



## Separation and determination of arsenic species in water by selective exchange and hybrid resins

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### ABSTRACT

A simple and efficient method for separation and determination of inorganic arsenic (iAs) and organic arsenic (oAs) in drinking, natural and wastewater was developed. If arsenic is present in water prevailing forms are inorganic acids of As(III) and As(V). oAs can be found in traces as monomethylarsenic acid, MMA(V), and dimethylarsenic acid, DMAs(V). Three types of resins: a strong base anion exchange (SBAE) and two hybrid (HY) resins: HY-Fe and HY-AgCl, based on the activity of hydrated iron oxides and a silver chloride were investigated. It was found that the sorption processes (ion exchange, adsorption and chemisorptions) of arsenic species on SBAE (ion exchange) and HY resins depend on pH values of water. The quantitative separation of molecular and ionic forms of iAs and oAs was achieved by SBAE and pH adjustment, the molecular form of As(III) that exists in the water at pH <8.0 was not bonded with SBAE, which was convenient for direct determination of As(III) concentration in the effluent. HY-Fe resin retained all arsenic species except DMAs(V), which makes possible direct measurements of this specie in the effluent. HY-AgCl resin retained all iAs which was convenient for direct determination of oAs species concentration in the effluent. The selective bonding of arsenic species on three types of resins makes possible the development of the procedure for measuring and calculation of all arsenic species in water. In order to determine capacity of resins the preliminary investigations were performed in batch system and fixed bed flow system. Resin capacities were calculated according to breakthrough points in a fixed bed flow system which is the first step in designing of solid phase extraction (SPE) module for arsenic speciation separation and determination. Arsenic adsorption behavior in the presence of impurities showed tolerance with the respect to potential interference of anionic compounds commonly found in natural water. Proposed method was established performing standard procedures: with external standard, certified reference material and standard addition method. Two analytical techniques: the inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectroscopy-hydride generation (AAS-GH) were comparatively applied for the determination of arsenic in all arsenic species in water. ICP-MS detection limit was  $0.2 \mu\text{g L}^{-1}$  and relative standard deviation (RSD) of all arsenic species investigated was between 3.5 and 5.1%.

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## 1. Introduction

### 1.1. Arsenic in water

Arsenic contamination of environment has been reported as a critical issue in many articles which reflects the latest state-of-the-art understanding of the occurrence and behavior of arsenic as a natural and anthropogenic toxic element [1,2]. Depending on the physical, chemical and biogeochemical processes

(such as oxido-reduction, precipitation/solubilisation, adsorption/desorption and microbiological processes) and condition of the environment, various arsenic species can be present in water [3,4]. Water soluble arsenic species existing in natural water are inorganic arsenic (iAs) species as arsenite, As(III) and arsenate, As(V) and organic arsenic (oAs) species as monomethylarsenic acid, MMAs(V) and dimethylarsenic acid, DMAs(V). As(V), MMAs(V) and DMAs(V) are stable in oxidized systems, while As(III) is unstable under oxidizing conditions and is readily oxidized [1]. All acidic species, according to the chemical equilibrium and successive acid dissociation constants ( $\text{pK}_a$ ), have well recognized neutral and ionic forms in water. As(III), having successive acid dissociation constants ( $\text{pK}_a$ ) of 9.2, 12.1 and 13.4, is present as a neutral species in the form of arsenous acid,  $\text{H}_3\text{AsO}_3$ , at pH values less than 8.0.

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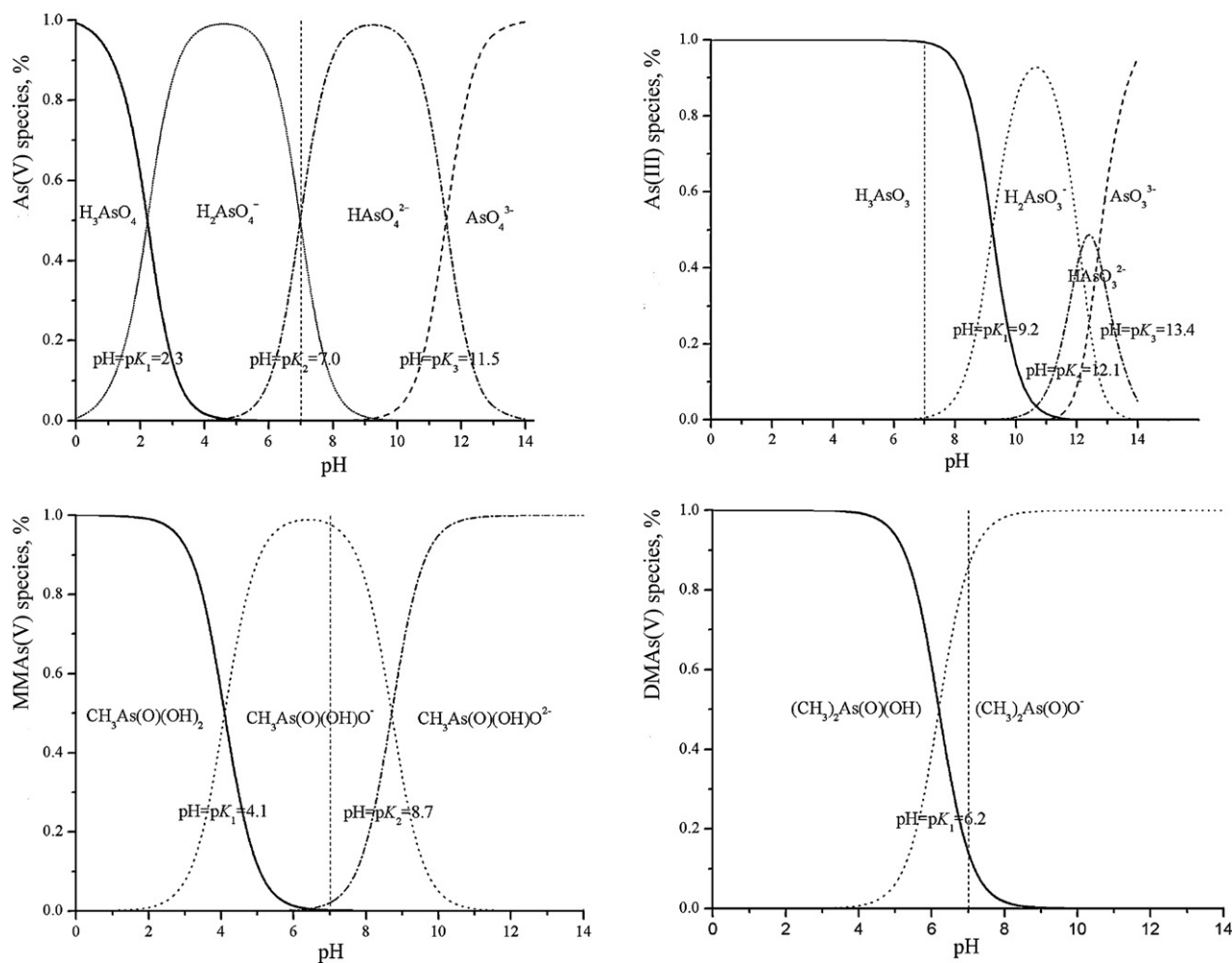


Fig. 1. The distribution of iAs and oAs species as a function of pH values of water.

As(V) has  $pK_a$  values 2.3, 7.0 and 11.5 and it exist mainly as anionic species at wide range of pH. The As(V) exists in neutral water as monovalent or divalent anion ( $H_2AsO_4^-$  and  $HAsO_4^{2-}$ ) [1]. In general, arsenite is normally found in groundwater (assuming anaerobic conditions), while oxidized arsenate is found in surface water (assuming aerobic conditions). MMAs(V) has  $pK_a$  values 4.1 and 8.7 and it exists as a neutral species (pH < 4) or as anionic species (pH > 4). DMAs(V) with a  $pK_a$  value of 6.2 exists as neutral species or even as a cation in acidic medium [5–10]. The distribution of iAs and oAs species as a function of pH value of water is presented in Fig. 1.

EPA proposed a maximum concentration level of  $10 \mu\text{g L}^{-1}$  arsenic for the community water systems (USEPA, 2002). This value is related to the total concentration of arsenic, but it was recognized that arsenic toxicity for human depends strongly on its chemical form. It was estimated that the iAs species are more toxic than the oAs species, As(III) is almost 70 times more toxic than the methylated forms of oAs [MMAs(V) and DMAs(V)] and 10 times more toxic than As(V) [6]. Due to increasingly stringent environmental regulations, selective and accurate measurements of arsenic species are required. Separation and preconcentration of arsenic from water samples was the object of many scientific works. Silica gel bonded with octadecyl functional groups, yeast immobilized on controlled pore glass, activated alumina, immobilized macrocyclic material [5], ion-pairing complex with Pyronine B in the presence of cetyl pyridinium chloride [9], waste materials as sand and iron slag [10] have been employed as selective sorbent material for arsenic. In our previous work [7], a simple procedure for the preliminary

preconcentration and separation of iAs species [As(III) and As(V)] on two resins was developed and proposed. In this work, the procedure was extended to separation and determination of iAs and oAs introducing a new hybrid resin based on active silver ion, which can separate iAs and oAs species. A new hybrid resin was prepared and tested and in generally form, the analytical results are obtained in spiked and real samples. The methodology presented requires very simple sample treatment and it is an alternative to chromatographic techniques.

## 1.2. Methods for the determination of different arsenic species in water

The total concentration of arsenic in drinking water (mostly traces of arsenic, level of  $\mu\text{g L}^{-1}$  or less) can be detected only by sophisticated analytical techniques as inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GF-AAS). For iAs species the hydride generation atomic absorption and fluorescence spectrometry (HG-AAS and HG-AFS) methods are applicable. However, coupled analytical techniques are the most convenient for selective and sensitive determination of arsenic species with essentially uniform qualitative and quantitative response. In many works, nowadays, arsenic species are determined by ICP-MS coupled with various chromatographic methods as ion chromatography (IC) [8–11] or high performance liquid chromatography (HPLC) [12,13]. Parallel investigations were devoted to evaluate some selective sorbents

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