



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

Mei Sun^{a,b,*}, Guijian Liu^{a,**}, Qianghua Wu^c, Wenqi Liu^b

^a CAS Key Laboratory of Crust-Mantle Materials and Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China

^b Hefei National Laboratory for Physical Sciences on Microscale, University of Science and Technology of China, Hefei 230026, China

^c Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

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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⁻¹H₃PO₄ and 0.1 mol L⁻¹ascorbic 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% ($c=10.0 \mu\text{g L}^{-1}$, $n=7$), 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.

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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 As³⁺ and As⁵⁺(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

* Corresponding authors at: CAS Key Laboratory of Crust-Mantle Materials and Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China. Tel.: +86 551 3602811; fax: +86 551 3602803.

** Corresponding author.

E-mail addresses: sunmei@ustc.edu.cn (M. Sun), lgj@ustc.edu.cn (G. Liu).

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 (AsO₄³⁻) 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 LD₅₀ 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 a 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], atmospheric 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 H₃PO₄ 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 essential 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. H₃PO₄ (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 mol L⁻¹ (NH₄)₂HPO₄ 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 KBH₄ 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

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