

# XAS ANALYSIS OF ARSENIC COMPOUNDS IN TERRESTRIAL PLANTS



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## Background

Arsenic (As) is a naturally occurring element often found complexed with sulfide minerals, or released into the environment through anthropogenic activities such as mining, industrial and agricultural processes<sup>1,2</sup>. Arsenic is perhaps best known for its toxicity; however, arsenic toxicity varies depending on its chemical form (Fig. 2). Commonly used methods for detecting arsenic compounds such as High Performance Liquid Chromatography - Atomic Absorption Spectrometry (HPLC-AAS) and HPLC - Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS), involve both physical and chemical manipulation of the sample. This sample manipulation may alter the chemical form of the arsenic being studied. X-ray Absorption Spectroscopy (XAS) provides an alternate means of sample analysis which may minimize this concern. To fully understand the risk posed by arsenic contaminated soil to human and wildlife populations, it is important to understand how arsenic is taken up by plants and subsequently transformed<sup>3</sup>.



Fig. 1: Experiments utilized soils with high concentrations of arsenic collected from Yellowknife, Northwest Territories, Canada. This location has elevated levels of arsenic both as a result of natural geology, and anthropogenic inputs from a once thriving gold mining industry.

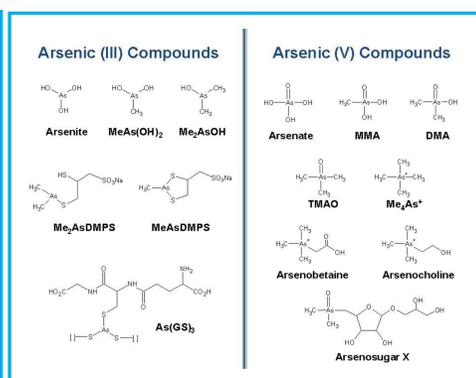


Fig. 2: Structures of the 14 arsenic standards selected for analysis  
 MMA = monomethylarsonic acid  
 DMA = dimethylarsinic acid  
 TMAO = trimethylethylarsine oxide

## Research Interests

Our research group is interested in assessing the extent to which X-ray Absorption Spectroscopy (XAS) can be used in the determination of the chemical forms of arsenic in the terrestrial environment, focusing on plants. To date we have used XAS to:

1. Establish a standards library of biologically important arsenic compounds.
2. Examine arsenic compounds in the roots, stems and leaves of radishes grown in arsenic contaminated soil from Yellowknife in the Northwest Territories, Canada (Fig. 1).

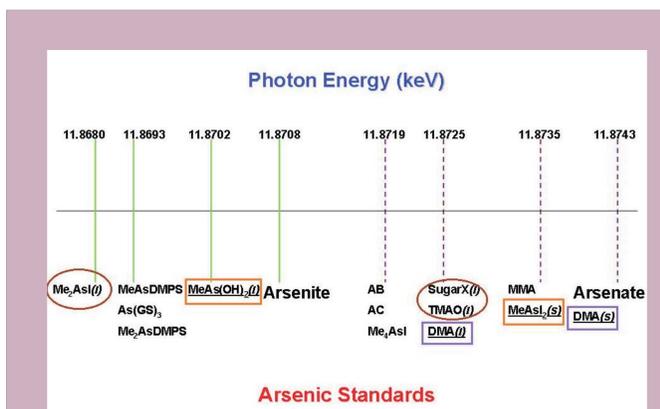


Fig. 3: Representation of edge position energies (keV) for arsenic standards. Standards labeled (s) = solid, (l) = solution, unlabeled standards represent solid and solution forms. Underlined standards had different edge energies for liquid and solid forms. Dotted vertical lines represent pentavalent species (except MeAs<sub>3</sub>(s)), solid vertical lines represent trivalent species. (AB = arsenobetaine; AC = Arsenocholine)

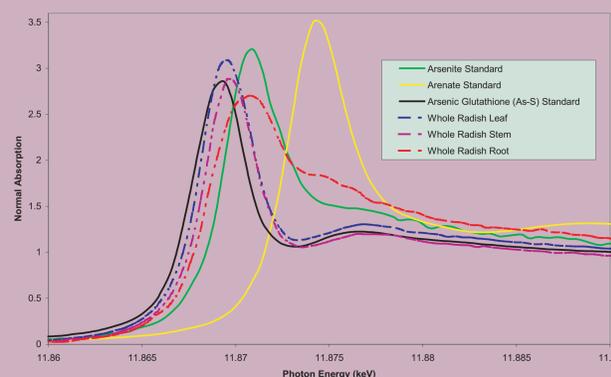


Fig. 4: Comparison of XANES spectra for three known arsenic standards, to XANES spectra from root, stem and leaf of radish samples, for identification of arsenic compounds within radishes.

## Other Interesting Findings

XAS was used to confirm the presence of arsenobetaine in terrestrial Yellowknife fungus. Arsenobetaine is commonly found in marine environments and its identification in terrestrial samples is relatively recent.

XAS was also used to examine residual arsenic compounds produced in laboratory bioreactors. These bioreactors were modelled after a system in B.C. which is being used successfully to remove arsenic from contaminated smelter effluent.

## Protocol

XAS absorption spectra were collected using the PNC-CAT bending magnet beamline with a silicon (III) double-crystal monochromator, rhodium coated harmonic rejection mirror, and either a single-element solid state Canberra detector or an argon filled ionization detector. Fourteen arsenic standards were selected based on their availability and biological significance (Fig. 2). Standards were analyzed as solids and solutions, while radish samples were analyzed as whole and ground samples.

## Results

As seen in Figure 3, edge positions from XANES spectra can be used to identify many biologically important arsenic compounds. These energies were used in a novel study to identify arsenic compounds within the roots, stems and leaves of radishes (Fig. 4). An arsenic sulfur compound was observed as the main arsenic species in whole samples of radish stems and leaves (Fig. 5), which supports the recent hypothesis that arsenic is transported throughout plants in this form<sup>4</sup>. In addition XANES data may be valuable in distinguishing arsenic compounds in the solid state from those in solution.



Radishes growing in arsenic contaminated soil after 7 days (top left); 18 days (top right); 28 days (bottom).

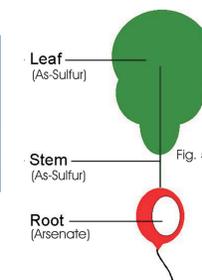


Fig. 5: Major arsenic compounds in whole radish samples.

## Future Objectives

1. Search for a link between plant structure and arsenic compartmentalization using a microprobe to map arsenic compound location on a smaller scale.
2. Explore XAS as a tool to validate more traditional analysis methods for the identification of arsenic species.
3. Use XAS to examine Yellowknife samples containing arsenic compounds that remain unidentified, or unexplained, after laboratory analysis with more traditional methods.

### References

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