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Arsenic fractionation in agricultural soil using an automated three-step sequential extraction method coupled to hydride generation-atomic fluorescence spectrometry

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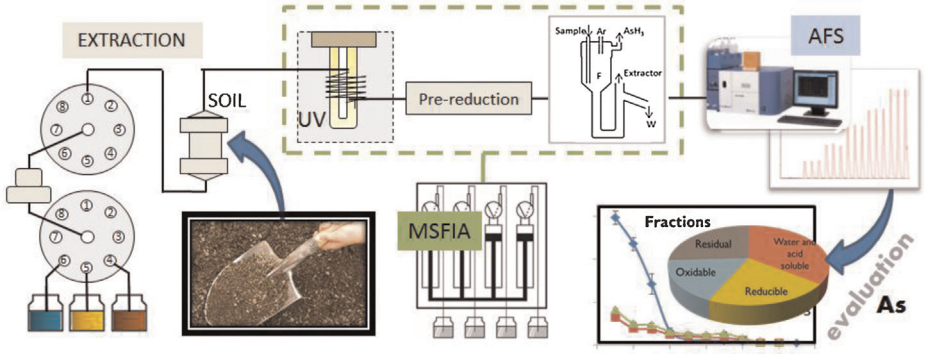
HIGHLIGHTS

- A fully automated flow-based modified-BCR extraction method was developed to evaluate the extractable As of soil.
- The MSFIA–HG-AFS system included an UV photo-oxidation step for organic species degradation.
- The accuracy and precision of the proposed method were found satisfactory.
- The time analysis can be reduced up to eight times by using the proposed flow-based BCR method.
- The labile As (F1 + F2) was <50% of total As in soil samples from As-contaminated-mining zones.

GRAPHICAL ABSTRACT



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ABSTRACT

A fully automated modified three-step BCR flow-through sequential extraction method was developed for the fractionation of the arsenic (As) content from agricultural soil based on a multi-syringe flow injection analysis (MSFIA) system coupled to hydride generation-atomic fluorescence spectrometry (HG-AFS). Critical parameters that affect the performance of the automated system were optimized by exploiting a multivariate approach using a Doehlert design. The validation of the flow-based modified-BCR method was carried out by comparison with the conventional BCR method. Thus, the total As content was determined in the following three fractions: fraction 1 (F1), the acid-soluble or interchangeable fraction; fraction 2 (F2), the reducible fraction; and fraction 3 (F3), the oxidizable fraction. The limits of detection (LOD) were 4.0, 3.4, and 23.6 $\mu g\,L^{-1}$ for F1, F2, and F3, respectively. A wide working concentration range was obtained for the analysis of each fraction, i.e., 0.013–0.800, 0.011–0.900 and 0.079–1.400 $mg\,L^{-1}$ for F1, F2, and F3, respectively. The precision of the automated MSFIA–HG-AFS system, expressed as the relative standard deviation (RSD), was evaluated for a 200 $\mu g\,L^{-1}$ As standard solution, and RSD values between 5 and 8% were achieved for the three BCR fractions. The new modified

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three-step BCR flow-based sequential extraction method was satisfactorily applied for arsenic fractionation in real agricultural soil samples from an arsenic-contaminated mining zone to evaluate its extractability. The frequency of analysis of the proposed method was eight times higher than that of the conventional BCR method (6 vs 48 h), and the kinetics of lixiviation were established for each fraction.

1. Introduction

High arsenic (As) levels in the environment constitute an important public health problem. It is known that chronic exposure to a low dose of arsenic can cause skin lesions, neurological defects, atherosclerosis and cancer [1]. In addition, this metalloid has been classified by the U.S. Environmental Protection Agency (EPA) as a human carcinogen [2]. Natural sources, such as volcanic rocks, marine sedimentary rocks, hydrothermal deposits and fossil fuels (coal and oil), and anthropogenic activities, including mining, industrial activities and the use of arsenic pesticides, have contributed to an increase in the amount of As in agricultural zones [3–5]. Arsenic can be absorbed by the root systems of plants and vegetables through agricultural soil and irrigation water and thereby gain access into the food chain. The intake of water and agricultural products contaminated with arsenic is considered the principal pathway for human exposure [6]. The binding between soil and As in the contaminated soil can dramatically affect the mobility of As underwater and thus its bioavailability for plants and animals. The mobility varies from one place to another due to variability in the chemical properties of the soil.

The three-step BCR sequential extraction method is a batch-wise protocol proposed by the European Community Bureau of Reference in 1993 (now the Standards Measurement and Testing Program) in order to harmonize the fractionation of heavy metals in soil samples according to the chemical processes involved according to: (1) the acid soluble or interchangeable fraction, (2) the reducible fraction, and (3) the oxidizable fraction [7]. This method has been widely used for the fractionation of elements in substrates such as soil and sediments [8–10]. The acid soluble and reducible fractions are considered the most bioavailable [11]. However, the conventional BCR sequential extraction method presents some drawbacks, such as an inadequacy for determining the extraction kinetics of the leaching process for elements under the action of the corresponding extracted solutions, a low frequency of analysis, and the risk of bias in the experimental results of each step due to the arsenic re-adsorption process [12]. To solve these disadvantages, the application of flow-based analysis techniques has been highlighted in several studies [13–15]. Multi-syringe flow injection analysis (MSFIA) has the advantages of flow injection analysis (FIA) methodologies and the robustness and reagent saving ability of a sequential injection system (SIA). The basic element of this method is a multi-syringe burette allowing the simultaneous movement of four syringes, which are connected in block to the same step-by-step motor. By coupling three-way solenoid valves on the syringe head to this burette, reagents are saved because they are only injected into the system at the precise moment when the analytical determination is performed [16].

Among the techniques used for As detection, hydride generation (HG) coupled to atomic fluorescence spectrometry (AFS) is widely used to detect trace levels of As. The HG-AFS technique offers a high sensitivity, specificity and relatively low cost [13].

To evaluate the total extractable arsenic fractions in agricultural soil using a more rapid and efficient extraction method than the conventional BCR procedure, a new flow-through modified-BCR extraction method is proposed in this work based on the use of a MSFIA system coupled to HG-AFS. Taking into account the lower HG efficiency observed in dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), and As(V) species (approximately 70% lower for DMA and MMA, and up to 38% for As(V)) compared with As(III) [17], the developed system includes a UV photo-oxidation step for the degradation of organic As species extracted during the BCR procedure and the reduction of the As(V) to As(III) species for the proper quantification of the total As content.

2. Experimental

2.1. Reagents

All of the chemicals were of analytical reagent grade. All of the solutions were made with Milli-Q water provided by a Direct-8 purification system (resistivity >18 MΩ cm, Millipore Iberica, Spain). All of the glassware was carefully cleaned, soaked in 10% (v v^{-1}) HNO_3 for 24 h and rinsed with Milli-Q water prior to use.

The reagents and operational conditions used in the flow-based and conventional BCR methods are summarized in Table 1. Sodium arsenate ($Na_2HAsO_4{\cdot}7H_2O$, As(V)) and dimethylarsinic acid ($C_2H_7AsO_2$, DMA) were purchased from Sigma–Aldrich (Spain). Stock solutions of As(V) and DMA at concentrations of 20 mg L^{-1} were prepared by dissolving each compound in ultra-pure water. Working solutions of As were prepared daily by the dilution of the stock solution with 0.11 mol L^{-1} acetic acid, 0.5 mol L^{-1} $HONH_2{\cdot}HCl$ (pH 1.5) and 8.8 mol L^{-1} H_2O_2 (pH 2). Hydrochloric acid 0.6–3.0 mol L^{-1} (5–25% v v^{-1}, Scharlau, Spain) was used for hydride generation from the total inorganic As content. The reducing solution of 0.5–2.5% w v^{-1} $NaBH_4$ (Scharlau, Spain) was prepared daily by dissolving an appropriate amount of sodium tetrahydroborate in 0.2 g L^{-1} NaOH (Scharlau, Spain).

In this study, two reducing agent and one oxidizing agent solutions were used, which are as follows: 1.5–4.5% w v^{-1} thiourea (Panreac, Spain) prepared with 22% w w^{-1} ascorbic acid (Scharlau, Spain), 2–6 mol L^{-1} $HONH_2{\cdot}HCl$ (Scharlau, Spain); and 1.5% and 5.4% $K_2S_20_8$ (Scharlau, Spain) in 0.5% NaOH, to assist in As hydride generation and the UV-oxidation steps of the organic species, respectively.

2.2. As-enriched soil preparation and agricultural soil samples

The parameters of the flow-based extraction method were firstly optimized using a bulk 500 g As-enriched soil sample prepared following an established protocol for a soil certified reference material [19]. A surface soil sample was dried to a constant weight (80 ± 5 °C) and sieved. Then, 500 g of soil <63 μm were mixed with 200 mL of a 50 mg L^{-1} As solution (from $Na_2HAsO_4{\cdot}7H_2O$), placed in an airtight container and stored 1 month in the dark at room temperature. Then, the As-enriched soil sample was dried to constant weight (80 ± 5 °C) and homogenized in a ball mill for 48 h. A homogeneity study was performed to determine the total As content in 5 subsamples. No significant differences (95% confidence level) between the average values of the analyzed subsamples were found by applying a one-way ANOVA test. This homogeneous As-enriched soil bulk allows the optimization of the proposed system in order to found the best sensibility and reproducibility.