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EFFECTS OF pH AND COMPETING ANIONS ON THE SOLUTION SPECIATION OF ARSENIC BY ION EXCHANGE RESINS

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Introduction

Anion exchange resins (AER) can be used to differentiate As species. This ability is due to the fact that As(V) is theoretically a negatively charged species between the pH values 4 and 10 (as $H_2AsO_4^-$ or $HAsO_4^{2-}$) while As(III) exists predominantly as uncharged species (H_3AsO_3 and $HAsO_2$)[1]. Thus, the AER retains charged As(V) species while allowing uncharged As(III) species to pass through. As(V) is calculated by subtracting the concentration of As(III) from the total As concentration in the sample. The vast majority of research concerning the speciation of As using resins has focused on freshwater. Ficklin[2] employed Dowex 1X8 resin (100-200 mesh, acetate form) for differentiation of As(V) and As(III). Edwards et al.[3] used a slightly modified procedure based on the procedure by Ficklin for use in the field. This study also examined interference from SO_4^{2-} due to sample preservation with H_2SO_4. Several researchers have also included separation of monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) in addition to the inorganic species. Henry and Thorpe[4] employed combina- tions of cation and anion exchange resins to separate As species for analysis by differential pulse polarography. Yalcin and Le[5] investigated a wide range of solid phase extraction cartridges for speciation of As(III), As(V), MMA, and DMA.

Many other researchers have presented schemes for the separation of As(III), As(V), MMA, and DMA[6-9]. These methods are based on separation of the As species by loading the sample onto cation and/or anion exchange resins in conjunction with elution by various chemical solutions.

Inorganic As species dominate the overall As chemistry in soils[10] and in surface and ground waters[11]. This study focuses on speciation of inorganic As. In assessing resins contained in commercially available anion exchange cartridges, emphasis was placed on ease-of-use. It is desirable to employ a cartridge that is able to work as-is, without pre-preparation or conversion of functional groups to some other form. The methodolo- gy should be simple and rapid to facilitate work in the field as well as in the laboratory. Lastly, the research presented here assesses the efficacy of cartridges for As speciation in a 0.01 M $NaNO_3$ background electrolyte (BG) which is meant to mimic the solution ionic strength of soils and sediments. The objectives of this work are to: 1) Identify a cartridge and optimal conditions for As speciation 2) Assess the impact of anions commonly found in environmental samples on the speciation process 3) Calculate loading rates for the cartridges.

Methods and Materials

Two cartridges containing different AERs were selected for examination based on results from previous work[5]. The syringe-shaped cartridge contained LC-SAX, a silica-based AER with quaternary amine functional groups (Supelco, Bellefonte, PA Cat.# 57017). The cylindrical-shaped cartridge contained QMA, a silica-based AER (Waters Corporation, Milford, MA Cat.#WAT020545). All standards, spikes, and sam- ples were made in 0.01 M $NaNO_3$ BG. Stock solutions (4000 mg/L) of SO_4^{2-}, HPO_4^{2}, Cl^-, and HCO_3^- were made in 18 mohm DI H_2O. As(V) and As(III) stock solutions (10,000 mg/L) were made in 0.01 M $NaNO_3$ BG. All solutions were analyzed by inductively coupled argon plasma spectrometry (ICAP).

Retention of As(III) was examined first by passing 0.1 mg/L solutions through the cartridges at a rate of 5mL/min (approximately 2 drops/sec). Preliminary results indicated that there were differences (in both cartridges) between pre-wetting the cartridge with the BG and loading the solution on a dry cartridge. Both scenarios were tested. Initial As(III) concentrations were compared with concentrations after passing through the cartridge and As(III) retention was assessed. Based on these results, the LC-SAX cartridge was eliminated from further study.

The QMA cartridges were chosen for further testing on As(V) breakthrough. Appropriate amounts of the stock solutions were used to create solutions in BG containing 0.3 mg/L As(V) with and without individual competing anions. Blank BG was also included in the experiment. The sequential order of samples was determined by a random numbers table[12]. The final concentrations of competing anions were as follows: 1.0 mM (35 mg/L) SO_4^{2-}, 0.1 mM (10 mg/L) HPO_4^{2-}, 1.0 mM (35 mg/L) Cl^-, and 0.1 mM (10 mg/L) HCO_3^-. These values were chosen as being representative of concentrations found in a "typical" soil pore water[13]. Runs in As(V) spiked BG provide information on interference from NO_3^- (0.01 M or

620 mg/L). The solutions were then adjusted to the appropriate pH (4, 6, or 8) with 0.1 M NaOH or 0.1 M HNO_3 and brought to a final volume of 100 mL with BG. The solutions were then loaded onto the cartridges at a rate of 5 mL/min (which roughly equates to 2 drops/sec) by a peristaltic pump (Ismatec #78017-10, Zurich, Switzerland). The solution passing through the cartridges was caught by a fraction collector (Spectrachrom CF-1, Spectrum Chromatography, Houston, TX) set at 1 tube/min. Each tube containing 5 mL of solution was analyzed for pH and then acidified by adding 10 mL of concentrated HNO_3. All samples were analyzed by inductively coupled argon plasma spectrometry (ICAP). All solutions were run in duplicate. Breakthrough curves were calculated for each solution and compared graphically to identify differences to pH and/or competing anions. Five Matrix (BG) spikes were passed through the cartridges containing 50µg/L each of As(III) and As(V) and method detection limits (MDL) were calculated.

Results and Discussion

Figure 1 shows the comparisons of both the QMA and LC-SAX cartridges after passing As(III) through pre-wetted and dry columns (n=5 for each bar). As(III) retention was greatest on the LC-SAX cartridges under these conditions. These preliminary results also indicated that the QMA cartridge performed better without a pre-wetting step with BG. After establishing conditions for minimal retention of As(III), the QMA cartridges were assessed for As(V) breakthrough. Figure 2 shows the effects of pH on As retention by the QMA cartridges.

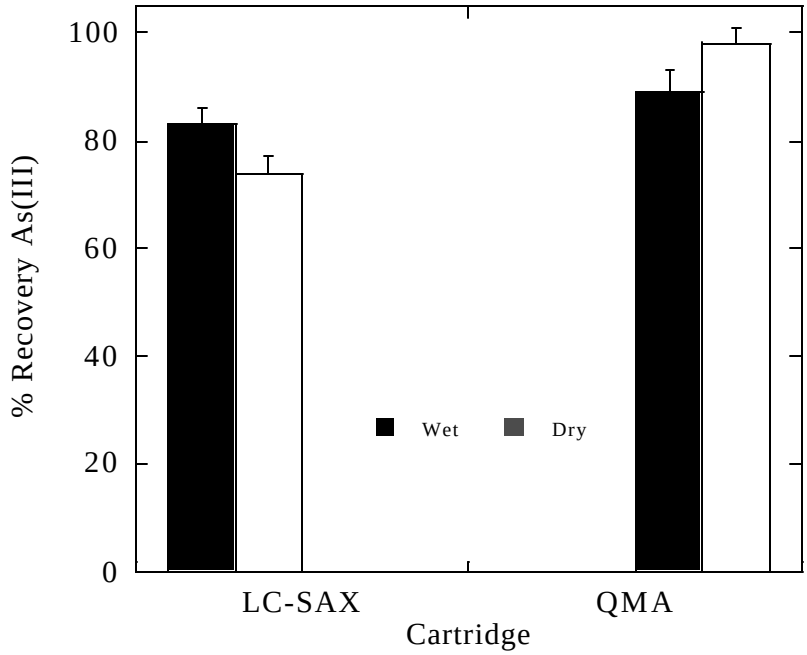

Figure 1. Recovery of As(III) by AER cartridges and effects of prewetting (n=5 for each).

Breakthrough occurs, conservatively, at 20 mL. Thus, in the presence of 0.01 M (620mg/L) NO_3^-, the QMA cartridge has the ability to retain 0.006 mg As(V). This correlates to a 5 mL sample with a concentration of 1.2 mg/L. An interesting effect is seen at pH 4. Note that af-

ter breakthrough the data suggest that As(V) is flushed from the ion-exchange media. A similar phenomenon was noted for SO_4^- and as noted in that research, this could have consequences for water treatment operations employing ion exchange media to treat for As.

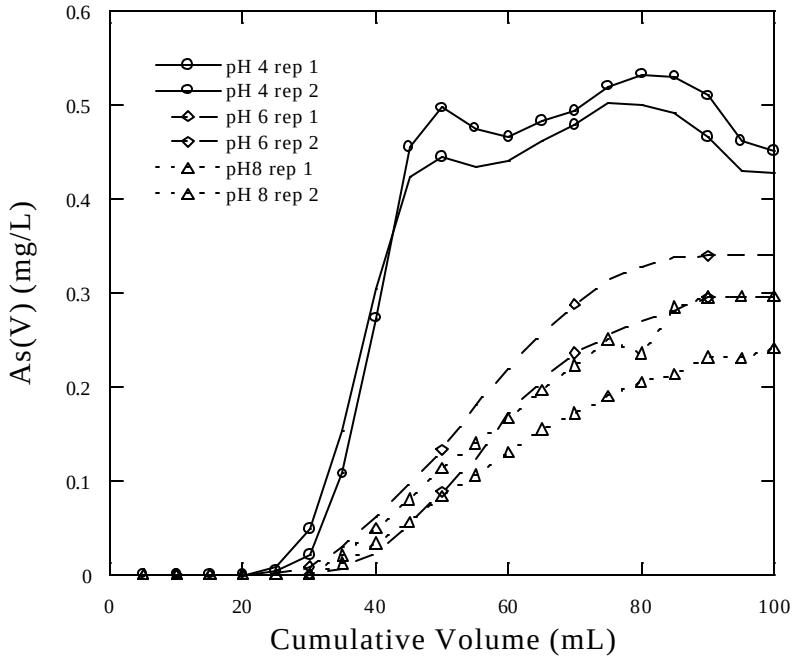

Figure 2. Effects of pH on As(V) breakthrough

At all pH values, at the anion concentrations examined, only HPO_4^{2-} had an effect on the breakthrough of As(V) as shown in figure 3. In the worse case, at pH 8, the As(V) breakthrough was detected in the 15 mL cumulative volume fraction. Thus we conserva- tively estimate the loading rate for As(V) at 10 mL which corresponds to a total As mass loading of 0.003 mg. Thus, a five mL sample containing 0.6 mg/L As could be safely speciated under these conditions.

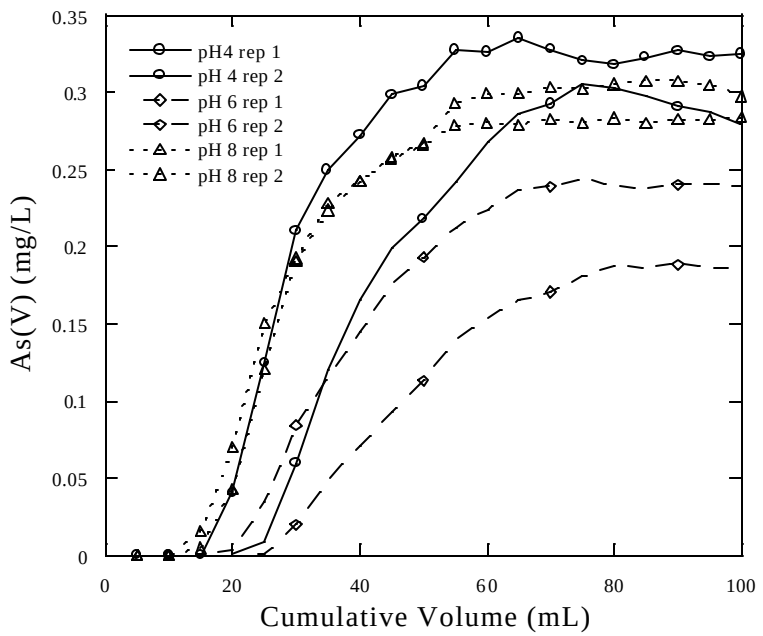

Figure 3. Effects of HPO_4^{2-} on As(V) breakthrough.

Lastly, MDLs were calculated to be 0.006 mg/L for As(V) and 0.005 mg/L for As(III). The spike concentration:MDL ratio was approximately 9 for each As species. In future work the spike concentration will be lowered and MDLs recalculated until a spike concentration:MDL ratio of less than 5 is achieved.

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