditions: 100 ng/mL As(III) and 80 ng/mL As(V), other condition as in Tables 1 and 2 except $NaBH_4$ concentration.

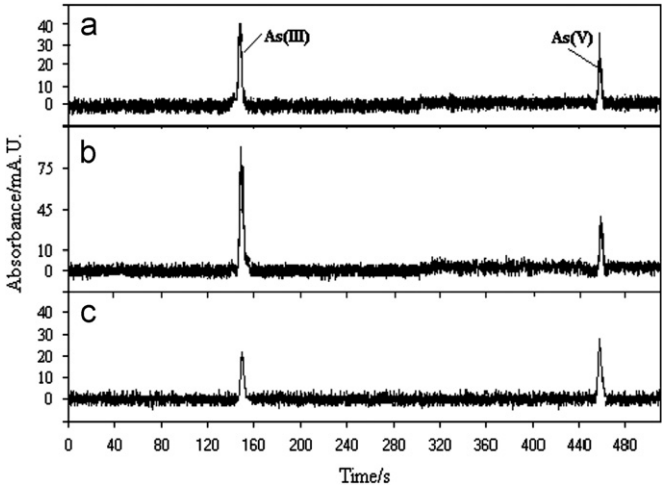

Fig. 5. Electropherogram of arsenic speciation by CE–HG–ETAAS. Detection conditions: 100 ng/mL As(III) and 100 ng/mL As(V) (a), 200 ng/mL As(III) and 100 ng/mL As(V) (b), sediment sample (c), other condition as in Tables 1 and 2.

the electropherogram was almost not changed. Therefore, the first peak in Fig. 5 was As(III).

3.6. Analytical figures of merits

Under the optimized experimental conditions, the eleven times have been measured for 50 ng/mL of As(III) and As(V) standard solution. The relative standard deviations (RSD) of As(III) and As(V) were 1.2% and 1.5%, respectively. The detection limits of As(III) and As(V) (three times the standard deviation of the blank), based on 11 replicates of the blank, were 135 ng/g and 160 ng/g, respectively. The linear concentration ranges of As(III) and As(V) were from 550 ng/g to 100,000 ng/g and from 650 ng/g to 125,000 ng/g, respectively.

3.7. Application

Introduction of the application of the CE–HG–ETAAS interface was demonstrated through the analysis of extract from sediment. The electropherogram of extract from sediment was shown in Fig. 5c. The peaks of As(III) and As(V) were achieved. According to absorbance from the calibration curve, the contents of As(III) and As(V) in the dry sediment were 0.45 mg/kg and 0.81 mg/kg, respectively. The recoveries of As(III) and As(V) in the sample with spiking concentration of 2500 ng/g As(III) and 5000 ng/g As(V) were 97.6% and 96.7% for five repeatable determinations, respectively. The RSDs of As(III) and As(V) were 1.7% and 2.5% for five replicates, respectively. As indicated from these results, the total arsenic concentration was 1.26 mg/kg in the dry sediment. The total concentration of arsenic in the sediment sample directly measured by HG–ETAAS was found to be 1.29 mg/kg; the recovery of arsenic species with the current described CE–HG–ETAAS method was 97.7%.

4. Conclusions

The results in the present work have demonstrated the feasibility of the self-designed capillary electrophoresis hydride generation electrothermal atomic absorption spectrometry for arsenic speciation. Electrophoretic separation of the two arsenic species can be obtained within 8 min with detection limits less than 160 ng/g for each species. The low cost, easy operation, less dead volume, simple structure, good conductivity, good gas–liquid separation efficiency and good selectivity of ETAAS make it attractive as an on-line element-specific detector of CE for speciation of hydride-forming elements.

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