

Arsenic in the Environment: XAS Analysis of Arsenic Compounds in Terrestrial Plants

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Introduction

Arsenic (As) is a naturally occurring element that is best recognized as a component of toxic, even carcinogenic, compounds. A large number of As compounds exist in the environment, and their toxicity varies with their chemical form (species). From an environmental perspective, it is important to know the As species present in a sample in order to properly evaluate the associated risk.

As speciation analysis traditionally involves the separation of compounds (e.g., high pressure liquid chromatography) followed by detection (e.g., atomic absorption spectroscopy or inductively coupled plasma mass spectrometry). However, As must first be extracted from solid samples (e.g., soils, tissues). Extraction involves both physical and chemical manipulation that may alter the form of the As being studied. X-ray absorption spectroscopy (XAS) is a less obtrusive means of speciation analysis that minimizes the possibility of such transformations.

Methods and Materials

XAS absorption spectra were collected by using the PNC-CAT bending magnet beamline at the APS 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 As standards were selected on the basis of their availability and biological significance. These standards were analyzed in solid and liquid states. Solid samples were sealed into an aluminum holder with Kapton[®] tape. They included bioreactor solids as well as whole, ground, and extracted (by methanol-water or gastric fluid method), leaves, roots, and stems of radishes. Both extraction methods recover the biologically available arsenic, but gastric fluid extractions more accurately simulate conditions in the mammalian digestive tract.

Results and Discussion

To fully understand the risk posed by As-contaminated soil to human and wildlife populations, it is important to understand how As is taken up by plants and subsequently transformed [1]. XAS has been used to identify As compounds in the roots, stems, and leaves

of radish (*Raphanus sativus*) plants grown both hydroponically and in contaminated soil collected from Yellowknife in the Northwest Territories. XAS was also used to confirm the presence of arsenobetaine in terrestrial Yellowknife fungus. (Arsenobetaine is commonly found in marine environments, its identification in terrestrial samples is relatively recent.)

XAS Characterization of Standards

XANES analyses of 13 biologically important As compounds (Fig. 1) were conducted to provide standards for later use. The stability (within the beam and over time, Fig. 2) of As species in liquid and solid states was examined. With few exceptions, no degradation of standards was observed within the beam or over time, and most liquid and solid states of a single standard shared the same white line.

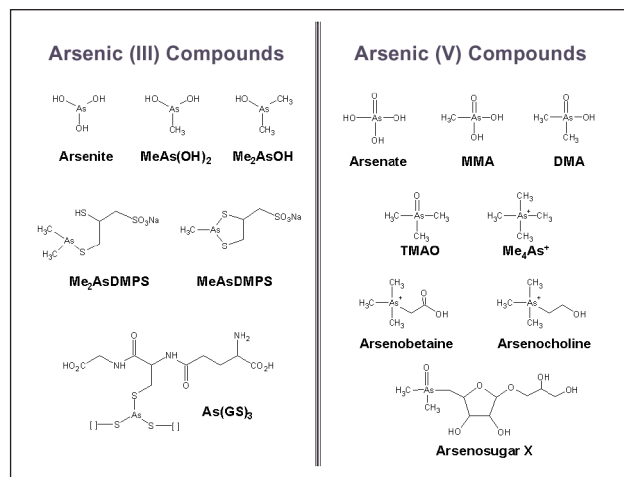


FIG. 1. Structures of the 14 arsenic standards selected for analysis. (MMA = monomethylarsonic acid, DMA = dimethylarsinic acid, and TMAO = trimethylethylarsine oxide.)

Radish Results

X-ray absorption near-edge structure (XANES) spectra from biologically important As compounds were used in a novel study to identify As species within the roots, stems, and leaves of radishes (Fig. 3).

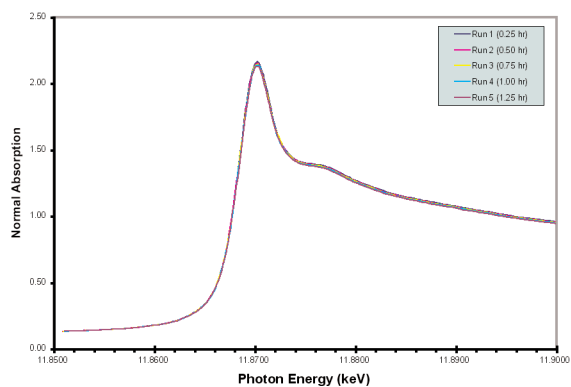


FIG. 2. Extended x-ray analysis fine structure (EXAFS) analysis demonstrates the stability of 1000 ppm MMA(III) over a period of 1.5 hours.

- Root = As(III)
- Stem = arsenic-sulfur
- Leaf = As(III)/As-sulfur
- Soil = As(V)

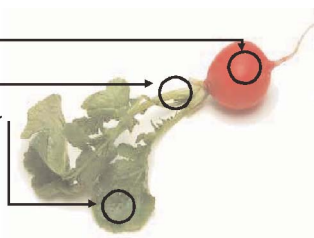


FIG. 3. Arsenic in *Raphanus sativus*.

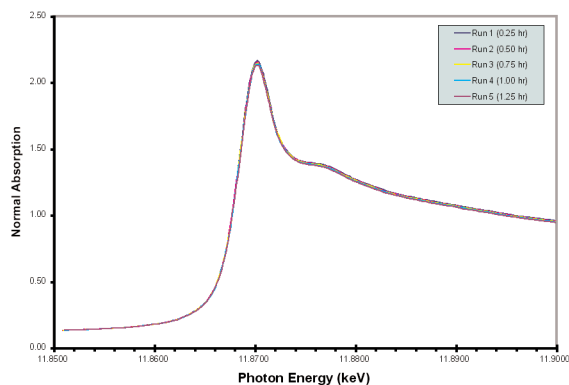


FIG. 4. Comparison of whole radish leaves with wet/dry ground samples and methanol-water (MW)/gastric fluid extraction (GFE) residues. As(V) appeared to be present only in MW samples, whereas As(III) was present in wet, dry, and MW samples. GFE residues appeared to be most similar to whole leaves; both contained an As-S compound.

Arsenate [As(V)] from contaminated soils may be transported into the radish root, where it is converted to arsenite [As(III)]. An As(III)-sulfur compound, not identified with more traditional techniques, was observed to be the main As species in whole samples of radish stems. This finding supports the recent hypothesis that As is transported throughout plants in this form [2]. Ground radish leaves contained predominantly As(III); however, an As-sulfur(s) compound was later identified in whole leaves, suggesting that As(III)-S compounds may have been transformed to As(III) during grinding. The main As species in leaf residues from gastric fluid extraction was an As-S compound, while methanol-water As residue contained a combination of As(III) and As(V) (Fig. 4). In the latter case, evaporation of methanol from residues may have dried the samples and promoted oxidation of the As that was present.

Future projects will incorporate microprobe mapping and microXANES in the search for a link between plant structure and As compartmentalization. Terrestrial plants native to contaminated sites in Yellowknife and Ontario will be examined, and XAS will be used to investigate samples containing As compounds that were unidentified after analysis with more common techniques. As speciation information collected by using XAS complements and contributes to results obtained by more traditional analytical methods, and XAS is a valuable tool for the study of As in the environment.

Acknowledgments

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References

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