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# Iron-complexed adsorptive membrane for As(V) species in water

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## HIGHLIGHTS

- Functionalized membrane was prepared by graft polymerization in host membrane.
- $Fe^{3+}$ ions fixed in membrane made it selective for As(V) ions.
- As(V) preconcentrated selectively in membrane samples was quantified by INAA.
- As(V) in ground water sample was easily quantified in 2–3 ppb using membrane.
- Total inorganic arsenic could be quantified by oxidation of As(III) to As(V).

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## ABSTRACT

Selective preconcentration of a target analyte in the solid phase is an effective route not only to enhance detection limit of the conventional analytical method but also for elimination of interfering matrix. An adsorptive membrane was developed for selective preconcentration and quantification of ultra-trace (ppb) amounts of As(V) present in a variety of aqueous samples. The precursor membrane was prepared by UV-initiator induced graft polymerization of sulphate and phosphate bearing monomers (1:1 mol proportion) in pores of the host microporous poly(propylene) membrane. $Fe^{3+}$ ions were loaded in the precursor membrane to make it selective for As(V) ions. The presence of phosphate functional groups prevent leaching of $Fe^{3+}$ ions from the membrane when it comes in contact with solution like seawater having high ionic strength. The optimized membrane was characterized in terms of its physical structure, chemical structure and experimental conditions affecting As(V) uptake in the membrane. The possibility of quantifying total preconcentration of As content was also explored by converting As(III) to As(V). To quantify As(V), the membrane samples were subjected to instrumental neutron activation analysis (INAA). The studies carried in the present work showed that quantification of inorganic arsenic species in natural water samples is easily possible in 2–3 ppb concentration range.



## 1. Introduction

Arsenic is one of the most important hazardous elements widely present in atmosphere, soils, rocks, natural waters and bio-organisms. It is the 20th most abundant element in nature, 14th in the seawater, and 12th in the human body [1]. The nature and quantities of the various arsenical compounds found in dietary seafood and their metabolic processing and fate has been reviewed by Borak and Hosgood [2]. The primary sources of arsenic are erosion of rocks along with anthropogenic inputs like pesticides, wood preservatives, mining activities and electronic equipments [3]. Contamination of ground water with arsenic has become a worldwide important environmental issue [4]. The World Health Organization (WHO), US Environmental Protection Agency (US-EPA) and other agencies have introduced a standard that led to reduction of permissible arsenic maximum contaminant level (MCL) in drinking water from 50 ppb to 10 ppb [5–7]. This has resulted in a series of research and development activities to evolve analytical method for As speciation and quantification in aqueous sample at ultra-trace level, and also search for cost effective arsenic treatment technologies as evident from the recent reviews [3,8,9].

There are several conventional analytical methods that can be used for quantification of As in the samples depending upon their chemical compositions [10,11]. However, the arsenic speciation at ultra-trace level requires techniques such as high pressure liquid chromatography (HPLC), capillary electrophoresis (CE), ion chromatography (IC); solid phase extraction, cloud point extraction; and hydride generation, diffusive gradients in thin films (DGT), etc. [10,12–19]. For enhancing the detection limit for As(III) in

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drinking water, the electrochemical assay based on self-assembled monolayers (SAMs) [20] and surface-enhanced Raman scattering (SERS) platform based on glutathione (GSH)/4-mercaptopyridine (4-MPY)-modified silver nanoparticles (AgNPs) [21] have been developed. Multi-elements analyses in the environmental samples are possible with the instrumental neutron activation analysis (INAA) and inductively coupled plasma-mass spectrometry (ICP-MS) [22]. A radiochemical neutron activation analysis method has been developed for determination of arsenic in the biological samples [23]. However, a selective preconcentration step can be effective not only for enhancing reliable analytical range to ppb level but also for elimination of interfering matrix from aqueous samples. The solid phase extraction has advantages that it provides high preconcentration factor and amenable to direct quantification of the target analytes preconcentrated in it by elemental techniques like energy dispersive X-ray fluorescence (EDXRF) and INAA [24].

The arsenite, the trivalent form, is far more toxic in the biological systems than arsenate whereas toxicity of organic-arsenic species is generally lower than that of inorganic arsenic species [25,26]. Organic, inorganic and inorganic–organic hybrid materials like calix[4]arene appended resin [27], *N*-methyl-D-glucamine resins [28], iron phosphate [29], several iron(III) oxides [30–32], ferrihydrite [33], zerovalent iron [34], rare earth oxides [35], porous polymers loaded with monoclinic hydrous zirconium oxide [36], Zr-loaded lysine diacetic acid chelating resin [37], zirconium(IV) loaded phosphoric chelate adsorbent [38,39], metal-loaded chelating resins [40], PVDF/zirconia blend flat sheet membrane [41] and inorganic particles loaded chitosan [42–44] etc. have been developed for removal of the arsenic species from aqueous media. For analytical application, a sorbent should be in a reproducible geometrical form, have non-interfering matrix, easy to use for preconcentration, and should be amenable to quantification of the analyte in sorbent's matrix. The flat sheet functionalized polymer sorbents offer such advantages for the analytical applications [24].

Fe(III) has strong affinity towards oxyanions of arsenic. Therefore, Fe(III) ions have been loaded in chelating resins (weak-base and iminodiacetic chelating resins Chelex 100) [45,46], amberlite resin [47], poly(hydroxamic acid) [48], chelating resin having a lysine-$N^{\alpha}$,$N^{\alpha}$-diacetic acid [49], chitosan [50] and sulfonic acid functionalized polystyrene (Purolite C-145) [51]. There are two possibility to stabilized Fe(III) in a polymer matrix i.e. precipitate it as hydroxide in polymer matrix or form strong complex with chelating group attached covalently to polymer chains. The phosphate moiety on polymer chains forms strong complex with Fe(III) that may prevent its leaching in aqueous media having extreme chemical conditions like high acidity or salt.

In the present work, a flat sheet polymer sorbent (adsorptive membrane) has been developed for preconcentration and determination of the inorganic arsenic in natural water samples. The membrane was prepared by UV-initiator induced in situ polymerization of monomers 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) with or without co-monomer bis[2-(methacryloyloxy)-ethyl] phosphate (MEP) (1:1 mol ratio) along with a crosslinker methylene-bis-acrylamide (MBA) in pores of the poly(propylene) microporous host membrane. The membrane thus formed has reproducible geometry, and close proximity of binding sites in pores results in formation of the channels for ion-hopping. The stability of anchored polymer in pores is attributed to entanglement of host-guest polymer chains, crosslinking and grafting. The pores are completely blocked and crosslinking provides mesh like structure to micro-gels anchored. The microporous host membrane acts as a mechanical containment to micro-gel and guest component makes the membrane selective to target ions. The precursor membrane has been made selective to As(V) by loading $Fe^{3+}$ ions. The $Fe^{3+}$-loaded membrane was characterized by different techniques and then subjected to studies for quantifying ultra-trace concentrations of inorganic arsenic species in natural water samples using INAA.

## 2. Experimental

### 2.1. Reagents and apparatus

The microporous poly(propylene) flat sheet membrane (Accurel® 1E R/P from Membrana) having nominal pore size of 0.1 μm and thickness of 92.5 μm was used as a host membrane. Bis[(2-methacryloyloxy)-ethyl] phosphate (MEP), N-N'-methylene-bis-acrylamide (MBA), 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and α,α'-dimethoxy-α'-phenyl acetophenone (DMPA) were obtained from Sigma–Aldrich (Steinheim, Switzerland). Tetrahydrofuran (THF), methanol, and N, N' dimethylformamide (DMF) were obtained from Merck (Mumbai, India). Thicknesses of the membrane samples were measured using a digital micrometer (Mitutoyo, Japan) with a precision of ±0.001 mm. Multilamps photoreactor from Heber Scientific (model No. HML-SW-MW-LW-888) having six UV lamps (8 Watt) arranged in a circle was used for photo-initiator induced grafting. EDXRF measurements were carried out using an EX 3600-M spectrometer, Jordon valley AR Ltd. (Migdal Haemek, Israel). $^{59}$Fe and $^{131}$I radiotracers in aqueous solutions were obtained from Board of Radiation and Isotope Technology, Mumbai, India. $^{76}$As ($t_{1/2}$ = 26.3 h, $E_{\gamma}$ = 559 keV, $a_{\gamma}$ = 45%) radiotracer was obtained by irradiating sodium meta-arsenite ($NaAsO_2$) and sodium arsenate ($Na_2HAsO_4$) for 1 min in pneumatic carrier facility (PCF) (flux = $5 \times 10^{14}$ n cm$^{-2}$ s$^{-1}$) of Dhruva research reactor, BARC, Mumbai. The gamma activity of $^{76}$As (559 keV) and $^{131}$I (364 keV) were monitored by using HPGe detector connected to multichannel analyzer. The longer lived radiotracer $^{74}$As ($t_{1/2}$ = 18 d, $E_{\gamma}$ = 595–635 keV) was prepared by $^{74}$Ge (p, n) $^{74}$As nuclear reaction using proton beam (10 MeV) at VECC, Kolkata, India. Natural germanium foil of 0.4 mm thickness was irradiated for 3 days with 10 MeV proton at a beam current of 1 μA [52]. Irradiated Ge target was dissolved in aqua regia under IR lamp. The solution was then evaporated to near dryness and re-dissolved in 3 mL conc. HCl. 30% $H_2O_2$ was added drop wise (100 μL) to oxidize arsenic completely into As(V) [52]. The pH of equilibrating solution was monitored by the pH meter (420A, Thermo Orion, USA), which was calibrated using pH 4, 7 and 10 standard buffer solutions (Hamilton).

### 2.2. Preparation of membrane

The polymerizing solution was prepared by dissolving appropriate amounts of monomer MEP or combination of monomers MEP + AMPS (1:1 mol proportion) along with a cross-linker MBA (5 mol% of monomers) and a UV initiator DMPA (1 wt%) in mix solvent having 1:1 vol of DMF and THF. The host poly(propylene) microporous membranes ($5 \times 5$ cm$^2$ area) were soaked in polymerizing solution for overnight. The excess of polymerizing solution adhering on surfaces of the membranes was removed. The solution filled membranes were sandwiched between two glass plates to prevent any possible loss of solution from the membrane. Care was taken to remove excess grafting solution and air bubbles trapped between the membrane and glass plates. Finally, the sandwiched membranes were exposed to 365 nm UV light in a multilamps photoreactor for a period of 15 min. After exposure in photoreactor, the membranes were washed thoroughly with hot DMF and hot water repeatedly to remove soluble components. The membrane samples were washed till a constant weight of membrane obtained. The membrane samples were equilibrated with well-stirred 100 mL of 0.01 M $FeCl_3$ aqueous solutions having pH 2 for 5 h. Finally, the