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RESEARCH PAPER

Determination of Inorganic Arsenic Speciation in Municipal Solid Waste Incineration Fly Ash by High Performance Liquid Chromatography-Hydride Generation-Atomic Fluorescence Spectroscopy with Phosphoric Acid as Extracting Agent

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Abstract: A method for the determination of arsenic speciation in municipal solid waste incineration fly ash was developed by high performance liquid chromatography (HPLC) coupled with hydride generation atomic fluorescence spectroscopy (HG-AFS). Before determination, various forms of arsenic were extracted with phosphoric acid through microwave digestion. The effect of phosphoric acid in the extracted solution on the speciation analysis of inorganic arsenic (As(III)/As(V)) was studied in detail. The results showed that when using diammonium phosphate as the mobile phase, the determination of As(V) was adversely affected. The increasing flow rate of mobile phase hardly reduced the adverse influence caused by phosphoric acid. The adverse influence was effectively suppressed when a mixed solution of disodium hydrogen phosphate/potassium dihydrogen phosphate (pH = 6.864) was used as the mobile phase. By using the improved method, As(III) and As(V) could be separated in 5 min, and the detection limits of As(III) and As(V) were 0.063 μg L^{-1} and 0.110 μg L^{-1}, respectively. The recovery rate of As(III) and As(V) in spiked standard sample was satisfactory (86.9%–102.6%). The determination of arsenic species in fly ashes sampled from four different municipal solid waste incineration plants were successfully accomplished by using the method. The results showed that the arsenic was predominantly in the form of As(V).

Key Words: Inorganic arsenic; Speciation analysis; Hydride generation atomic fluorescence spectroscopy coupled with high performance liquid chromatography; Municipal solid waste incineration fly ash

1 Introduction

In recent years, municipal solid waste (MSW) incineration has been widely used in China[1]. MSW could be effectively disposed by incineration. However, a considerable amount of fly ash is produced in the incineration procedure. Arsenic is easily volatilized during MSW incineration and most of the arsenic is enriched in fly ash[2], which would release into the environment and poses a great threat to the ecological environment. The toxicity of arsenic not only depends on its content, but also on its speciation. The arsenic in MSW incineration fly ash was mainly in the form of inorganic arsenic[3]. Among the inorganic arsenic, the toxicity of As(III) was much higher than that of As(V)[4]. Therefore, the speciation of arsenic must be analyzed accurately to make a reasonable assessment of the threat caused by arsenic in MSW incineration fly ash.

Generally, the determination of arsenic speciation is accomplished by hyphenated technique. Arsenic in various species could be separated and determined by the coupling of

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separation techniques such as high performance liquid chromatography (HPLC) with determination techniques such as inductively coupled plasma mass spectrometry (ICP-MS), atomic fluorescence spectroscopy (AFS) and atomic absorption spectroscopy (AAS)[5,6]. Among these techniques, the hyphenated technique of HPLC-HG-AFS was widely used due to its advantages such as lower detection limit, shorter separation time and better determination stability[7–9].

In addition, before the speciation analysis of arsenic in solid samples like soil and coal, arsenic should be effectively extracted from samples by proper extractant. Alam[10] and Giral[11] found that phosphoric acid was an efficient and moderate extractant for the extraction of arsenic in soil. Recently, phosphoric acid was widely used as the extractant for extraction of arsenic from coal and atmospheric particulate matter and etc[12,13]. However, in our previous study, the determination of As(V) was strongly affected by using phosphoric acid as extractant and the peak shape of As(V) was deformed when detecting the speciation of arsenic in MSW incineration fly ash by HPLC-HG-AFS. The similar phenomenon was also reported by Georgiadis[14], however, no further investigation has been studied yet. It is important to solve this problem regarding the adverse effect caused by the existence of phosphoric acid in the extracted solution when using HPLC-HG-AFS for the detection of arsenic speciation.

In this study, the HPLC conditions were optimized to minimize the adverse effect on the analysis of arsenic speciation when using HPLC-HG-AFS at the presence of phosphoric acid. Furthermore, various forms of arsenic were extracted from the MSW incineration fly ash through the microwave digestion method with the mixed solution of phosphoric acid and ascorbic acid as the extractant. The optimized method of HPLC-HG-AFS for the determination of arsenic speciation was applied to determine the speciation of arsenic in the extracted solution. Moreover, the arsenic speciation was determined in spiked standard samples to verify the accuracy of this method.

2 Experimental

2.1 Apparatus and reagents

The following instruments were used in this study: anion exchange column of Hamilton PRP-X100 (250 mm × 4.1 mm i.d., 10 μm) with guard column; Atomic fluorescence spectroscopy with arsenic hollow cathode lamp (AFS-8220, Beijing Titian Instruments Co., Ltd.); High pressure constant flow pump (P230, Dalian Elite Analytical Instruments Co., Ltd.); Ultrasonic cleaningapparatus (KQ-3200DE, Kunshan Shumei Ultrasonic Instruments Co.,Ltd.); Ultra-pure Water Purifier (American Millipore Instruments Co., Ltd.).

$(NH_4)_2HPO_4$, KH_2PO_4 and Na_2HPO_4 were all analytically pure, and the hydrochloricacid was metal-oxide-semiconductor level. The standard samples including arsenite solution (GBW 08666), arsenate solution (GBW 08667) and standard coal fly ash (GBW 08401) were purchased from National Analysis and Research Center for Certified Reference Materials (China).

2.2 Collection of samples

The fly ash samples were collected from bag filters in four typical MSW incineration plants in China. The samples of fly ash were smashed, homogenized and then dried. The four fly ash samples were labeled as sample 1, sample 2, sample 3 and sample 4, respectively.

2.3 Extraction of As(III) and As(V)

About 0.2 g sample and 20 mL mixed solution composed of H_3PO_4 (1.0 M) and ascorbic acid (0.5 M) were put into a digestion tank. The extraction procedure was carried out with microwave. The extractant was firstly heated from room temperature to 80 °C within 10 min, and kept for 20 min to make the arsenic be effectively extracted, then the extracted solution was cooled down to room temperature. The extracted solution was collected through filter membrane. Meanwhile, the residue was rinsed three times with deionized water. The eluate was collected and mixed with the extracted solution. The obtained mixture was then diluted to a constant volume of 100 mL for analysis.

2.4 Determination of As(III) and As(V)

As(III) and As(V) in the extracted solution were determined by HPCL-HG-AFS. The mixed standard solutions of As(III) and As(V) with five different concentration (20, 40, 60, 80 and 100 $\mu g\ L^{-1}$) were prepared. The detection results of standard solutions were assumed as the standard curve. The initial HPLC conditions and the operating parameters of AFS are listed in Table 1. The mobile phase mentioned in Table1 was labeled as mobile phase A. HPLC and AFS were connected by a hydride generator. The liquid sample separated by HPLC reacted with hydrochloric acid and potassium borohydride, leading to the formation of arsine. The arsine was separated from the redundant liquid sample by a liquid-gas separator and then entered the AFS to be determined by the carrier gas of argon.

3 Results and discussion

3.1 Optimization of HPLC conditions

3.1.1 Interference of phosphoric acid on determination of As(III) and As(V)