Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 65 (2005) 627–631

Talanta

www.elsevier.com/locate/talanta

On-line coupling of flow injection sequential extraction to hydride generation atomic fluorescence spectrometry for fractionation of arsenic in soils

Li-Ming Dong, Xiu-Ping Yan*

Research Center for Analytical Sciences, College of Chemistry, Nankai University, 94 Weijin Road, Tianjin 300071, China

Received 28 March 2004; received in revised form 15 July 2004; accepted 21 July 2004
Available online 21 August 2004

Abstract

A new flow injection on-line sequential extraction procedure coupled with hydride generation atomic fluorescence spectrometry (HG-AFS) was developed for rapid and automatic fractionation of arsenic in soils. The developed methodology involved a three-step sequential extraction procedure with deionized water, KOH solution, and HCl solution. 25 mg of the soil sample packed into a microcolumn (4 mm i.d. × 3 cm long) was dynamically extracted by continuously pumping each individual extractant through the column. The extracted arsenic solution was merged with 4% (m/v) $K_2S_2O_8$ solution for on-line oxidation of all arsenic species into As^V. The total extracted arsenic was on-line detected by HG-AFS, and quantitated using an on-line standard addition calibration strategy. The total time for the three-step sequential extraction and on-line detection lasted only 10 min. The developed methodology offers several advantages over conventional batch sequential extraction protocols, including minimization of readsorption/redistribution problem, improvement of accuracy, high speed, less amounts of sample/reagents required, less risk of contamination and analyte loss. The developed methodology was successfully applied to the fractionation of arsenic in certified soil reference materials.

Keywords: On-line sequential extraction; Arsenic; Soil; Flow injection; Atomic fluorescence spectrometry

1. Introduction

Arsenic is one of the elements of public concern because of its highly toxic and carcinogenic properties. It may accumulate in soils due to the use of arsenic pesticides, application of fertilizers, irrigation, oxidation of volatile arsine in air, dust from the burning of fossil fuels and disposal of industrial, municipal and animal wastes [1]. Soils are typically heterogeneous mixtures of sands, silts, and clay minerals, along with natural organic matter. In addition, these solid phases may be coated with organics or amorphous oxides. Therefore, soil provides a variety of surfaces to which contaminants such as arsenic may adsorb. As a result, arsenic may be adsorbed to several coexisting phases. These different physical forms of arsenic can give widely varying apparent environmental availability [2]. Hence, identification of the main binding sites and phase associations of arsenic in soil helps in understanding geochemical processes in order to evaluate the remobilization potential and the risks induced.

Sequential extraction technique has been widely used for fractionation of toxic elements in soils and sediments. From 1980s till now, many extraction procedures have been developed to evaluate the behavior of metal cation [3–5]. Typically, sequential extractions involve the successive leaching of a contaminated soil with extractant solutions that are chemically increasingly aggressive. Leaching is usually completed by batch extraction, which involves thorough mixing between the entire sample and the extractant at a defined solution/soil ratio and for a defined time period and reaction temperature. The extractant is then separated from the solid phase by centrifugation or filtration, the leachate and any rinse solutions

---

* Corresponding author. Tel.: +86 22 23508724; fax: +86 22 23508724.
E-mail address: xpyan@nankai.edu.cn (X.-P. Yan).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.07.028

are analyzed for the contaminant, and the remaining solid phase is used in the subsequent extraction steps. Such batch sequential extraction procedures are time-consuming and tedious, suffering great risk of contamination and analyte loss. Also the batch sequential extraction procedures provide the potential for readsorption/redistribution of elements among phases during extraction [3].

Recently, a flow-through sequential extraction reactor was developed to overcome some of the above-mentioned problems in conventional batch sequential extraction procedures [6]. With appropriate design, a flow-through system allows extraction of the contaminant and the associated solid phase followed by extractant flow out of the system and away from the remaining solid phase, thereby minimizing the possibility of readsorption/redistribution. The flow extraction system was off-line coupled with graphite furnace atomic absorption spectrometric detection for As fractionation in soil [6].

With on-line sequential extraction using flow injection (FI) techniques, the drawbacks of batchwise operation can be overcome to a great extent. The low cost, easy operation, high selectivity and sensitivity of hydride generation atomic fluorescence spectrometry (HG-AFS) make it attractive as an on-line detector of the on-line sequential extraction. Unfortunately, no such on-line combination has been reported before.

This work was undertaken to develop a new hyphenated technique for rapid, sensitive and automatic fractionation of arsenic in soils by on-line coupling of FI sequential extraction system to HG-AFS. The new technique offers several advantages over traditional batch-mode sequential extraction and currently available flow-through sequential extraction schemes with off-line detection and quantification, such as minimization of readsorption/redistribution, improvement of accuracy, high speed, less amounts of sample/reagents required, less risk of contamination and analyte loss.

2. Experimental

2.1. Instrumentation

The FI on-line sequential extraction, on-line oxidation, hydride generation and standard addition calibration were performed on a model FIA-3100 flow injection analyzer (Vital Instrumental Co. Ltd., Beijing, China). The FIA-3100 consists of two peristaltic pumps and a standard rotary injection valve (8-channel 16-port multifunctional injector).

A model XGY-1011A non-dispersive atomic fluorescence spectrometer (Institute of Geophysical and Geochemical Exploration (IGGE), Langfang, China) fitted with an arsenic hollow cathode lamp (Ningqiang Light Sources Co. Ltd., Hengshui, China) is employed for on-line detection of the extracted arsenic from soil. A laboratory-made gas–liquid separator (GLS) is used to isolate the generated arsenic vapor from the reaction mixture solution, and an argon flow is used to transport the arsenic vapor into the atomizer (7 mm i.d. × 14 cm quartz tube) of AFS. The signal was recorded by Qianpu Chromatography Workstation (Nanjing Qianpu Software Co. Ltd., Nanjing, China). The optimized operating parameters of the AFS instrument are given in Table 1. Details about the AFS system can be found elsewhere [7–9].

Table 1
Optimized operating parameters of AFS

Parameter	Setting
Lamp	Arsenic hollow cathode lamp
Primary current (mA)	60
Boost current (mA)	60
Quartz furnace temperature (°C)	200
Quartz furnace height (mm)	7
Negative high voltage of photomultiplier (V)	260

2.2. Reagents

All the reagents used are at least of analytical grade. Doubly deionized water (DDW, 18 MΩ cm) obtained from a WaterPro water system (Labconco Corporation, Kansas, MO, USA) was used throughout. All glasswares are soaked in 10% (v/v) nitric acid solution for at least 24 h and rinsed with DDW before use.

The As^{III} stock solution of 1000 mg l^{-1} was prepared by dissolving 0.1320 g As_2O_3 (Beijing Chemicals Co. Ltd., Beijing, China) in 10 ml of 1.0 mol l^{-1} KOH solution, neutralized with 5 mol l^{-1} HCl and diluted to 100 ml with DDW. The As^V stock solution of 1000 mg l^{-1} was prepared by dissolving $Na_2HAsO_4{\cdot}7H_2O$ (Beijing Chemicals Co. Ltd.) in DDW directly. Working standards solutions were prepared daily by successive dilution to the required concentration just before use. A 3% (m/v) KBH_4 solution was prepared daily by dissolving KBH_4 (Tianjin Institute of Chemical Reagents, Tianjin, China) in 0.5% (m/v) KOH (Taixing Chemicals Co., Tianjin, China) solution. A 4% (m/v) $K_2S_2O_8$ (Beijing Chemicals Co. Ltd.) solution containing 4% (m/v) KOH was prepared for on-line oxidation.

2.3. Soil samples

Two certified soil reference materials, GBW 08302 and GBW 07405 (National Center for Standard Materials, Beijing, China) were used for the validation of the developed methodology.

2.4. Procedures for arsenic fractionation

A sample microcolumn was prepared by loosely packing 25 mg of soil into a 4 mm i.d. × 3 cm long microcolumn between quartz wool plugs, and integrated into the flow injection manifold for flow injection on-line extraction.

The FI on-line sequential extraction procedure consists of three single extraction sequences with deionized water, 1.4 mol l^{-1} KOH solution and 1.0 mol l^{-1} HCl, sequentially.

Each single extraction sequence ran through three steps. The FI manifold for the present on-line sequential extraction coupled with HG-AFS is shown in Fig. 1. Details of FI programs and steps of operation are described in Table 2. In step 1, the injector valve was in the fill position and pump1 was active to fill the As^{V} standard solution or deionized water into a (300 μl) for standard addition calibration. Meanwhile, the HCl and KBH_4 solution mixed to produce an Ar–H_2 flame for a baseline. In step 2, pump 2 started running while the injector valve was still in the fill position. In this step, the extractant solution was introduced to pass through the sample microcolumn to extract arsenic from the sample, reacted with a mixture of 4% (m/v) $K_2S_2O_8$ and 4% (m/v) KOH solution to oxidize the extracted As^{III} to As^{V}. In step 3, the injector valve turned to the inject position while the two pumps were still running. The standard solution in the loop was driven by a flow of HCl solution to merge with the extract solution, and then reacted with KBH_4 solution for hydride generation. The generated gaseous mixture was transported to the atomizer with an argon flow at 400 ml min^{-1}. At the same time, the atomic fluorescence signal was detected by AFS. Step 3 lasted until the signal returned to the baseline level or became steady. The above latter two steps repeated for a subsequent extraction. The total time for the three-step dynamic sequential extraction, online detection and online quantitation lasted only 10 min.

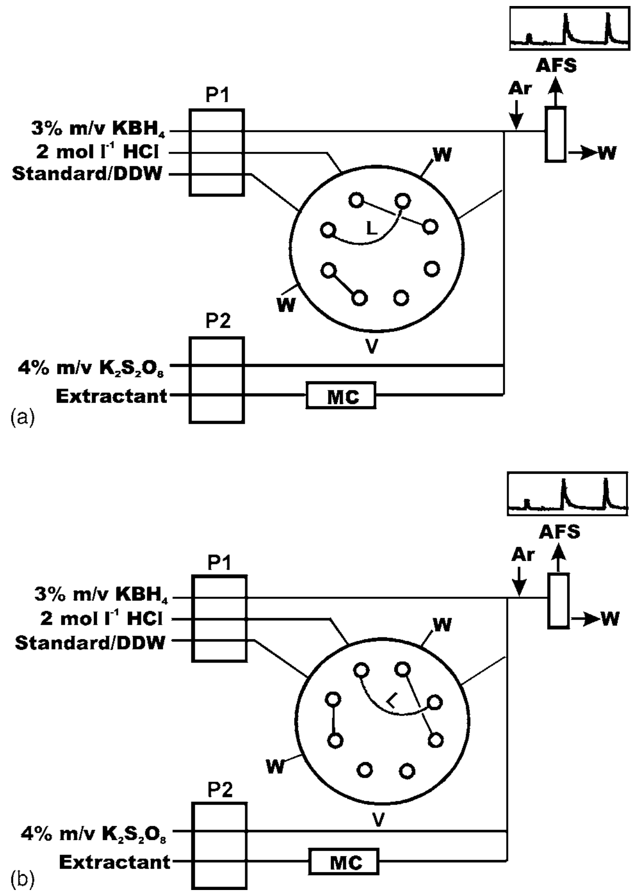

Fig. 1. FI manifold for the on-line sequential extraction coupled with HG-AFS and standard addition calibration. P1, P2, peristaltic pump; W, waste; L, standard solution loop (300-μl); V, injector valve (the inner is the rotor); GLS, gas–liquid separator; Standard, As^{V} standard solution, MC, microcolumn (4 mm i.d. × 3 cm long) packed with 25 mg of soil. Injector valve position: (a) fill and (b) inject.

3. Results and discussion

While many sequential extraction procedures have been developed to evaluate the behavior of cationic species, only a limited number of schemes have been reported for the fractionation of elements giving anionic species, such as arsenic, selenium and phosphorous [3]. Based on previous publications on arsenic fractionation in soil [10–15], we considered the following three fractions of arsenic in soil to demonstrate the feasibility of the present hyphenated technique for rapid fractionation of arsenic in solid materials in this work: (a) water soluble; (b) KOH extractable for the As fraction adsorbed by iron hydroxide precipitates [12]; (c) HCl extractable for the Ca-associated As fraction [11,16]. The factors affecting the on-line extraction, online oxidation of arsenic species into As^{V}, hydride generation, online calibration were investigated in detail. These factors include the concentration and flow rate of the extractants, the concentration of the oxidizing agent, the concentration of KBH_4 and HCl carrier solution.

3.1. Effect of the extractant concentration

The effects of KOH concentration (extractant) on the extraction of arsenic from the two certified reference materials (GBW 08302 and GBW 07405) were studied with a fixed flow rate of 3.0 ml min^{-1}. The results showed that the KOH extractable concentration of arsenic from GBW 07405 increased significantly as the concentration of KOH increased up to 1.0 mol l^{-1}, then kept almost constant from 1.0 to 2.0 mol l^{-1} KOH. The concentration of extractable As for GBW 08302 was also dependent on the concentration of KOH. The maximum extractable As concentration for GBW 08302 was achieved in the KOH concentration range of 0.7–1.8 mol l^{-1}. Pierce and Moore [15] investigated the adsorption of arsenite and arsenate on amorphous iron hydroxide, and found that at $pH > 10$ no adsorption took place. Therefore, in a batch sequential extraction procedure, 1 mol l^{-1} KOH was used to release the As fraction adsorbed by iron hydroxide precipitates by Daus et al. [12]. The optimum KOH concentration found in this work is generally in consistent with these previous observations [12,15]. For further experiments, a 1.4 mol l^{-1} KOH solution was used as the extractant for GBW 08302 and GBW 07405.

The effect of HCl concentration on the extracted As concentration was investigated within a concentration range of 0.2–1.6 mol l^{-1} at a flow rate of 3.0 ml min^{-1}. It was found that the HCl extractable As in GBW 07405 incremented with increasing of HCl concentration from 0.2 to 0.8 mol l^{-1}, and leveled off in the range of 0.8–1.6 mol l^{-1} HCl. The HCl ex-

Table 2
Program of FIA-3100 for the FI on-line sequential extraction coupled with HG-AFS and on-line standard addition calibration

Step	Time (s)	Valve position	Pumped medium		Flow rate (ml min^{-1})		Function
			Pump 1	Pump 2	Pump 1	Pump 2	
1 (Fig. 1a)	20	Fill	Standard/DDW; 2 mol l^{-1} HCl (carrier); 3% (m/v) KBH_4		3.5	Off	Fill standard solution into the loop
2 (Fig. 1a)	10	Fill	2 mol l^{-1} HCl (carrier); 3% (m/v) KBH_4	Extractant; 4% (m/v) $K_2S_2O_8$	3.5	3.0	Start extraction; oxidize the extract
3 (Fig. 1b)	Variable[a]	Inject	2 mol l^{-1} HCl (carrier); 3% (m/v) KBH_4	Extractant; 4% (m/v) $K_2S_2O_8$	3.5	3.0	Continue extraction; oxidize the extract; add standard; generate hydride

[a] Variable with extractant: 100 s for deionized water, 200 s for 1.4 mol l^{-1} KOH, and 120 s for 1.0 mol l^{-1} HCl.

tractable As for GBW 08302 increased as the concentration of HCl increased up to 0.6 mol l^{-1}. The maximum HCl extractable As was obtained within the HCl concentration range of 0.6–1.2 mol l^{-1}. The optimum HCl concentration observed in this work was in good agreement with the concentration of HCl (1 mol l^{-1}) used to dissolve the Ca-associated As fraction in soil in batch sequential extraction procedures reported by McLaren et al. [11] and Jones et al. [16]. Accordingly, a 1.0 mol l^{-1} of HCl solution was used as the third extractant for GBW 08302 and for GBW 07405.

3.2. Effect of the extractant flow rate

The extractant flow rates for efficient extraction may depend on the type of soil and particle size, so optimization of the flow rate should be carried out. Studies on the effect of the extractant flow rate showed that the concentration of extracted As slightly decreased as the extractant flow rate increased from 1.5 to 4 ml min^{-1}. Further increase in the extractant flow rate significantly diminished the concentration of the extracted As.

3.3. On-line oxidation of As^{III} and organic arsenic species into As^{V}

The arsenic extracted from soil could exist in different oxidation states, such as As^{III} and As^{V}. In order to quantify the total extracted As concentration in each fraction by HG-AFS, all the extracted As species should be reduced or oxidized to an identical valence state. The reducing reagent for convert As^{V} to As^{III} are typically potassium iodide and L-cysteine. However, a heating step should be integrated for the application of these reagents for online reduction of As^{V} to As^{III}, making it inconvenient to design the online extraction procedure. Here, we employ a $K_2S_2O_8$ solution as the oxidizing reagent for the oxidation of As^{III} and organic arsenic species into As^{V}. Studies on the effect of the $K_2S_2O_8$ solution concentration showed that a 4% (m/v) $K_2S_2O_8$ solution could rapidly and efficiently oxidize all the As species to the As^{V} at room temperature, making it easy to integrate the on-line oxidation into a dynamic extraction procedure.

3.4. Hydride generation and delivery

Potential factors affecting the hydride generation and transfer were investigated in light of the sensitivity and precision, including the concentration of KBH_4 and HCl in the carrier solution, and the argon gas flow rate. To ensure good sensitivity, acceptable precision, and minimum reagent consumption, a 3% (m/v) KBH_4 solution, a 2 mol l^{-1} HCl carrier solution, and an argon flow rate of 400 ml min^{-1} were selected.

3.5. On-line standard addition calibration

Because the extracts contain large amounts of dissolved salts, the standard additions technique is required for calibration to overcome the matrix effect on the determination of arsenic in the extracts. However, off-line standard addition calibration needs manual collection of the extracts and addition of a series of standard solutions to the extracts. Thus, considerable volumetric manipulation is involved, and such a calibration procedure is a tedious operation, suffering great risk of contamination and analyte loss. To overcome the shortcomings involved in the off-line calibration, an FI on-line standard additions method was incorporated into the flow system. The on-line calibration was achieved by injecting a standard solution into a carrier stream (2 mol l^{-1} HCl solution) to be merged with the extract for generation of a concentration profile by precise timing.

3.6. Application to the fractionation of arsenic in soils

The developed technique was applied to the fractionation of arsenic in two certified soil reference materials, GBW 08302 and GBW 07405. The results are given in Table 3. The arsenic extractograms for GBW 07405 obtained by the present online hyphenated technique under optimal conditions are shown in Fig. 2. The concentration of As in residue after three-step sequential extraction was determined by HG-AFS with HNO_3–HF digestion. Good agreement between the sum of the As concentration in each extracted fraction from these soil samples and the certified total arsenic concentration demonstrates the accuracy of the developed

Table 3
Sequential extraction results for arsenic (mean ± σ, $n = 3$, $\mu g\,g^{-1}$) in soils by the developed FI on-line sequential extraction coupled with HG-AFS

Fraction	GBW 08302	GBW 07405
Water extractable	1.23 ± 0.06	12.9 ± 1.2
KOH extractable	0.34 ± 0.04	49.3 ± 1.9
HCl extractable	0.42 ± 0.03	38.5 ± 2.1
Residue[a]	1.50 ± 0.20	308.3 ± 1.6
Sum	3.49 ± 0.21	408.7 ± 3.5
Certified total As	3.8 ± 0.4	412 ± 24

[a] Determined by HG-AFS after complete acid digestion.

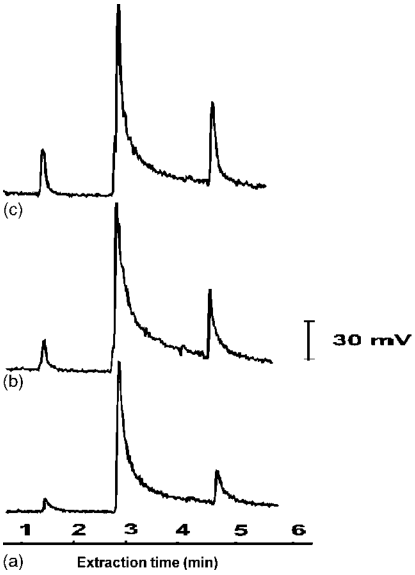

Fig. 2. Arsenic extractograms for GBW 07405: (a) without standard addition; (b) addition of 300 μl of 5 $\mu g\,l^{-1}$ As^{V} standard solution during deionized water extraction, 300 μl of 10 $\mu g\,l^{-1}$ As^{V} standard solution during 8% (m/v) KOH and 10% (v/v) HCl extraction; (c) addition of 300 μl of 10 $\mu g\,l^{-1}$ As^{V} standard solution during deionized water, 300 μl of 20 $\mu g\,l^{-1}$ As^{V} standard solution during 1.4 mol l^{-1} KOH and 1.0 mol l^{-1} HCl extraction at a flow rate of 3.0 ml min^{-1}.

technique.

4. Conclusions

An FI on-line sequential extraction coupled with HG-AFS and FI standard addition calibration has been developed and demonstrated for the first time for rapid, automatic and sensitive fractionation of arsenic in soils. Compared with traditional batch-mode sequential extraction and currently available flow-through sequential extraction schemes with off-line detection and quantification, the present methodology offers several advantages, such as minimization of readsorption/redistribution, improvement of accuracy, high speed, less sample/reagent consumption, less risk of contamination and analyte loss. We expect that it will become a useful and powerful technique for the study of the mobility, leaching kinetics and the environmental geochemistry of arsenic in contaminated solid materials, such as soils, sediments, solid wastes and air particulates.

Acknowledgements

This work was supported by the National Natural Science Foundation of China for Distinguished Young Scholars (No. 20275019, 20025516).

References

[1] M.G.M. Alam, S. Tokunaga, T. Maekawa, Chemosphere 43 (2001) 1035.
[2] H. Kurosaki, S.M. Loyland Asbury, J.D. Navratil, S.B. Clark, Environ. Sci. Technol. 36 (2002) 4880.
[3] C. Gleyzes, S. Tellier, M. Astruc, Trends Anal. Chem. 21 (2002) 451.
[4] A. Tessier, P.G.C. Campbell, M. Bisson, Anal. Chem. 51 (1979) 844.
[5] Ph. Quevauviller, G. Rauret, H. Muntau, A.M. Ure, R. Rubio, J.F. López-Sánchez, H.D. Fiedler, B. Griepink, Fresenius J. Anal. Chem. 349 (1994) 808.
[6] J. Shiowatana, R.G. McLaren, N. Chanmekha, A. Samphao, J. Environ. Qual. 30 (2001) 1940.
[7] X.-P. Yan, X.-B. Yin, X.-W. He, Y. Jiang, Anal. Chem. 74 (2002) 2162.
[8] X.-B. Yin, X.-P. Yan, Y. Jiang, X.-W. He, Anal. Chem. 74 (2002) 3720.
[9] X.-P. Yan, X.-B. Yin, D.-Q. Jiang, X.-W. He, Anal. Chem. 75 (2003) 1726.
[10] J.-B. Shi, Z.-Y. Tang, Z.-X. Jin, Q. Chi, B. He, G.-B. Jiang, Anal. Chim. Acta 477 (2003) 139.
[11] R.G. McLaren, R. Naidu, J. Smith, K.G. Tiller, J. Environ. Qual. 27 (1998) 348.
[12] B. Daus, R. Weiß, Wennrich, Talanta 46 (1998) 867.
[13] V. Ruban, J.F. López-Sánchez, P. Pardo, G. Rauret, H. Muntau, Ph. Quevauviller, J. Environ. Monit. 1 (1999) 51.
[14] K.P. Dai, Y. Li, Chin. J. Environ. Sci. 14 (1993) 26.
[15] M.L. Pierce, C.B. Moore, Water Res. 16 (1982) 1247.
[16] C.A. Jones, W.P. Inskeep, J.W. Bauder, K.E. Keith, J. Environ. Qual. 28 (1999) 1314.