Selective Extraction of Trace Arsenite Ions Using a Highly Porous Aluminum Oxide Membrane with Ordered Nanopores

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ABSTRACT: Metal ion extraction and determination at trace level concentration are challenging due to sample complexity or spectral interferences. Herein, we prepared a through-hole aluminum oxide membrane (AOM) by electrochemical anodization of aluminum substrates. The prepared AOM was characterized by scanning electron microscopy, surface area analysis, porosity measurements, and X-ray photoelectron spectroscopy. The AOM with ordered nanopores was highly porous and possess inherent binding sites for selective arsenite sorption. The AOM was used as a novel sorbent for solid-phase microextraction and preconcentration of arsenite ions in water samples. The AOM’s sub-micrometer thickness allows water molecules to flow freely across the pores. Before instrumental determination, the suggested microextraction approach removes spectral interferents and improves the analyte ion concentration, with a detection limit of 0.02 μg L⁻¹. Analyzing a standard reference material was used to validate the procedure. Student’s t-test value was less than critical Student’s t-value of 4.303 at a 95% confidence level. With coefficients of variation of 3.25%, good precision was achieved.

INTRODUCTION

The increased usage of heavy metals has resulted in water pollution, which has become a major environmental concern worldwide. Groundwater is regularly discovered with inorganic arsenic species, which is regarded as a 21st century environmental disaster. As a class I carcinogen, arsenic causes acute and chronic harm. Arsenic poisoning causes damage to the lungs, skin, liver, kidneys, and blood vessels in humans and it is recognized as a health risk. Depending on the type of exposure, As(III)-polluted water consumption affects around 144 million people worldwide, including the United States, Canada, Spain, and Asia. Moreover, cereals such as rice and wheat acquire significantly more arsenic than other cereal grains, which constitute the principal diet content for billions of people. The cumulative and additive effects of arsenic in food and water have resulted in a significant increase in arsenic toxicity in Asia. The USEPA has designated arsenic as a strong toxin among priority pollutants, and the maximum contaminant limit has been reduced from 50 to 10 parts per billion. The WHO has actually advocated for a more stringent arsenic drinking water standard, with a maximum permitted content of 10 ppb. As(III) is more mobile under aqueous conditions and is significantly more hazardous to humans than As(V). Because of the low concentration of analyte ions and/or matrix interferences, direct detection of ultratrace As(III) concentrations using spectroscopic techniques remains difficult. These sophisticated instruments are not sensitive enough to detect low-level concentrations with a complex sample matrix. The development of trace metal ion measurement methods, on the other hand, could help improve their monitoring and assessment and therefore reduce the occurrence of health problems linked to heavy metal ions. The quantification of new toxins is a common research topic that may be used to track contamination levels, evaluate control measure effectiveness, and assess biota consequences. Therefore, to eliminate matrix components and improve the detection limit, sample extraction and preconcentration procedures should be employed.

For the pretreatment of environmental samples, solid-phase extraction (SPE) has been frequently used. The method is easy, quick, and economical, and it provides for a high enrichment factor in a short extraction time while using minimal materials and solvent. For the extraction of arsenic and other metal ions, several metal oxides such as titanium dioxide, ferric/ferrous oxide, manganese oxide, copper oxide,
zinc oxide, and their composites have been explored.\textsuperscript{30,33–36}
These metal oxides can be applied directly to a solid surface or after immobilization. In the adsorption of organic and inorganic contaminants, alumina has been shown to be an effective sorbent.\textsuperscript{37–40} It has good affinity and selectivity for As(III) in the presence of As(V) and other heavy metal ions, based on Lewis acid–base interactions.\textsuperscript{41,42} Anodic aluminum oxide, with its regular hexagonal array of monodisperse pores, has become widely used for simple and cost-effective nanofabrication since the pioneering work of Masuda and Fukuda.\textsuperscript{43} The resulting one-dimensional nanostructure arrays with well-organized pores and large surface areas have been used to develop complex architectures for adsorption, catalysis, and sensing.\textsuperscript{44–46} Such materials could have a fast adsorption rate and high adsorption capacity for binding metal ions due to their large pore size and high pore volume. Maghsodi et al.\textsuperscript{47} prepared anodic aluminum oxide and optimized the synthesis parameters; after surface modification with Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2} nanoparticles, the prepared material was studied for adsorbent removal of arsenic at higher concentrations from aqueous solution. Similarly, in another report, anodic aluminum oxide after modification with graphene oxide has been studied for the

Figure 1. (A,B) FESEM image of the AOM at varying resolutions and (C) cross-sectional view of the AOM.

Figure 2. Elemental mapping images of the AOM after As(III) sorption.

Figure 3. XPS survey spectra of the AOM (A) and deconvoluted core-energy peaks of (B) Al 2p and (C) O 1s and (D) As 3d of the AOM sorbent.
extraction of metal ions.48 Wei et al. report the successful adsorption/extraction of phosphopeptides from complex human serum using anodic aluminum oxide.49 However, no research has been done to date to look into the use of anodic aluminum oxide membranes in sample cleansing and metal ion enrichment at trace level concentration. The use of a porous AOM advantageously lacks pressure drop during flow through experiments (column operation) compared to activated alumina in column operation. This is due to the high porosity of the AOM and cross-through channels for water permeation. The SPE adsorbent in the disk format has a wide cross-sectional area, allowing for rapid mass transfer in a short loading time, reduced column plugging risk, and, as a result, a faster flow rate. The goal of this research is to prepare an AOM for the preconcentration of trace arsenite ions in a column procedure. The resultant AOM was described, and flow-through tests were used to assess the selective enrichment of arsenite ions (trace and ultratrace levels). Controlling the sample pH and flow rate allowed for selective extraction of arsenite ions from other heavy metals including alkali- and alkaline-earth metals. The AOM has a high extraction efficiency for arsenite ions and good flow rate features. The entire analysis time was much less than that of other SPE procedures, including sample preconcentration.

# RESULTS AND DISCUSSION

Characterization. The field emission scanning electron microscopy (FESEM) image of the AOM shows a dense and orderly array of hexagonally packed cylindrical pores with an average pore diameter of 105 nm and a pore-to-pore minimum spacing of 15 nm (from SEM) with an average pore diameter of 105 nm (Figure 1A,B). Figure 1C shows a cross-sectional picture of the AOM, which reveals the thickness of the material and parallel nanochannels with a pore depth of 505 nm. Figure 2 shows the surface elemental composition of the AOM after As(III) sorption as determined by EDS. After As(III) sorption, the XPS scan of the AOM (Figure 3A) revealed the significant Al 2p and O 1s peaks at their respective binding energy levels and the As peak. The Al 2p peak at a binding energy of 74.4 eV in the deconvoluted XPS spectra of Al reveals the Al–O–Al bonding of the AOM framework (Figure 3B). This signal indicated a covalent bonding between the AOM units (Al₂O₃). The shoulder peak in the Al 2p spectrum at 73.5 eV was also attributed to Al–Al metallic bonding. The Al–O–H and Al–O bonding was attributed to the deconvoluted O 1s peaks seen at binding energies of 532.15 and 531 eV, respectively (Figure 3C). After As(III) sorption onto the AOM, the deconvoluted As 3d peaks are indicated in Figure 3D.50,51 According to the water contact angle measurements, the AOM has a good surface hydrophilicity for the SPE of As(III) from aqueous fluids (Figure 4).

Effect of Sample pH. The sample pH has a significant impact on the distribution of the arsenic species’ ionic states and hence plays an important role in the sorption process. As(III) is commonly found in the neutral form (H₃AsO₄) at pH 1–9, but As(V) is commonly found in the neutral form (H₂AsO₄⁻) at acidic pH 1–2 and remains negatively charged as H₂AsO₄⁻ at pH 2–7 and HAsO₄²⁻ at pH 7–10. A series of model solutions (50 mL) each containing 100 μg mL⁻¹ As(III) ions were passed through an AOM-packed column to investigate the effect of pH on the sorption/extraction of As(III). At pH 1–9, the sorption of As(V) was also investigated. Surface complexation with oxygen moieties at

![Figure 4. Water contact angle measurement of the AOM sorbent.](image)

Al–O bonds and positively charged aluminum ions can result in the sorption of As(III) ion species on the active sites of the AOM (Al₂O₃). The experimental and theoretical studies demonstrated clearly that the adsorption of As(III) onto the aluminum oxide surface positively occurs by formation of inner-sphere bidentate–binuclear configuration complexes along with outer-sphere complexes.52–54 Figure 5 shows the sorption trend of As(III) onto the AOM as a function of pH. At all the pH levels investigated, the sorption/extraction of As(III) is more or less identical. When the sample pH was changed, no significant variations in sorption efficiency were detected. Furthermore, no substantial sorption of As(V) was seen at any of the pH levels investigated. At pH 3–7, there was a full recovery of As(III) of around 97–100%. Finally, in later trials, a pH value of 6 was shown to be optimal for As(III) sorption.

Flow Rate of the Samples. In the recovery of analytes, the sorption flow rate is a critical element that impacts not only the analyte extraction efficiency but also the analysis time. In general, effective extraction is aided by a sample flow rate that permits a sufficient contact time between the analyte and the sorbent substrate. The effect of the sorption flow rate on As(III) preconcentration was examined by passing 50 mL of sample solutions containing 100 μg mL⁻¹ As(III) at a flow rate of 2–10 mL min⁻¹ at pH 6.0 (Figure 6). After a flow rate of 5 mL min⁻¹, it was discovered that as the sorption flow increased, the percent recovery of arsenic decreased. The As(III) recovery decreased by 10% when the sample flow was increased to 6 mL min⁻¹, owing to an insufficient contact time between the As(III) ions and AOM active sites. As a result, for the next studies, 5 mL min⁻¹ sorption flow was chosen.

Reusability and Elution. A high extraction efficiency and 100% recovery of adsorbed metal ions from the adsorbent are two important qualities of an ideal adsorbent for ensuring reusability. Hydrochloric, nitric, and sulfuric acids at different concentrations (0.25–1.0 M) and volumes were used to study
complete desorption of the adsorbed heavy metal ions from the AOM-packed column (2−5 mL). The eluents were pumped through the column at a volume ranging from 2 to 5 mL. The eluent solution of sulfuric acids resulted in a quantitative recovery of analyte ions, and 3 mL of 0.5 M sulfuric acid at a flow rate of 3 mL min\(^{-1}\) completely desorbed the As(III) (recovery >99.9%) and regenerated the column for the next sorption cycle. Nitric and hydrochloric acids, on the other hand, were less effective (recovery 80−95%). Figure 7 shows the obtained data. As a result, for the following studies, 3 mL of 0.5 M sulfuric acid at a flow rate of 3 mL min\(^{-1}\) was utilized as the eluent.

To test the reusability of the AOM-packed column, 30 successive extraction cycles under optimum circumstances were performed. Figure 8A depicts the results. During repeated usage, good extraction (>98 percent) of the As(III) ions was observed, demonstrating the AOM-packed column’s reusability in the extraction of As(III) from samples without loss of extraction performance. After 30 cycles, the FESEM picture of the AOM revealed no significant changes in the surface morphology (Figure 8B).

**Effect of Alkali- and Alkaline-Earth Metals.** Co-existing ions such as alkali- and alkaline-earth metals, nitrate, carbonate, chloride, sulphate, phosphate, and heavy metal ions that show spectral interferences and may interfere with the sorption of As(III) ions were investigated, and the results are provided in Table 1. The tolerance limit was chosen at the highest concentration of interferent ions that might cause a 5% divergence in arsenic sorption/recovery. Under optimal circumstances, 50 mL of model solution containing 10 \(\mu\)g L\(^{-1}\) As(III) and different concentrations of co-ions was passed through the AOM-packed column to determine the tolerance limit. The results showed that there were no substantial interferences in the sorption and detection of arsenic for the entire added ions, with an analyte recovery of 96−100 percent.

| co-ion | salt          | amount added (\(\mu\)g L\(^{-1}\)) | recovery % (RSD) |
|--------|---------------|----------------------------------|-----------------|
| CO\(_3\)^{2−} | Na\(_2\)CO\(_3\) | 50 \times 10^3 | 96.5 (3.5) |
| SO\(_4\)^{2−} | Na\(_2\)SO\(_4\) | 50 \times 10^3 | 98.0 (4.2) |
| PO\(_4\)^{3−} | Na\(_3\)PO\(_4\) | 50 \times 10^3 | 95.5 (3.7) |
| NO\(_3\)^{−} | NaNO\(_3\) | 50 \times 10^3 | 99.8 (3.6) |
| Cl\(^{−}\) | NaCl | 50 \times 10^3 | 98.0 (2.8) |
| Na\(^{+}\) | NaCl | 25 \times 10^3 | 98.5 (3.9) |
| K\(^{+}\) | KCl | 25 \times 10^3 | 95.5 (4.3) |
| Ca\(^{2+}\) | CaCl\(_2\) | 25 \times 10^3 | 98.0 (3.2) |
| Mg\(^{2+}\) | MgCl\(_2\) | 25 \times 10^3 | 96.2 (3.8) |
| Fe\(^{3+}\) | Fe(NO\(_3\))\(_3\) | 15 \times 10^3 | 98.6 (3.1) |
| Pb\(^{2+}\) | Pb(NO\(_3\))\(_2\) | 15 \times 10^3 | 98.5 (3.7) |
| Cu\(^{2+}\) | Cu(NO\(_3\))\(_2\) | 15 \times 10^3 | 98.0 (2.8) |
| Cd\(^{2+}\) | CdCl\(_2\) | 15 \times 10^3 | 98.0 (4.2) |
| Zn\(^{2+}\) | ZnCl\(_2\) | 15 \times 10^3 | 98.5 (4.8) |
| Ni\(^{2+}\) | Ni(NO\(_3\))\(_2\) | 15 \times 10^3 | 98.6 (4.5) |
| Co\(^{2+}\) | Co(NO\(_3\))\(_2\) | 15 \times 10^3 | 99.0 (3.4) |

In conclusion, successful recovery of As(III) in the vicinity of other heavy metal ions in the concentration range of up to 250 mg L\(^{-1}\), for quantitative determination, can be achieved under optimized experimental conditions.

**Preconcentration.** The goal of the present study is to use an AOM adsorbent to separate the sample matrix and enhance the analyte concentration above the instrumental detection limit. Using a preconcentration process, the trace As(III) ions can be transferred from a complex sample with a larger volume into a cleaner sample with a smaller volume, eliminating spectrum interferences and allowing for reliable instrumental analysis. After preconcentrating model samples of variable sizes (volume) containing a set number of As(III) ions (1 \(\mu\)g), the minimum As(III) concentration at which quantitative recovery
is possible was examined. Up to a sample volume of 1800 mL, a great recovery (100%) was achieved; however, as the amount is increased, the recovery drops to 92% at a sample volume of 1900 mL. With a preconcentration factor of 600, a preconcentration limit of 0.5 μg L⁻¹ was obtained. Such a fairly good preconcentration factor promotes the AOM appropriateness in the enrichment of real samples prior to instrumental analysis.

**Analytical Method Validation and Reliability.** Under optimum experimental conditions, the analytical properties of the method were evaluated, including linearity (calibration), precision, the limit of detection (LOD), accuracy, reliability, and robustness. After preconcentrating As(III) standards in the range of 1–5000 μg L⁻¹, a calibration plot was generated with a correlation coefficient (R²) value of 0.9998. The method’s precision was tested by analyzing 10 replicate samples (1 μg in 50 mL). The relative standard deviation (RSD) for repeated analyses was found to be 3.25%, with high recovery values of 99–100%, indicating the method’s precision. For 20 replicate blank measurements, the limit of detection was estimated as three times the signal-to-noise ratio (s/n) of a mean blank sample and was found to be 0.02 μg L⁻¹. By recovering the spiked amount (5 and 10 μg) to real samples and assessing SRMs, the accuracy was confirmed. With RSD levels of less than 5%, the recovery percentage of the spiked amount was 98–100%. Tables 2 and 3 present these findings. Student’s t-test results were significantly lower than the essential Student’s t-value of 4.303 (95 percent confidence level; N = 3) (Table 2). There were no methodological errors found. The difference between the preconcentrates’ mean concentration values and the certified values was statistically insignificant. The method’s robustness was tested by changing the sample pH value to ±1.0 and the flow rate to ±0.5 mL min⁻¹. The recovery of As(III) ions showed no significant variations (recovery >98%).

**Application to the Analysis of Real Samples.** In this study, the AOM-packed column was utilized to preconcentrate trace quantities of As(III) from real-sample matrices (50 mL), including potable water, ground water, river water, and wastewater samples, prior to their measurement by ICP-OES. As illustrated in Tables 3 and by the recovery of the spiked amount, the AOM-packed column successfully preconcentrates As(III) from a complex sample matrix while simultaneously enriching the analyte ions for further detection with high precision. The mean percentage recoveries for the increased quantity of As(III) vary from 99 to 100%, with an RSD value of <5%.

### CONCLUSIONS

Wet anodization was used to create a highly porous aluminum oxide membrane with a higher pore size, which was used to recover and concentrate trace As(III) ions from complicated sample matrices. As(III) is selectively absorbed onto the AOM via Al–O bonds and positively charged aluminum ions. The AOM has a wide surface area (195 m² g⁻¹), a big pore size (average 100 nm), a high pore volume (0.38 cm³ g⁻¹), and a high density of binding sites, all of which are thought to promote increased As(III) ion sorption with a low detection limit (0.02 g L⁻¹). The suggested method was effectively used to clean the sample while also reducing the sample size to concentrate As(III) ions prior to instrumental analysis. As a result, reliable identification of trace As(III) ions in actual samples may be possible. The results of the SRM study verified the suggested method’s dependability and its accuracy and precision. The AOM-packed column may be used to analyze As(III) in ambient water samples on a regular basis. Spectral interferences produced by the co-existing ions may usually impair direct sample analysis. When analyzing the samples using the AOM-packed column, however, no spectral interferences were found.

### EXPERIMENTAL SECTION

**Materials.** Analytical-grade chemicals and metal salts were used. Alfa Aesar provided an aluminum (Al) sheet (99.997% pure, 0.25 mm thick with a size of 10 × 10 cm²) and a platinum (Pt) mesh (China). Thermo Fisher Scientific (China) provided the metal salts. In addition, the As(III) solution used (1000 mg L⁻¹ in 1% HNO₃) was procured from Agilent (Australia) and As(V) oxide hydrate (As₂O₃ 7H₂O) was purchased from Sigma-Aldrich (Germany). Required working solutions were prepared from stock solutions after dilutions using deionized water (18.2 MΩm-cm). Merck (Germany) supplied sulfuric acid, oxalic acid, hydrochloric acid, phosphoric acid, sodium hydroxide, and potassium hydroxide pellets. Princeton Applied Research provided the reference electrode (K2625 Ag/AgCl, 3 mol L⁻¹ KCl) (India). The National Institute of Environmental Studies provided standard reference materials (SRM NIES 2669). (Ibaraki, Japan) also provided the metal salts. In addition, the As(III) solution used (1000 mg L⁻¹ in 1% HNO₃) was procured from Agilent (Australia) and As(V) oxide hydrate (As₂O₃ 7H₂O) was purchased from Sigma-Aldrich (Germany).

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edges of the Al sample. To obtain a through-hole AOM, polystyrene (PS) coating was applied to the back side and charge-coupled detector, was used to determine the axial mode for observing plasma, with an ultrasonic nebulizer calibration standards for ICP-OES.

**Preparation of the AOM.** The permeable AOM with self-ordered nanochannels was fabricated using a two-electrode system and two-step anodization of the aluminum sheet. In 0.3 M oxalic acid, an aluminum sheet was employed as an anode with platinum mesh as a cathode, using 50 V at 5 °C for 8 h. The anodized layer was removed after step I by immersing the templates in a chemical mixture etchant of chromic and phosphoric acid (1:8.6 wt %) at 60 °C for 1 h and then re-anodized under similar conditions for 5 h. To avoid back-side anodization and offer a limited surface area, a polystyrene (PS) coating was applied to the back side and edges of the Al sample. To obtain a through-hole AOM, residual Al was etched using a standard mixture etchant of CuCl₂/HCl (0.1mol L⁻¹, 20 wt %), followed by pore widening and barrier layer etching in 5 wt % H₃PO₄ at ambient temperature. The resultant AOM was then soaked in chloroform for 20 min to remove the PS covering completely. The AOM was then cleaned with ethanol and deionized water to eliminate any remaining contaminants before being characterized.

**Characterization.** For the microcompositional study, field emission scanning electron microscope (JSM-7800F, JEOL, Japan) with an energy dispersive X-ray spectrometer (QUANTAX X129 eV, Bruker) was used to analyze the chemical bonding, with a digital camera was used to assess the surface hydrophilicity of the AOM. The water contact angle was determined by placing a deionized water droplet (5 μL) on the AOM surface and using the sessile drop method. Photographs of water droplets were taken digitally. The measurement was carried out five times at random locations, with the average values provided.

**Arsenic Preconcentration and Extraction Procedure.** The preconcentration tests were carried out on a polytetrafluoroethylene (PTFE) column (10 × 0.8 cm) packed with five AOM SPE discs (bed height/thickness ≈1.0 cm). The column was purged with N₂ gas before passing the sample solution. A sample flow of 5.0 mL⁻¹ was attained by passing 50 mL of sample solutions at a sufficient As(III) concentration through the column under optimal pressure. In all tests, the pH of the sample solutions was tuned and kept at 6.0. The sorbed As(III) ion was eluted with 3 mL of 0.5 M H₂SO₄ solution after flushing the column with deionized water. ICP-OES in the axial mode for observing plasma, with an ultrasonic nebulizer and charge-coupled detector, was used to determine the amounts of eluted As(III) ions. The following were the instrument’s operational parameters: 1.5 kW; alumina injector 2.0; Ar (8 L min⁻¹); auxiliary gas (0.2 L min⁻¹); nebulizer gas (0.7 L min⁻¹); pressure: 3.2 bar; read time: 2 mL min⁻¹; and wavelength: 188.979 nm.

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**Notes**

The authors declare no competing financial interest.

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