

X-RAY ABSORPTION SPECTROSCOPY AS A PROBE OF ELEMENTAL SPECIATION

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ABSTRACT: An effective bioremediation strategy for metals and metalloids must take the chemical state of the contaminants into account. The oxidation state and local atomic environment of contaminants critically affect such factors as their mobility, reactivity and toxicity, and hence the remediation strategy which might be applied. Since contamination exists in diverse environments, it is very likely that the chemical state of the contaminant will be site specific. X-ray absorption spectroscopy provides a unique tool for determining the chemical form of contaminants in most matrices with minimal pretreatment of the sample.

INTRODUCTION

There are increasing regulatory and public pressures for remediating contamination at industrial, agricultural and municipal sites. While organic and nitrogen-containing contaminants can be mineralized to harmless gaseous species under favorable conditions, most other elements must be removed by solubilization and extraction. Both biological and non-biological treatments may be able to achieve this goal, and the chemical nature of the contaminants at the site will determine the most effective remediation strategy. There are many approaches to determining this speciation, but most require extensive chemical treatment, and in many cases only some of the potential forms of a contaminant can be detected.

X-ray absorption spectroscopy is unique in detecting all forms of any element in any physical state (gaseous, liquid or solid). Furthermore, there are no unexpected interferences from chemically similar species. Providing concentrations are above a few ppm, there is typically no need to concentrate the sample and no other pretreatment is required for the speciation.

Since X-ray absorption spectroscopy detects all atoms of any element under study, the spectrum of a sample is the sum of the spectra of all the species of this atom in the sample. In favorable cases, curve fitting can be used to deconvolute the spectrum into its component spectra, and thereby allow an estimation of the species present (George et al., 1991). Of course this requires that a library of spectra of model compounds is available, and that one has some intuition as to what sorts of compounds are likely to be in a sample. Curve fitting is obviously simplest when the potential components of the mixture have significantly different spectra. Here we will focus on three examples where this is true.

X-ray absorption spectroscopy. X-ray absorption spectroscopy requires a tunable source of X-rays, and typically only synchrotron light sources are bright enough that they can serve this purpose. The X-ray absorption spectrum of an element may be considered in two parts. The spectrum of the X-ray absorption edge contains information about the redox state, symmetry and chemical nature of ligands to the element. The spectrum beyond the edge, often called the extended X-ray absorption fine structure (EXAFS), contains information that can be used to obtain very precise estimates of the bond lengths of ligands to the atom. It should be noted that while it is possible to determine absolute concentrations of species using X-ray spectroscopy, this is cumbersome, and such information is more simply obtained by other techniques, such as atomic absorption spectrometry.

All the spectra reported here were collected at the Stanford Synchrotron Radiation Laboratory. In all cases the spectra have been normalized to equivalent amounts of the element under consideration.

Chromium. Chromium is present at many contaminated sites as a relic of smelting, industrial processing and waste disposal. There is particular concern that Cr(VI) is more mobile and more hazardous than Cr(III), and regulatory limits are typically lower for Cr(VI) than Cr(III). There are several ways of estimating the amount of chromium in a sample, and several approaches to determining how much of the chromium is in the +6 redox state. X-ray absorption spectroscopy is a particularly elegant way of achieving this goal. As shown in Figure 1, the K-absorption edge spectrum of a compound containing Cr(VI) tetrahedrally

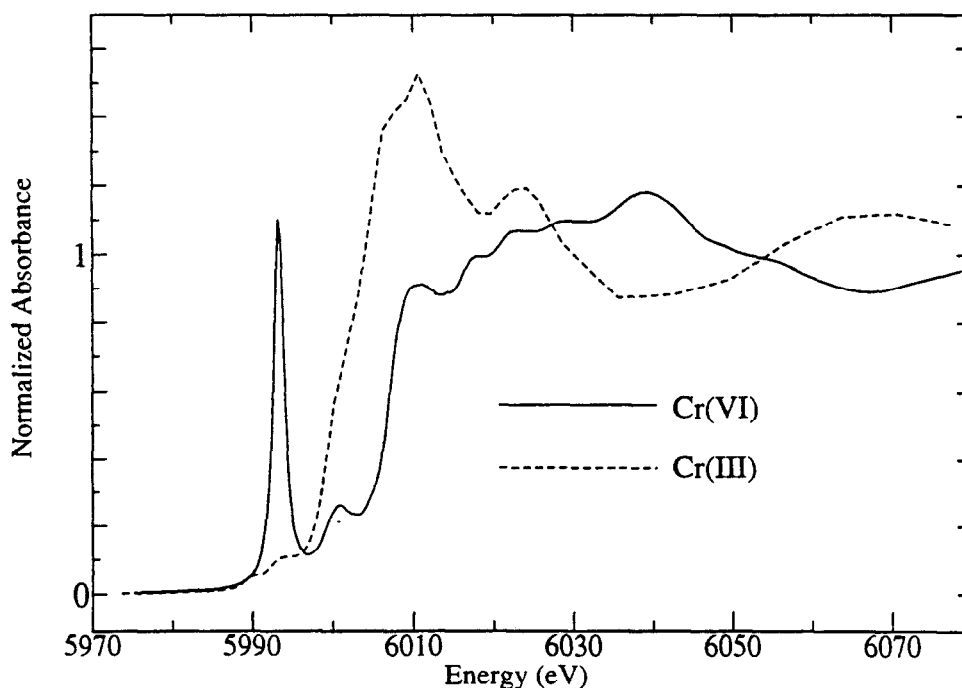


Figure 1. Chromium K-edge X-ray absorption spectra of representative compounds containing Cr(VI) [K_2CrO_4] and Cr(III) [Cr_2O_3].

coordinated by oxygen has a very distinctive sharp absorption feature before the edge, while the Cr(III) compound, which has octahedral oxygen coordination, lacks this feature. The peak is a formally dipole forbidden $1s \rightarrow 3d$ transition, which gains significant intensity in noncentrosymmetric atomic symmetries (such as tetrahedral Cr(VI)) from admixing with unoccupied 4p levels in the metal. Under favorable conditions it should thus be possible to detect a few percent Cr(VI) in a sample containing Cr(III) with no chemical pretreatment.

To date, most remediation options for chromium contaminated soil have involved removal to a secure landfill, or capping with enough clean soil that the contamination is thought to be effectively removed from the biosphere. Chromium is not known to play a vital role in microbial metabolism, but there is a potential for exploiting microbial reduction of Cr(VI) to Cr(III), both in solid and liquid matrices. The generation of sulfide by sulfate-reducing bacteria, and the reduction of Cr(VI) to Cr(III) by this sulfide is one such approach (Fude et al., 1994). The availability of a tool to monitor the level of Cr(VI) in solid matrices may prove to be an important part of validating this approach.

Selenium. Selenium is receiving considerable attention in light of the problems found in the disposal of agricultural drainage water in the Central Valley of California. Selenium is an essential element for many organisms, but higher amounts are toxic. Different forms of the element have radically different solubilities and bioavailabilities, and the need for remediation, and the options available, will depend on the selenium species present. Figure 2 shows, as an example, that the spectra of the two oxyanions selenate and selenite are very different, and are also very different from that of the elemental form. The shift of the edge to higher energy as the Se redox state increases is due to a decrease in shielding of the core 1s electrons as valence electrons are removed. The peak on top of the edge (traditionally called the "white line") is due to dipole-allowed $1s \rightarrow 4p$ transitions and increases in intensity as the number of 4p vacancies increases.

The spectra of Figure 2, together with those of other candidate species, have allowed the determination of their levels in samples collected from the Kesterson site in the Central Valley (Pickering et al., 1995). While there are other technologies for speciating selenium, most require that the element be present in a soluble form; X-ray absorption spectroscopy is able to determine selenium speciation in both solids and in solution.

To date, remediation options for contaminated soils have involved either covering with sufficient clean soil that the contamination is thought to be effectively removed from the biosphere, or removal to a secure landfill. More recent efforts involve potential biological treatments where the oxyanions are reduced by microbial metabolism to the elemental form (Oremland et al., 1994). This may provide a technology for removing insoluble elemental selenium from water, and for immobilizing selenium in soils. The availability of a tool to determine the speciation of selenium in solid matrices may prove to be an important part of validating this approach.

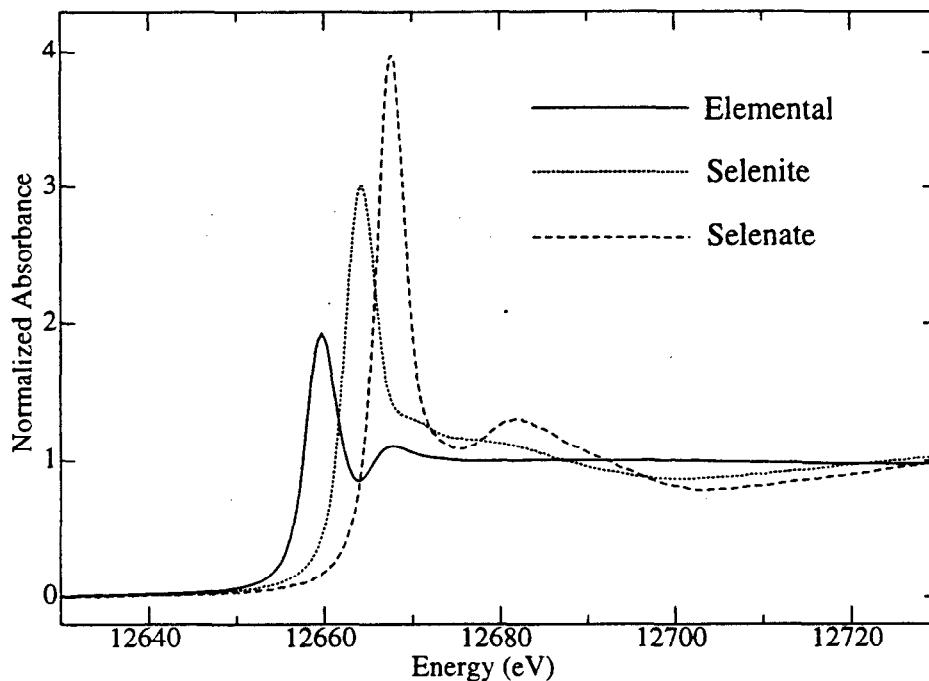


Figure 2. Selenium K-edge X-ray absorption spectra of elemental selenium (red, α -form), aqueous selenite ($[\text{SeO}_3]^{2-}$) and aqueous selenate ($[\text{SeO}_4]^{2-}$).

Cadmium. Cadmium is a notorious heavy metal present at a variety of smelting, industrial processing and waste disposal sites. It has no known vital biological role, but is of concern as a renal toxin and potential carcinogen. While cadmium ions can be removed from waste water streams by chemical treatments, remediation options for contaminated soils have to date involved removal to a secure landfill, or capping with enough clean soil that the contamination is thought to be effectively removed from the biosphere. More recently it has been suggested that certain plants may be able to accumulate cadmium, either on or in their roots, in which case they may provide an option for remediating water, or into their leaves and above-ground biomass. This might be useful for remediating contaminated soils.

X-ray absorption spectroscopy again provides a unique tool for investigating these options. Figure 3 shows an example of the phenomenon that compounds with cadmium-sulfur ligands have distinctly different spectra from those containing cadmium-oxygen ligands. Using this approach, we have been able to demonstrate that *Brassica juncea*, a mustard, accumulates cadmium in roots and leaves as a complex with sulfur ligands, most probably as a phytochelatin complex, but transports cadmium from the roots to the leaves in the xylem sap as a complex with oxygen or nitrogen ligands, perhaps complexed to organic acids (Salt et al., 1995).

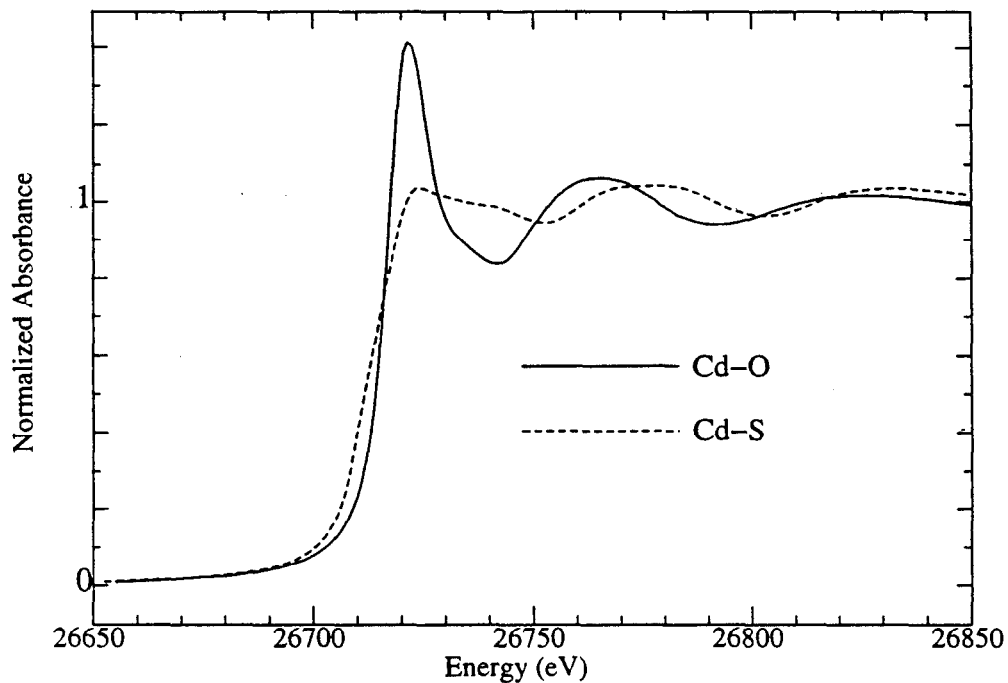


Figure 3. Cadmium K-edge X-ray absorption spectra of compounds containing cadmium-sulfur [CdS] and cadmium-oxygen [aqueous $\text{Cd}(\text{NO}_3)_2$] ligands.

SUMMARY

X-ray absorption spectroscopy provides a unique tool for studying the chemical nature of contaminant metals and metalloids in the environment.

- Unlike most other analytical tools, it detects all forms of the element under study, and can do so in solids, liquids and gases.
- In many cases, the absorption edge spectrum of different compounds is sufficiently distinctive that the approximate composition of simple mixtures can be determined by spectral fitting. Of course this requires a knowledge of the spectra of likely component species, and some intuition to begin the process with likely species.
- Detection limits depend on several factors, but samples with contaminants at the ppm level are usually amenable to characterization.
- The spectroscopy is element specific, and while there are rare instances where the X-ray absorption spectrum of one element interferes with the analysis of another, this is a well understood phenomenon, and the unwitting misidentification of an element need never occur.
- Extended X-ray absorption fine structure (EXAFS), while not addressed here, provides an additional avenue for the identification of chemical species in environmental samples (Manceau et al., 1996).

There is still much to be done to develop X-ray absorption spectroscopy for studying environmental samples, but as it is used as part of analytical protocols in

remediation research and validation, we expect that it will become an important and robust tool with broad applicability.

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