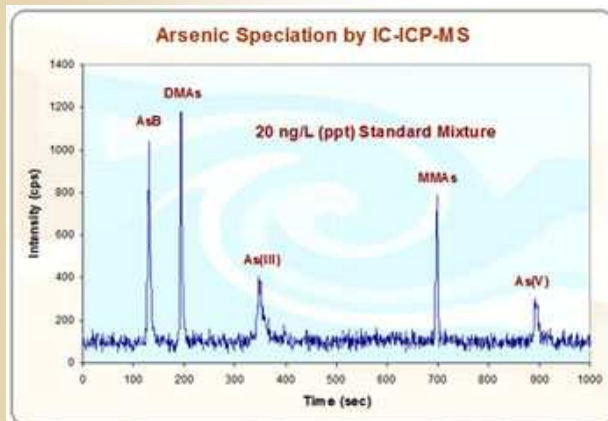




Arsenic Speciation in Soil and Sediments

Arsenic speciation analysis of soil and sediment can provide insightful information associated with risk assessment, fate and transport, and chemical equilibria within the substrate. The unparalleled degree of variability associated with soil and sediment matrices makes it one of the most technically difficult materials to extract representative data for arsenic speciation analysis. Applied Speciation and Consulting, LLC (ASC) understands the complexity of soil and sediment systems and applies appropriate quality control measures and analytical method necessary for quantification.



The sorption of various arsenic species onto Fe, Mn, and Al have been well documented throughout literature. Due to the ubiquitous nature of Fe, Mn and Al, their concentrations and molecular structures can vary significantly impacting interactions with the different arsenic species. The pH and Eh of the substrate must also be taken into consideration as those parameters drive the equilibrium of the As, Fe, Mn, and Al species as well as their degree of protonation. The complexity of soil and sediment matrices cannot be understated; therefore, understanding the interactions and experience involved with different extraction methods becomes of paramount importance when quantifying arsenic species.

Extraction procedures must meet three qualifiers: (1) the extracting solution must solubilize all forms of arsenic, (2) the conditions of the extraction must not induce reduction of native arsenate to arsenite, and (3) the method must not cause oxidation of native arsenite contained in the sample to arsenate. Due to their chemical properties arsenite and arsenate are the most efficiently adsorbed by the sample matrix. Many arsenic extraction procedures apply ligand exchange to reduce readsorption which is a function of the extraction solution. Often these procedures involve the application of phosphate (PO_4^{3-}) at different pH values. The similar molecular structures and chemical properties of phosphate and arsenate allow for competitive binding resulting in higher extraction efficiencies and a reduction in readsorption.

Multiple extraction procedures are applied as the extraction efficiencies for the different arsenic species are pH dependant. The ability to alter the extraction solutions to optimize the specificity for target arsenic species is limited; therefore, speciation must be performed on every extract. The extraction efficiencies can often be correlated with the different components of the soil or sediment. An excellent example is the different sorption efficiencies for arsenite and arsenate onto goethite and amorphous Fe. Low recoveries of arsenite using phosphate at pH ~3 may suggest that goethite is not the major Fe species; rather, amorphous Fe which may have resulted from deposition of precipitated Fe is the controlling factor. This would

Highlights

Research Level Analysis with High Quality QA/QC

Confirmation of Extraction Efficiencies with Speciation Analysis

Free Consultation for Sampling Protocols

Experienced and Knowledgeable Scientists and Project Managers

suggest that the matrix may act as a viable sink for arsenite inferring the arsenic contaminated site may have less impact on the local aquifer than initially expected. Unfortunately, assumptions are often made toward the specificity of the extraction solutions which is represented by only performing a total arsenic analysis of the extract.

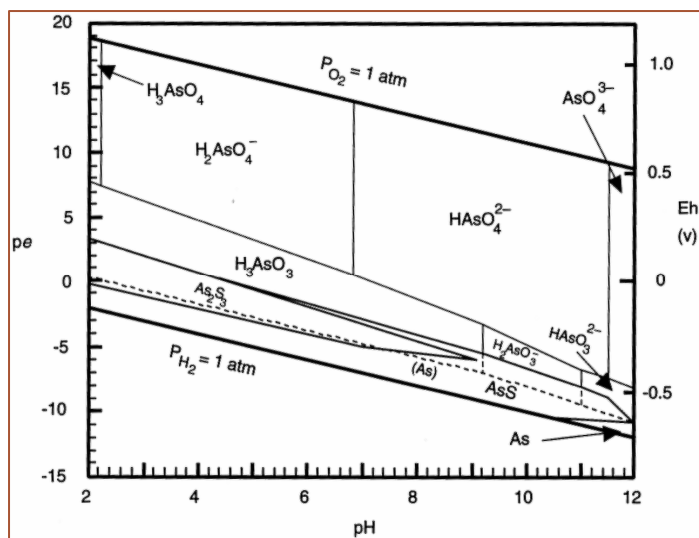


Other extraction procedures may facilitate hydroxide, sulfate, chloride, or other anionic molecules. While these options may result in consistent high extraction efficiencies, meeting the

first qualifier as previously mentioned, they often result in speciation conversion which cannot be accounted for unless speciation analysis is performed on the extracts. This leads to the importance of meeting the three main qualifiers for identifying viable extraction procedures.

In addition to speciating the sample extracts, equilibrium shifts must also be monitored in the form of matrix spikes and laboratory control samples for every target species. Due to the variability inherent with soil and sediment matrices the application of a certified reference material would not be representative of sound scientific practices; therefore, the best representation of the method efficiency are matrix spikes. Although matrix spikes are artificial representations of the extraction efficiencies they do identify issues with readsorption and species conversion. Other standard quality control measures (e.g. preparation blanks, laboratory control samples, matrix duplicates, etc.) must also be employed to identify accuracy and precision associated with the applied methods. The limitations of some analytical methods for arsenic speciation may hinder the applicability of the different quality control parameters; therefore, the importance of analytical method selection also contributes to the confidence in generated results.

Applied Speciation and Consulting applies ion chromatography inductively coupled plasma - mass spectrometry (IC-ICP-MS), the most robust and widely accepted method for speciation analysis of arsenic and other metalloids. Sample extracts can be introduced directly into an ion exchange column which separates the different metalloid species according to their interactions with the column packing material. The eluting species are then introduced into an ICP-MS serving as a very sensitive elemental detector. In addition to matching retention times of known standards for species identification ancillary elements can also be monitored for confirmational purposes. Correlating molar ratios of arsenic and other elements can also facilitate the identification of new arsenic species which may assist in identifying transitional species for modeling purposes.



Our experience allows us to choose different ion exchange columns and eluants for different matrices to provide better resolution of target species. More importantly, for higher profile cases, secondary confirmation using different columns and eluants can provide indisputable data when necessary.



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