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Speciation analysis of inorganic arsenic in coal samples by microwave-assisted extraction and high performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry

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ABSTRACT

A new method was developed for the speciation analysis of inorganic arsenic in coal samples by high performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry after microwave-assisted extraction. Effective extract of As(III) and As(V) in coal sample was achieved by 1.0 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} ascorbic acid. Under the optimized conditions, the limits of detection (LOD) were 0.01 μg L^{-1} and 0.02 μg L^{-1}, the relative standard deviations (RSD) were 2.4% and 3.3% (c=10.0 μg L^{-1}, n=7), recoveries were 102.5% and 96.5% for As(III) and As(V). The proposed method was successfully applied for the determination of speciation of inorganic arsenic in coal samples and GBW11117 coal standard reference material with complex matrix.

1. Introduction

Arsenic(As) is ubiquitous in the environment. As and its compounds have been classified as Group I carcinogens [1]. As poisoning may cause non-cancer effects such as hypertension, cardiovascular and cerebrovascular diseases, diabetes mellitus, keratosis and neurotoxicity as well as cancers of skin, lung, bladder and liver. Because of the high toxicity and mobility of As, and the direct health impacts in epidemic areas, As contamination in air, water, and soil from both geological and anthropogenic sources and the occurrence, distribution, and mobility of As have received significant attention in recent years. It has become a public environmental health concern [2].

One of the major sources of As contamination arises from the combustion of As-containing coal. Coal is the predominant energy resource in China, with a consumption of 3.49 billion tonnes in 2011[3]. Coal contains more than 80 elements, among which C, H, O, N, Na, Mg, Al, Si, S, K, Ca, Ti and Fe are major elements in coal, with the content of above 0.1% [4], the remaining elements within coal are present in minor or trace amounts. The trace element concentration of coal is influenced by a variety of factors such as the intake of trace elements during plant growth, enrichment during plant decay, sedimentation and diagenesis, burial and coalification, and late mineralization [5]. More than 20 trace elements are hazardous in coal, the hazardous trace elements may be released into the environment during the processes of mining, transporting, processing and using, and thereby pollute the environment.

The arsenic species in the feed coals has been examined using As X-ray absorption fine structure(XAFS) spectroscopy, the feed coals can be grouped based on their contents of arsenic associated with pyrite(As/pyr) and as As^{3+} and As^{5+}(arsenate) species [6]. Arsenic can have a wide range of association modes in coal. Generally, coals with high sulfur and pyrite contents have high arsenic contents, X-ray absorption fine structure (XAFS) studies by Huggins and Huffman [7] indicated that arsenic occurs in pyrite by substituting for sulfur in the pyrite structure. Other forms of occurrence for arsenic in coal are typically minor. For example, Finkelman et al. [8] concluded that a small portion ($<10\%$) of the arsenic present in the coals they investigated may also be organically associated or in a chelated form. In the same study, small amounts ($<10\%$) of arsenic were also thought to be included in silicates. Arsenic in the feed coal is dominated by

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arsenical pyrite and less toxic As^{+5} in arsenate forms [9]. Huggins [10] also found that arsenic in coal and ash by XAFS reveals significant oxidation of the arsenic associated with pyrite to arsenate (AsO_4^{3-}) species.

It is very well-known that toxicity depends not only on the concentration but also on the chemical species in which this analyte is present [11]. Toxicity studies of arsenic have shown that different forms exhibit different toxicities, thus inorganic arsenic species are more toxic than organic compounds and toxicity generally decreases with increasing degree of methylation. The LD_{50} values of arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid are 14, 20, 700-1800 and 700–2600 mg kg^{-1}, respectively [12]. Therefore, the determination of toxic arsenic species, especially inorganic arsenic, is necessary.

Several methods based on high performance liquid chromatography (HPLC), ion chromatography(IC), and capillary electrophoresis (CE) coupled with different detection methods have appeared in the literature for arsenic speciation analysis in various samples [13–16]. HPLC-inductively coupled plasma mass spectrometry (ICP-MS) is the most frequently used hyphenated technique for arsenic speciation [17–21]. However, the hydride generation-atomic fluorescence spectrometry (HG-AFS) coupled to HPLC represents a suitable alternative to this technique [22,23]. HG-AFS has been reported to be similar to ICP-MS regarding sensitivity and linear calibration range, and it has some advantages for arsenic speciation analysis, such as simplicity, lower acquisition and running costs [24].

HG-AFS could, in this sense, combine all the benefits associated with HPLC to a sensitive instrumental technique. In recent years, HPLC as an separation technique prior to the HG-AFS determination of speciation of arsenic in fruit [25] and vegetable[25,26], sediment samples [27], human urine [28], atomspheric particulate matter [29] and soil [30]. However, the research work on determination of arsenic speciation in coal samples by HG-AFS has not been reported at present.

The main purpose of this study is to develop a simple, sensitive and accurate method for speciation analysis of inorganic arsenic in coal samples. A new method is developed for direct determination of speciation of inorganic arsenic in coal samples by HPLC–HG-AFS after microwave assisted extraction with 1.0 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} ascorbic acid as extractant. The proposed method is successfully applied for the determination of speciation of inorganic arsenic in coal samples and GBW11117 coal standard reference material.

2. Materials and methods

2.1. Instrumentation

Microwave assisted extraction was conducted using a CEM MARS XPress microwave oven (CEM, Matthews, NC, USA) with Pyrex extraction vessels. The temperature was monitored in a control vessel by an armored fiber-optic temperature control probe.

AFS-9130 double-channel non-dispersive atomic fluorescence spectrometer (Beijing Titan Instruments Co., Ltd., Beijing, China) including the AS-90 autosampler was used. As atomic fluorescence high strength hollow cathode lamp (General research institute for non-ferrous metals, China) was used as the radiation source. SAP-10 atomic fluorescence pretreatment device for speciation analyzer, which was equipped with LC-15C essentia liquid chromatograph (Shimadzu). Chromatographic separations were carried out in a Hamilton PRP-X100 anion exchange column(Hamilton, Reno, NV). The corresponding guard column was used in order to preserve the analytical column. PHS-3C Lei-ci precision acidimeter (Shanghai precision scientific instrument Co., Ltd., China) was used to monitor acidity.

2.2. Reagents

All solutions were prepared from analytical reagent grade chemicals using deionized water obtained from a Millipore water purification system (Millipore Corp., Bedford, MA, USA). As(III) and As(V) stock standard solutions were purchased from National Institute of Metrology (China). All the stock solutions were kept at 4 °C, and further diluted solutions for the analysis were prepared daily. H_3PO_4 (MOS grade, Tianjing Fengchuan Chemical Reagent Science and Technology Co. Ltd., China) was used as an extractant. Ascorbic acid (A.R., Chinese Medicine Group Shanghai Chemical Reagent Company, China) was used as an antioxidant of As(III) during microwave extraction. 15 m mol L^{-1} $(NH_4)_2HPO_4$ solution was used as mobile phase for anion exchange chromatographic method, with the acidity of pH 6.0 adjusted with 10% formic acid (98%, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China). The mobile phase was filtered through a 0.45 μm filters and degassed before use by ultrasonic shaking. Furthermore, the coal extracts were filtered through 0.45 μm water system filtration membrane before their injection into the HPLC system.

Potassium borohydride solution 2%(w/v) was prepared by dissolving KBH_4 powder (95%, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) in deionized water and stabilizing it with 0.5%(w/v) sodium hydroxide (G.R., Tianjin no. 3 Chemical Reagent Factory, China). It was prepared daily. 7% (v/v) hydrochloric acid solution was prepared by dilution of 37% (v/v) HCl (MOS grade, Tianjing Fengchuan Chemical Reagent Science and Technology Co. Ltd., China). Both solutions were used in the hydride generation step.

The GBW11117 arsenic and phosphorus in coal standard reference material (Coal scientific research institute MeiHuaSuo Beijing, China). Light magnesium oxide (A.R., Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and anhydrous sodium carbonate (G.R., Beijing Chemical Works, Beijing, China) were used to digest the coal samples for determination of total arsenic.

2.3. Coal samples

Coal samples from China and America were collected, ground to a fine powder by a high speed crusher, sieved through a 0.25 mm fine-mesh sieve, and kept into pre-cleaned glass bottles at room temperature for subsequent analyses.

The reference material GBW11117 arsenic and phosphorus in coal (Coal scientific research institute MeiHuaSuo Beijing, China), certified for total arsenic, and was used for quality control purposes.

2.4. Experimental

2.4.1. Sample treatment

The coal standard reference material and samples were digested according to the following procedure [31]. The 1.0 g of each sample was weighed into nickel crucible, in which the 2 g of light magnesium oxide and anhydrous sodium carbonate ($m/m=2:1$) was placed in advance. The mixture was stirred with glass bar. Then another 1 g of light magnesium oxide and anhydrous sodium carbonate ($m/m=2:1$) was added into the samples. The crucibles were placed in muffle and heated at 800 °C, which were taken out from the muffle and cooled to room temperature after 2 h. The residual ash was dissolved by the 30 mL of HCl ($v:v=1:1$) and then the solution was transferred to a 100 mL volumetric flask, which was diluted with deionized water to volume. In the end, transfer 2.0 mL of this solution to a 50 mL

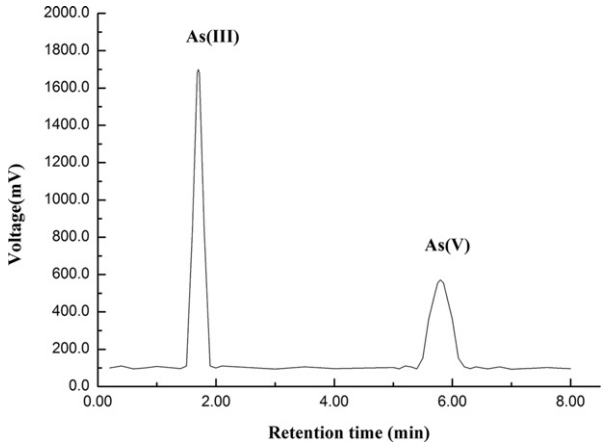

Fig. 1. Chromatogram of inorganic arsenic species. The concentration of As(III) and As(V) in injected solution was 100 ng mL^{-1}, respectively.

volumetric flask with the addition of 2.5 mL of concentrated HCl, 0.5 g of thiourea and 0.5 g of ascorbic acid, and diluted with deionized water to volume. The clear sample solutions were used for HG-AFS determination.

The H_2O or H_3PO_4 was chosen as extractant for coal and coal fly ash samples [32,33]. In this paper, inorganic arsenic species were extracted with 1 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} ascorbic acid (10 mL extractant per 0.30 g of coal sample) following microwave-assisted extraction method (extraction temperature of 80 °C and a retention time of 20 min). The coal extracts were filtered through 0.45 μm water system filtration membrane before HPLC analysis.

2.4.2. Chromatographic separation and detection

The inorganic arsenic species in coal extracts were analyzed by HPLC–HG-AFS. The separation of arsenic species was realized by the anion exchange chromatographic method, the chromatographic separation of As(III) and As(V) was carried out by injection standard or extract solution onto the anion exchange column, and eluting with 15 mmol L^{-1} $(NH_4)_2HPO_4$ solution (pH=6.0) at a flow rate of 1.6 mL min^{-1}. The anion exchange chromatographic method developed led us to the separation of two inorganic arsenic species in less than 8 min. The retention times are 1.7 min, 5.8 min for As(III) and As(V), respectively. The results could be seen from Fig. 1.

The eluted inorganic arsenic species were detected by HG-AFS, using the operation conditions given in Table 1.

Table 1
Experimental conditions for inorganic arsenic speciation by HPLC–HG-AFS.

HPLC	
Analytical column	Hamilton PRP—X100 (250 mm × 4.1 mm i.d., 10 μm)
Guard column	25 mm × 2.3 mm i.d., 12–20 μm
Mobile phase	15 mM$(NH_4)_2HPO_4$ (pH6.0)
Flow rate (mL min^{-1})	1.6
Injection volume (μL)	100
Hydride generation	
HCl (*v*/*v*)	7%
KBH_4 (*m*/*v*)	2.0%
NaOH (*m*/*v*)	0.5%
Ar flow rate (mL min^{-1})	250
AFS detection	
Detection wavelength (nm)	193.7
High negative voltage of PMT (V)	270
Lamp current (mA)	60
Auxiliary cathode (mA)	30
Atomizer height (mm)	8
Read time (min)	10
Carrier gas flow rate	300 mL min^{-1}
Shielding gas flow	500 mL min^{-1}
Read method	Peak area
Measure method	Standard curve

Table 2
Effects of H_3PO_4 concentration on extraction efficiency (n=3).

Concentration of H_3PO_4 (mol L^{-1})	Total arsenic extracted[a] (μg g^{-1})	Concentration of total arsenic[b] (μg g^{-1})	Extraction efficiency (%)
0	0.50 ± 0.06	29.68 ± 0.12	1.68
0.2	21.43 ± 0.06		72.20
0.4	24.75 ± 0.08		83.39
0.6	27.44 ± 0.12		92.45
0.8	28.52 ± 0.15		96.09
1.0	30.64 ± 0.09		103.23
1.2	29.24 ± 0.10		98.52

[a] The total arsenic concentration in the extract.
[b] Total arsenic in digested coal samples.

3. Results and discussion

3.1. Choice of microwave-assisted extraction condition

3.1.1. Choice of extractant concentration

Various concentrations of H_3PO_4 were chosen as extractant for a coal sample, in which total arsenic concentration is 29.68 ± 0.12 μg g^{-1}. The effects of H_3PO_4 concentration on extraction efficiency could be seen from Table 2. It could be found that extraction efficiency was higher when the concentration of H_3PO_4 was above 0.6 mol L^{-1}. Hence, 1.0 mol L^{-1} of H_3PO_4 was chosen for the subsequent work.

3.1.2. Effects of extraction temperature and time

Effects of extraction temperature and extraction time on extraction efficiency were studied. It was desirable to employ the shortest extraction time and the lowest possible extraction temperature. The dependence of extraction efficiency upon extraction temperature and time were studied with a range 60–100 °C and 10–30 min, respectively. A coal sample with total arsenic concentration of 3.34 ± 0.03 μg g^{-1} was chosen as sample. The results were shown in Table 3. The results showed that an extraction temperature of 80 °C and a retention time of 20 min were adequate to achieve high quantitative extraction efficiency considering using more moderate extraction condition and delaying working life of extraction tank.

3.1.3. The stability study for various arsenic species during the extraction processes

In any elemental speciation study, it is important to investigate whether the individual species are altered during any step of the method in order to confirm the reliability of the proposed analytical method. For this purpose, reference materials certified for arsenic species of interest would be ideal. However, the coal certified reference materials used in arsenic speciation studies cannot been gotten at present. Therefore, spiking of coal was used to assess the stability of arsenic species during the extraction procedure.

For study the stability for various inorganic arsenic species during the extraction process, the various concentration of ascorbic acid was added into 1.0 mol L^{-1} of H_3PO_4. Recovery experiments for inorganic arsenic species in the different extraction conditions

Table 3
Effects of extraction temperature and time on extraction efficiency ($n=3$).

Extraction temperature (°C)	Extraction time (min)	Total arsenic extracted [a] ($\mu g\,g^{-1}$)	Concentration of total arsenic [b] ($\mu g\,g^{-1}$)	Extraction efficiency (%)
60	10	2.48 ± 0.05	3.34 ± 0.03	74.3
	20	2.54 ± 0.03		76.0
	30	2.77 ± 0.08		82.9
80	10	2.91 ± 0.04		87.1
	20	3.35 ± 0.07		100.3
	30	3.28 ± 0.06		98.2
100	10	2.97 ± 0.04		88.9
	20	3.21 ± 0.05		96.1
	30	3.32 ± 0.06		99.4

[a] The total arsenic concentration in the extract.
[b] Total arsenic in digested coal samples.

Table 4
The recoveries test for inorganic arsenic species ($n=3$).

Concentration of ascorbic acid (mol L^{-1})	Species	Added concentration ($\mu g\,L^{-1}$)	Found concentration ($\mu g\,L^{-1}$)	Recovery (%)
0	As^{3+}	8.00	0	0
	As^{5+}	8.00	14.97 ± 0.23	187.1
0.05	As^{3+}	8.00	6.42 ± 0.16	80.2
	As^{5+}	8.00	9.87 ± 0.15	123.4
0.1	As^{3+}	8.00	8.20 ± 0.16	102.5
	As^{5+}	8.00	7.72 ± 0.14	96.5
0.2	As^{3+}	8.00	8.38 ± 0.23	104.8
	As^{5+}	8.00	6.15 ± 0.13	76.9
0.3	As^{3+}	8.00	10.06 ± 0.22	125.8
	As^{5+}	8.00	7.32 ± 0.14	91.5

were conducted as well for a coal sample. The results were shown in Table 4. From the results of experiment, recoveries were poor for As(III) and As(V) when the concentration of ascorbic acid is 0, the explain is As(III) was fully oxidized to As(V) in condition of microwave extraction. The recovery of As(III) was 125.8 when the concentration of ascorbic acid was 0.3 mol L^{-1}, because the As(V) was reduced As(III) when the concentration of ascorbic acid was higher. The recoveries obtained were the best for As(III) and As(V) when the concentration of ascorbic acid was 0.1 mol L^{-1}, so the mixed solution of 1.0 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} ascorbic acid was chosen as extracting agent.

3.2. Determination of total arsenic in coal samples

Total arsenic concentrations in coal samples were determined by HG-AFS according to Section 2.4.1. The accuracy of the method was assessed by determining the GBW11117 certified reference material. The result obtained ($48.54 \pm 0.23\ \mu g\,g^{-1}$) showed the absence of significant differences, at the 95% confidence level, between the As concentration found and the certified value ($51 \pm 3\ \mu g\,g^{-1}$). Therefore, the analytical method used has proved to be suitable for total arsenic determination in coal samples. The total arsenic concentrations found in Chinese coal samples varied over a wide range (1.50–3.34 $\mu g\,g^{-1}$).

3.3. Analytical performance of the method

The calibration equation and the other performance were examined, the calibration curve for As(III) and As(V) are linear up to 100 $\mu g\,L^{-1}$ with a correlation coefficient(r) of 0.9997, and 0.9991, the slope of working curve is 4216.8 and 2005.4. The intercept of working curve is 2730.9 and −2454.3. The LOD was

Table 5
Comparison of the published methods with the proposed method in this work.

Matrix/sample	Extractant method and reagent	Detection method	Concentration of As^{3+} and As^{5+} in the samples	Extraction efficiency (%)	Recovery (%)	Detection limit	Relative standard deviation (%)	References
Seaweed	Microwave-assisted extraction: 0.5m mol L^{-1} $(NH_4)_2CO_3$ + 1%MeOH (pH 8.5) and methanol	HPLC–ICP-MS	N.D.∼0.152 $\mu g\,g^{-1}$(As^{3+}); N.D.∼0.533 $\mu g\,g^{-1}$(As^{5+})	> 89	90–106	0.015 ng mL^{-1} (As^{3+}); 0.011 ng mL^{-1} (As^{5+})	> 9	[34]
Edible alga	Microwave-assisted extraction; deionized water	HPLC–AFS	N.D.∼77 $\mu g\,g^{-1}$(As^{3+}); N.D. (As^{5+})	49–98	93–115	0.019 $\mu g\,g^{-1}$ (As^{3+})∼0.028 $\mu g\,g^{-1}$(As^{5+})	2.6–4.6	[35]
Garlic	Ultrasound-assisted extraction; 1.0 mol L^{-1} H_2SO_4	HG–AFS	17.1–22.1 ng g^{-1} (As^{3+}); 54.7–67.6 ng g^{-1} (As^{5+})	98–100	98.9 for 17.5 ng g^{-1} (As^{3+}) and 56.3 ng g^{-1} (As^{5+})	0.8 ng g^{-1} (As^{3+}); 0.6 ng g^{-1} (As^{5+})	4 (As^{3+}); 7 (As^{5+})	[36]
Seafood materials	Ultrasound water-bath extraction; pepsin	HPLC–ICP-MS	< 0.011∼0.0876 $\mu g\,g^{-1}$ (As^{3+}); < 0.04∼0.207 $\mu g\,g^{-1}$(As^{5+})	–	96–105; for 2.3 ng mL^{-1} (As^{3+}); N.D.(As^{5+})	3.3 ng g^{-1} (As^{3+}); 12 ng g^{-1} (As^{5+})	11(As^{3+}) for 0.0876 $\mu g\,g^{-1}$	[37]
Edible oil	Microwave-assisted extraction; 0.5% v/v HNO_3 in 80% v/v methanol	IC–ICP-MS	1.62–2.60 ng g^{-1} (As^{3+}); 0.94–10.5 ng g^{-1}(As^{5+})	> 92	90–105	0.013ng mL^{-1} (As^{5+}); 0.024ng mL^{-1} (As^{3+})	< 8	[38]
Coal	Microwave-assisted extraction; 1.0 mol L^{-1} H_3PO_4 and 0.1 mol L^{-1} ascorbic acid	HPLC–HG-AFS	N.D.∼0.52 $\mu g\,g^{-1}$ (As^{3+}); 0.66–28.66 $\mu g\,g^{-1}$(As^{5+})	61.9–98.8	102.5% (for 0.49 $\mu g\,g^{-1}$$As^{3+}$); 96.5% (for 27.88 $\mu g\,g^{-1}$$As^{5+}$)	0.01 ng mL^{-1} (As^{3+}); 0.02 ng mL^{-1} (As^{5+})	2.4 (for 10 $\mu g\,L^{-1}$$As^{3+}$); 3.3 (for 10 $\mu g\,L^{-1}$$As^{5+}$)	This method

N.D. indicates not detected.

Table 6
Quantitative results for inorganic arsenic species in coal samples and GBW11117 ($n=3$).

Sample	Total arsenic in digested coal samples ($\mu g\,g^{-1}$)	Total arsenic extracted ($\mu g\,g^{-1}$)	Extraction efficiency (%)[a]	Inorganic arsenic species		Column recovery (%)[b]
				As(III) ($\mu g\,g^{-1}$)	As(V) ($\mu g\,g^{-1}$)	
1	3.34 ± 0.03	3.12 ± 0.08	93.4	N.D.	3.03 ± 0.06	97.12
2	1.50 ± 0.05	1.03 ± 0.05	68.7	0.09 ± 0.03	0.66 ± 0.05	72.82
3	2.58 ± 0.05	2.18 ± 0.06	84.5	0.32 ± 0.05	1.83 ± 0.08	98.62
4	29.68 ± 0.12	29.32 ± 0.14	98.8	0.52 ± 0.03	28.66 ± 0.23	99.52
GBW11117	48.54 ± 0.23	30.04 ± 0.25	61.9	0.49 ± 0.06	27.88 ± 0.26	94.44

N.D. indicates not detected.

[a] Calculated as the ratio between the total arsenic extracted concentration and the total arsenic in digested samples.

[b] Calculated as the ratio between the sum of inorganic arsenic species concentrations and the total arsenic concentration in the extract.

calculated as the concentrations that give signals equal to three times the standard deviations of the blank solution. The instrument LOD(3σ) of 0.01 $\mu g\,L^{-1}$ and 0.02 $\mu g\,L^{-1}$ were obtained for As(III) and As(V). The precision, evaluated as relative standard deviation (RSD), was calculated from seven independent replicates of a standard solution containing 10 $\mu g\,L^{-1}$ of inorganic arsenic per species. The observed RSD values for 11 replicate analyses at 10 $\mu g\,L^{-1}$ were 2.4% and 3.3% for As(III) and As(V). These data show that the present method has broad linear range, high sensitivity and good precision.

Table 5 compares the characteristic data of the present analytical method for inorganic arsenic speciation with those reported methods in literatures. Generally, the extraction efficiency and recovery obtained by the present method are comparable to those reported methods, the detection limit and the relative standard deviations are better than most of them.

3.4. Inorganic arsenic speciation in coal samples

Table 6 shows the total arsenic extracted in 1.0 mol $L^{-1}H_3PO_4$ and 0.1 mol L^{-1} ascorbic acid by the microwave-assisted extraction method for the coal samples studied, as well as for the reference material GBW11117. Extraction efficiencies, calculated as the ration of total arsenic in the extract to total arsenic in the coal, are shown in Table 6 and ranged from 61.9% to 98.8%. Most of the coals analyzed present a high percentage of arsenic compounds soluble in H_3PO_4, which was higher than 80% for 3 of the 5 samples analyzed. The arsenic fraction not extracted with H_3PO_4 could correspond to arsenic bound to compounds such as silicate.

Species quantification by HPLC–HG-AFS was carried out by external calibration. In arsenic speciation studies, mass balance between total arsenic concentration and the total arsenic extracted provides an estimation of the extraction yield. For quality assessment, column recovery must also be established to guarantee the suitability of the chromatographic separation. With this aim, the rations of the sum of the concentrations of the species eluted from the chromatographic column with the total arsenic concentration in the extract injected into the column were calculated. The values obtained for column recoveries are also shown in Table 6 and ranged between 72.82% and 99.52%, depending on the coal species and their origin. Low column recoveries could indicate the presence of species different from those studied, which cannot be detected with the chromatographic separations used, such as arsenic species present at concentration levels lower than the LOD of the developed methods or arsenic species that are not able to elute from the analytical column. Since some arsenic species are not able to elute from the analytical column, for extending the life of the column, the column was sequencely eluted by ultra-pure water and methanol–water solution (v:v=1:9) after the completion of each test, and the column was eluted by 50 mL of methanol with 1% HNO_3 (c=6 mol L^{-1}) after using for a long time.

Arsenic in coal samples studied is present under different chemical forms, with different toxicities. Therefore, from the results obtained, total arsenic content is not a useful parameter in the assessment of the toxicological implications. Therefore, study on toxic arsenic species, especially inorganic arsenic, is necessary. The analysis results for arsenic species in coal samples is shown in Table 6. It can be found that all of the coal samples analyzed present a high percentage of As(V) in inorganic arsenic species, and the proportion of inorganic arsenic with high toxicity is high, so it is required to pay attention to the environment pollution in the process of using coal.

4. Conclusions

In this work, the use of HPLC–HG-AFS method to other methods about speciation of inorganic arsenic speciation in coal samples offers several advantages including inexpensive, rapid, safe, high sensitivity, high recovery, low LOD and good precision. As(III) and As(V) are effectively separated with 1.0 mol $L^{-1}H_3PO_4$ and 0.1 mol L^{-1} ascorbic acid by microwave-assisted extraction. The results of this study demonstrate the possibility of using the HPLC–HG-AFS for separation and determination of inorganic arsenic speciation in coal samples with complicated matrixes.

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