



## Original article

# Supercritical fluid extraction and gas chromatography analysis of arsenic species from solid matrices



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## ABSTRACT

A method in combination with derivatization-supercritical fluid extraction (SFE) and gas chromatography (GC) for the speciation and quantitative determination of dimethylarsinate (DMA), monomethylarsonate (MMA) and inorganic arsenic in solid matrices was investigated. Thioglycolic acid methyl ester (TGM) and thioglycolic acid ethyl ester (TGE) were evaluated as derivatization reagents. The effects of pressure, temperature, flow rate of supercritical CO<sub>2</sub>, extraction time, modifier and microemulsion on the efficiency of extraction were systematically investigated. The procedure was applied to the analysis of real soil and sediment samples. Results showed that TGE was more effective for arsenic speciation as a derivatization reagent. Modifying supercritical CO<sub>2</sub> with methanol can greatly improve the extraction efficiency. Further, the addition of microemulsion containing surfactant Triton X-100 can further enhance recoveries of arsenic species. The optimum extraction conditions were 100 °C, 30 MPa, 10 min static and 25 min dynamic extraction with 5% (v/v) methanol, and surfactant modified supercritical CO<sub>2</sub>. Detection limits in solid matrices were 0.15, 0.3 and 1.2 mg/kg for DMA, MMA and inorganic arsenic, respectively. The method was validated by the recovery data. The resulting method was fast, easy to perform and selective in the extraction and detection of various arsenic species in solid matrices.

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## 1. Introduction

In recent years, supercritical fluid extraction (SFE) has become an attractive alternative to conventional solvent extraction in many separation processes for the sake of both analytical and technical applications [1–3]. Analytical SFE mostly uses supercritical CO<sub>2</sub> as an extractant because of low toxicity, relatively low costs and convenient critical properties (*i.e.*  $T_c = 31.1\text{ °C}$  and  $P_c = 7.38\text{ MPa}$ ) [4]. In the past two decades, an increasing number of CO<sub>2</sub> SFE studies that focus on metal ions have been published [5–8]. Direct extraction of metal ions by supercritical CO<sub>2</sub> is highly inefficient because of the charge neutralization requirement and weak solvent-solute interactions. One approach for metal ion extraction by supercritical CO<sub>2</sub> is suggested to convert charged metal ions into neutral metal complexes by using a derivatization reagent in supercritical CO<sub>2</sub> [9,10]. Besides metal ion extraction, metal speciation studies have also been conducted using SFE with neat or modified CO<sub>2</sub>, including organotin [11,12], organolead [13]

and organomercury [10,14]. However, there has been little research with a focus on arsenic speciation until now [15,16].

Arsenic is widely distributed in the environment. Global arsenic pollution has become a serious problem with various adverse effects on human health [17,18]. The most common arsenic species reported in environmental, clinical and other natural media include arsenite [As (III)], arsenate [As (V)], monomethylarsonate (MMA) and dimethylarsinate (DMA) [19]. Unlike other toxic trace elements (*e.g.*, tin, lead, and mercury), the above inorganic arsenic species are more toxic than organic ones, and therefore an available analytical methodology that permits the quantitative extraction and detection of arsenic species in various solid matrices is needed. So far, several reviews about arsenic speciation techniques have been reported [20–23]. Although high-performance liquid chromatography (HPLC) is the most commonly used separation technique for arsenic speciation, gas chromatography (GC) is often used after a prior derivatization step, which transforms original arsenic species into volatile and thermal stable derivatives such as trimethylsilyl derivatives [24], dithiocarbamate derivatives [25] and thioarsenite derivatives [26]. Among derivatization reagents, thioglycolic acid methyl ester (TGM) is used frequently. It does not only form thermally stable

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and lipophilic arsenic derivatives, but it can also convert alkylated organometallic forms MMA and DMA simultaneously with inorganic arsenic, as the sum of As (III) plus As (V), into volatile sulfur derivatives [27,28]. Therefore, it appeared possible to combine chemical derivatization-SFE with arsenic speciation in order to extract organic and inorganic arsenic species from solid matrices by SFE with on-matrix derivatization under supercritical conditions [29]. Compared with conventional sample extraction methods, this approach could reduce analysis time significantly by shortening the extraction period, eliminating the need for clean-up owing to extraction selectivity and providing the possibility of performing *in situ* derivatization reactions in fewer steps. Moreover, this procedure minimizes the usage of solvent and hazardous chemicals.

The main objective of the present study therefore was to develop a novel method in combination with *in situ* derivatization-SFE and GC for the speciation of MMA, DMA and inorganic arsenic in solid matrices using TGM as a derivatization reagent. As previous research has shown that TGM-derivatives might decompose under thermal stress at high temperatures, thioglycolic acid ethyl ester (TGE) was also evaluated as a derivatization reagent in order to avoid such degradation processes and get more stable arsenic derivatives [30]. The effects of pressure, temperature, flow rate of supercritical CO<sub>2</sub>, extraction time, modifier and microemulsion on extraction efficiency was studied. The procedure was also applied to the analysis of real soil and sediment samples.

## 2. Experimental

### 2.1. Chemicals and standards

Standard solutions of As(III) (1.011 mmol/L), As(V) (0.233 mmol/L), MMA (0.335 μmol/mL) and DMA (0.706 μmol/mL) were supplied by the China Standard Certification Center (CSC) and stored at 4 °C in PTFE bottles. Ultrapure water (18 MΩ), obtained by using a Milli-Q water purification system (Millipore, USA), was used throughout. All glassware was cleaned by using 10% (v/v) nitric acid (Merck KGaA, Germany), followed by multiple rinses with ultrapure water.

The supercritical grade carbon dioxide (99.99%) was supplied by Jinan Gas Factory of Shandong Province in China. TGM and TGE were purchased from Shanghai Chemical Reagent Company of the Medicine Group of China. Cyclohexane (Chemical Experimental Factory of Tianjin University, China) was used as the collecting solvent. HPLC grade methanol (TEDIA Co., USA) was used as modifier solvent. Triton X-100 (Beijing Reagent Factory, China) was used to form microemulsion, and silica gel (Ocean Chemical Factory of Qingdao, China) was used as the solid matrix. All other chemicals used were analytical grade reagents.

Nitrogen (99.99%, Jinan Gas Factory, China) was used as the carrier gas for GC. Tetradecane (Shanghai Chemical Reagent Co., Ltd., China) was added as the internal standard (IS) for chromatography in a 100 mg/L solution in cyclohexane.

The certified reference material soil GSS-1 and sediment GSD-10 were purchased from the Institute of Geophysical and Geochemical Exploration (IGGE) of China.

### 2.2. Instrumentation

SFE: The extraction experiments were performed using a SFE system (Applied Separation Co., USA), the schematic diagram of which is shown in Fig. 1. Two 5 mL stainless-steel extraction vessels were fitted with stainless-steel needle valves, which could be applied for two samples simultaneously. Two micro-metering valves were used as restrictor valves to control the flow rate of the supercritical CO<sub>2</sub> to the solvent collection. The

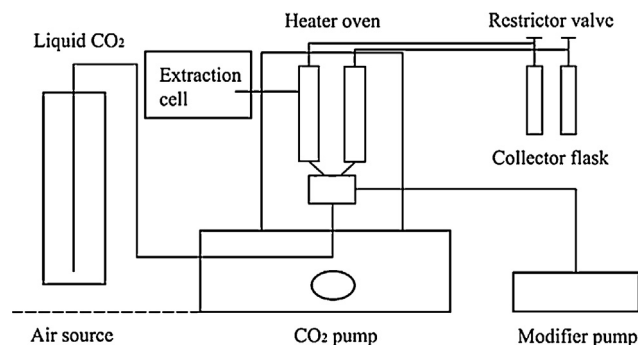


Fig. 1. The scheme diagram of the SFE system.

modifier (methanol) was added by an HPLC pump (WellChrom K-501, Germany) to the supercritical CO<sub>2</sub> stream. The extraction temperatures were monitored by a thermocouple with precision of ±1 °C.

GC: The arsenic derivatives were determined by a GC-2014 (Shimadzu, Japan) gas chromatograph equipped with a flame ionization detector (FID). The Shimadzu GC Solution Chromatography Data System was used to control and automate the GC systems, and for data acquisition and analysis. The column was a 30 m × 0.25 mm i.d. Restek Rtx-5 capillary column with a 0.25 μm film thickness (crossbond 5% diphenyl –95% dimethylpolysiloxane, Restek Co., USA). Nitrogen was used as the carrier gas at a flow rate of 3.0 mL/min. The temperature program adopted was as follows: set at 50 °C and held for 0.5 min initially, then increased up to 230 °C at 20 °C/min and then to 300 °C at 40 °C/min, where it was held for 1 min. Sample volumes of 2 μL were injected into a liner of 900 μL internal volume, in the splitless injection mode with an injection port temperature of 240 °C. The temperature of the detector was set at 300 °C.

### 2.3. Procedure

An aqueous arsenic solution was prepared by dilution from the standard solutions in ultrapure water and stored at 4 °C for not more than one week. The simulated sample was prepared as follows. A known amount of mixed arsenic solutions was spiked onto silica gel and dried at 105 °C. The dry sample was mixed well again. Concentrations were 5 mg/kg sample [As(III) and As(V)] and 1 mg/kg (MMA and DMA).

One of the end-fittings was removed and a plug of polypropylene wool was pushed into the closed end of the SFE vessel. The 5 mL vessel was filled with 2.0 g of the prepared simulated sample. The sample bed was packed firmly to ensure the uniform diffusion of supercritical CO<sub>2</sub> throughout the sample matrix. An aliquot (200 μL) of TGM or TGE was added and the remainder of the cell volume was also filled with polypropylene wool. Then the vessel was installed into the oven to perform the extraction. As the modifier solvent, the methanol solution was added into the extraction cell by the HPLC pump.

In order to find the optimum extraction conditions for arsenic derivatives, different pressures, temperatures, extraction time, flow rates of supercritical CO<sub>2</sub> and methanol modifier proportion were studied. Under the optimum conditions, a 1 mL aliquot of microemulsion, containing Triton X-100 (13.3% + cyclohexane 73.3% + 1-butanol 13.3%, w/w), was added to the extraction cell to study the effect of the surfactant on the extraction efficiency. The component and ratio of microemulsion coincided with the results found in previous studies [9,31]. The arsenic derivatives were collected in 2 mL of cyclohexane, and 2 μL of the liquid was injected and analyzed by GC as described in Section 2.2.

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