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Analytical Note

# Cloud point extraction for trace inorganic arsenic speciation analysis in water samples by hydride generation atomic fluorescence spectrometry

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ABSTRACT

A new cloud point extraction technique was established and used for the determination of trace inorganic arsenic species in water samples combined with hydride generation atomic fluorescence spectrometry (HGAFS). As(III) and As(V) were complexed with ammonium pyrrolidinedithiocarbamate and molybdate, respectively. The complexes were quantitatively extracted with the non-ionic surfactant (Triton X-114) by centrifugation. After addition of antifoam, the surfactant-rich phase containing As(III) was diluted with 5% HCl for HGAFS determination. For As(V) determination, 50% HCl was added to the surfactant-rich phase, and the mixture was placed in an ultrasonic bath at 70 °C for 30 min. As(V) was reduced to As(III) with thiourea–ascorbic acid solution, followed by HGAFS. Under the optimum conditions, limits of detection of 0.009 and 0.012 μg/L were obtained for As(III) and As(V), respectively. Concentration factors of 9.3 and 7.9, respectively, were obtained for a 50 mL sample. The precisions were 2.1% for As(III) and 2.3% for As(V). The proposed method was successfully used for the determination of trace As(III) and As(V) in water samples, with satisfactory recoveries.



## 1. Introduction

Contamination of natural water with Arsenic (As) is a global problem and has attracted much attention. Arsenic is a highly toxic substance and has various forms in the natural environmental. The toxic effects of As depend not only on its concentration, but also on its chemical form. Inorganic As [iAs; arsenite or As(III) and arsenate or As(V)]is more dangerous than organic As (iAs is classified as a non-threshold, class 1 human carcinogen) and compounds with As in the +3 oxidation state are more toxic than the analogous compounds with the +5 oxidation state [1,2]. Determination of the total concentration of As may not be sufficiently accurate for environmental and food safety assessments. Speciation methods, as well as sensitive and selective methods, are therefore required for As analyses. The direct determination of As has always been a challenge because of the complexity of the sample matrix and the low concentrations of As in water samples. Preliminary separation and preconcentration are therefore required prior to determination.

Recently, sample separation and pretreatment procedures such as solid phase extraction (SPE) [3–7], solvent extraction [8], and cloud point extraction (CPE) [9–11] have been used prior to determination of As species. The most versatile and simple method for preconcentration and extraction, i.e., CPE, is based on the observation that most non-ionic surfactants form micelles in aqueous solutions, and the solutions become turbid when heated to the cloud point temperature. Above the cloud point, the micellar solution separates into a surfactant-rich phase of small volume and a dilute aqueous phase [12]. The surfactant-rich phase separated under cloud point conditions is therefore able to extract and preconcentrate hydrophobic analytes from the aqueous phase. CPE is simple, cheap, rapid, and highly efficient. It also has low environmental toxicity because it does not use toxic volatile organic solvents. This process has been used for the separation, purification, and preconcentration of a variety of substances, including metal ions and organic compounds [13–16].

CPE has been used for extraction and preconcentration as the initial step in As determination using spectrophotometry [17], electrothermal atomic absorption spectroscopy [18–20], flame atomic absorption spectroscopy [21], and hydride generation atomic absorption spectroscopy [22]. HG coupled with atomic absorption spectroscopy [23–25] and atomic fluorescence spectrometry (AFS) [26–31] are sensitive analytical tools for the determination of trace levels of As, but HGAFS is superior to hydride generation atomic absorption spectroscopy in terms of sensitivity and linear calibration range, with the further advantages of simplicity, and lower acquisition and running costs [32]. The use of CPE as a preconcentration technique for iAs speciation analysis by HGAFS has not been reported previously. As(V) has frequently been determined based on the difference between total iAs and As(III), but this method may introduce errors when the concentration of one species is much higher than the other. Studies concentrating on separate determinations of As(III) and As(V) are rare.

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**Table 1**
HGAFS operating parameters.

| Parameter | Setting |
|---|---|
| Arsenic hollow cathode lamps | 30 mA |
| Atomizer temperature | 200 °C |
| Atomizer height | 8 mm |
| Negative high voltage of photomultiplier | 270 V |
| Carrier gas (argon) flow rate | 400 mL/min |
| Measurement mode | Peak height |

It is difficult to couple CPE with HGAFS, because the surfactant causes heavy foaming during hydride generation, which may interfere with the intensity and stability of the fluorescence signal. The addition of an antifoam solution before determination can quench surfactant foaming during hydride generation. Another reason for the limited use of CPE–HGAFS in As speciation analysis is that As(V) complexes cannot not be directly determined by HGAFS because of the inefficiency of $AsH_3$ generation in the HG process and reduction of the As(V) complex. To solve this problem, ultrasonication at 70 °C is used to release As(V) from the complex. Rapid and complete reduction of As(V) to As(III) can then be achieved, followed by direct HGAFS analysis.

The purpose of the present study was to optimize CPE methods using HGAFS for the determination of As(III) and As(V). As(III) and As(V) were preconcentrated by forming complexes with ammonium pyrrolidinedithiocarbamate (APDC) and molybdate, respectively, using Triton X-114 as a surfactant. An antifoam agent (0.4 mL) was added and the As(III) content of the surfactant-rich phase was diluted to 5.0 mL with 5% HCl, and then introduced into the HGAFS for analysis. The resulting As(V) complex was converted to free As(V) by ultrasonication, and determined using HGAFS after reduction of As(V) to As(III) with 10% (*m*/*v*) thiourea–ascorbic acid solution. The optimum conditions for iAs speciation analysis were also investigated in detail.

## 2. Materials and methods

### 2.1. Instrumentation

A dual-channel atomic fluorescence spectrometer (model AFS-920, Beijing Titan Analytical Instrument Co., Beijing, China) was used for all measurements. High-intensity As hollow cathode lamps (General Research Institute for Nonferrous Metals, Beijing, China) were used. Argon (>99.995%, Yaosheng Gas Co. Ltd., Guangzhou, China) was used as a protective and purging gas. The operating parameters for HGAFS determination of As(III) are given in Table 1. A DK-600 thermostated bath (Shanghai Precision Experimental Equipment Co., Ltd., Shanghai, China) maintained at the desired temperature was used in the CPE experiments. A centrifuge (TG12Y; Hunan Xiangli Scientific Instrument Factory, Hunan, China) was used to assist phase separation. The pH was measured using a PHS-3C precision pH meter (Shanghai Hongyi Instrumentation Co., Ltd., Shanghai, China). An SK2510LHC-type ultrasonic cleaner (Guangzhou Zhengyi Co., Ltd., Guangzhou, China) was used to speed up the reaction.

### 2.2. Reagents

All reagents used in this work were of at least analytical grade, and all solutions were prepared with ultrapure water prepared using an SZ-97 automatic triple water distiller (Shanghai Yarong Biochemical Instrument Factory, Shanghai, China). Working solutions of As(III) were prepared by serial dilution with ultrapure water of a stock solution (As(III) 1000 mg/L, Beijing Nuclear Industry Institute of Chemical Metallurgy, Beijing, China), and working solutions of As(V) were prepared by diluting a stock solution of $AsO_4^{3-}$ purchased from the National Center for Reference Materials (Beijing, China) with water. The following solutions were prepared: APDC (0.5%, *m*/*v*) in water, molybdate (0.2%, *m*/*v*) in water, Triton X-114 (5.0%, *m*/*v*) in water, thiourea and ascorbic acid mixed solution (10%, *m*/*v*) in water. $KBH_4$ solution was prepared by dissolving $KBH_4$ in 0.2% *m*/*v* KOH solution as the reductant and HCl (5% *v*/*v*) was used as the carrier. The antifoam solution (50%, *v*/*v*) was prepared using antifoam 204 (Sigma-Aldrich, St Louis, MO, USA) in 5% HCl. The certified reference arsenic water sample (GBW08605) was obtained from the National Institute of Metrology (China).

All laboratory glassware used for trace analyses was kept in 5% (*v*/*v*) nitric acid for at least 24 h, and then washed several times with ultrapure water before use.

### 2.3. Analysis of water samples

Prior to preconcentration, the pH values of lake water samples were adjusted to pH 2 using HCl. The water samples were then filtered with 0.45 μm membrane filters and stored at 4 °C. The analyses of As(III) and As(V) were accomplished on the same day to avoid risk of transformation of species.

A 100 mL portion of certified reference material (with dilution of 100-fold) or water samples was passed through a glass column with activated small sized $Al_2O_3$ to separate organic As species from inorganic As species by using a peristaltic pump at a flow rate of 1.0 mL/min. The oAs was not adsorbed on $Al_2O_3$ and the adsorbed iAs species were desorbed by 10 mL of 0.2 mol/L HCl and the volume was made up to 50 mL with ultrapure water. The desorbed solution was divided into two equal portions (25 mL of each) for the determination of As(III) and As(V) by CPE.

### 2.4. Procedures

#### 2.4.1. Determination of As(III)

For CPE preconcentration, an aliquot (50 mL) of the solution (pH 4.6) containing As(III) (2 μg/L), 0.8 mL of 5% (*m*/*v*) Triton X-114, and 2.0 mL of 0.5% (*m*/*v*) APDC was left in a thermostated bath at 40 °C for 15 min. Phase separation was achieved by centrifuging the mixture at 3500 rpm for 10 min, followed by cooling in an ice-bath for 10 min to increase the viscosity of the surfactant-rich phase. The supernatant aqueous phase was carefully removed with a pipette. Antifoam agent (0.4 mL) was added to the surfactant-rich phase to reduce its viscosity, followed by dilution to 5 mL with 5% HCl. The antifoam solution was added to quench foaming of the surfactant during hydride generation. The dilute surfactant-rich phase was introduced into the HGAFS for analysis.

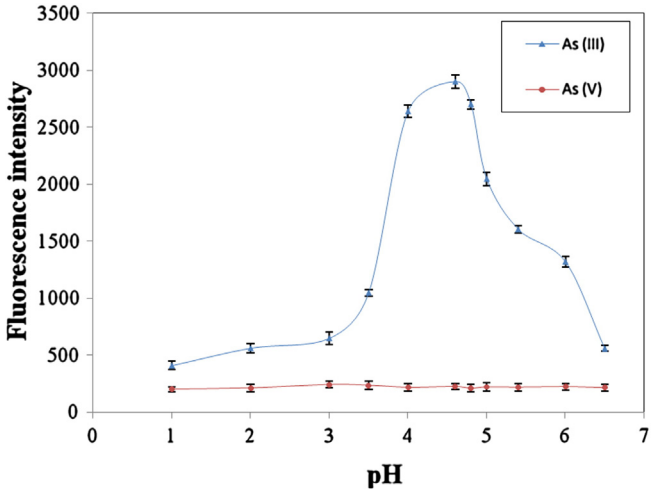


**Fig. 1.** Effect of pH on CPE of 2 μg $L^{-1}$ As (III) and As (V). Conditions: 0.015% (*m*/*v*) APDC; 0.08% (*m*/*v*) Triton X-114; equilibrium temperature 40 °C; equilibrium time 15 min. Error bar: mean of six experiments ± standard deviation.