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Survey of Chemical Speciation of Trace Elements
Using Synchrotron Radiation

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Survey of Chemical Speciation of Trace Elements
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Running Head: Chemical Speciation of Trace Elements

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ABSTRACT

Information concerning the chemical state of trace elements in biological systems generally has not been available. Such information for toxic elements and metals in metalloproteins could prove extremely valuable in the elucidation of their metabolism and other biological processes. The shielding of core electrons by binding electrons affect the energy required for creating inner-shell holes. Furthermore, the molecular binding and the symmetry of the local environment of an atom affect the absorption spectrum in the neighborhood of the absorption edge. X-ray absorption near-edge structure (XANES) using synchrotron radiation excitation can be used to provide chemical speciation information for trace elements at concentrations as low as 10 ppm. The structure and position of the absorption curve in the region of an edge can yield vital data about the local structure and oxidation state of the trace element in question. Data are most easily interpreted by comparing the observed edge structure and position with those of model compounds of the element covering the entire range of possible oxidation states. Examples of such analyses will be reviewed.

Index Entries

synchrotron radiation

x-ray fluorescence

absorption edge spectroscopy

chemical speciation

XANES

EXAFS

INTRODUCTION

X-ray spectroscopy has long been used to speciate chemical systems. The narrow energy resolution of crystal spectrometers has been used to determine chemical shifts in x-ray fluorescence originating in K-, L- and M-shell excitation of elements. Chemical information has also been determined by scanning the energy through the absorption edge of an element using the bremsstrahlung continuum spectrum of x-ray tubes. The variations in shielding of the core electrons by the outer binding electrons provide features in an absorption spectrum which can be related to oxidation state, bonding symmetry, types of ligands, etc. Until recently these techniques have been restricted to concentration levels of major and minor elements because of the limited brightness (photons/sec, source area, solid angle) of rotating anode x-ray tubes. Recently, synchrotron radiation x-ray sources have become available and are able to provide a continuous energy spectrum with a brightness about a factor of 10^5 greater than that of x-ray bremsstrahlung. This enables chemical speciation by x-ray absorption spectroscopy at trace concentration levels.

The x-ray absorption spectrum in the region of an absorption edge is illustrated in fig. 1. The spectrum is scanned at intervals of 1 eV bandwidth. An absorption spectrum is generally divided into two distinct regions, the XANES (x-ray absorption near edge structure) region and the EXAFS (extended x-ray absorption fine structure)

region. The XANES region contains information related to chemical speciation because it represents the energy region where a core electron is promoted to unfilled atomic and molecular states. The energy and intensities of such transitions depend on the chemical state of the absorbing atom. The EXAFS region represents those electrons whose kinetic energy is too great to be locally scattered but may be backscattered from the nearest neighbors causing the modulation that is characteristic of EXAFS spectra. This data may be interpreted to yield the distance from the absorbing atom to its nearest and next-nearest neighbors, but provides little chemical binding information. Fig. 1 shows a typical behavior of XANES spectra where the absorption edge of the oxidized species occurs at a greater energy than that of the reduced species because there is less shielding from the nucleus of the K electrons and thus more energy is required to produce a K hole. However, it is not clear that this is the explanation for the shift in the case of the hexaironcyanides(1).

EXPERIMENTAL METHODS

The traditional methods (2) of x-ray absorption spectroscopy considered here require the monochromatization of the x-ray source spectrum and the scanning of the selected energy range. This is usually accomplished with Bragg-diffracting crystals providing energy bandwidths of $\Delta E/E = 10^{-4}$. At major element concentrations the absorption mode of operation is used where an ion chamber is situated

both before and after the sample measuring I_0 and I_{abs} respectively. The absorption coefficient, α , is calculated from the relationship

$$\log \frac{I_0}{I} - C = \alpha FT$$

where F is the weight fraction of the element under study, T is the sample thickness and C is the sum of αFT products for the other elements in the sample. The factor C is essentially a constant since the range of energy being investigated is small and no abrupt changes are encountered. At minor and trace concentrations the factor C , representing the absorption by the bulk of the sample, approaches $\log(I_0/I)$ and the features of the absorption edge can not be seen. Under these conditions one can observe the effect of absorption by the desired element by measurement of the fluorescence x-rays or secondary charged particles. Fluorescence x-rays can be employed easily down to concentrations of a few hundred ppm using solid state detectors. The main source of background limiting the techniques is the scattered excitation energy at an energy just above the fluorescence energy. One detector method to circumvent this is the use of a barrel shaped Bragg-reflecting surface tuned to the fluorescence radiation with a geometric efficiency of 1.2%. (3). This system was used to obtain the EXAFS spectrum of 75 ppm Fe in Cu. Information of the XANES portion of the spectrum obviously could be obtained at lower concentrations because the spectrum features are more pronounced.

Another technique for XANES studies at trace levels utilizes an x-ray filter assembly between the sample and a large geometry detector together with the fluorescence mode(4). A critical filter with an absorption edge energy between that of the absorption edge energy of the element being studied and that of the fluorescence x-rays will absorb the scattered radiation from the target but will pass the fluorescence x rays with much greater efficiency. Soller slits are placed between the filter and the detector and collimated so as to allow x-rays from the target to pass. However, the fluorescence produced in the filter by the excitation radiation is isotropically distributed and most of this radiation directed towards the detector will be absorbed by the slit assembly. This arrangement improves the signal to background ratio by a factor of forty and has been used to measure the EXAFS spectrum of iron in a 1 mM aqueous solution(5).

DISCUSSION

The following studies are used to illustrate the range of systems studied and concepts used in the analysis of the data. Although considerable effort has gone into theoretical calculations to analyze and predict near-edge absorption spectra, most applications to systems of biochemical interest have consisted of comparisons of spectra with model compounds of the element being studied. The objective of one study was the determination of the oxidation state of molybdenum in nitrogenase(6). The positions of the absorption edge for model

compounds of Mo ranging from oxidation states +2 to +6 yielded a linear relationship when plotted against the "coordination charge," η , which is expressed as

$$\eta = Z - \sum nC$$

where Z is the formal oxidation state and the sum is over all types of bonds of number, n , and covalency, C , as obtained from Pauling's table of atomic electronegativities (7). The Mo in nitrogenase yielded an absorption edge position corresponding to a coordination number of 2.3 ± 0.3 . The oxidation state is somewhat ambiguous because of uncertainties of the bonding ligands. The results are consistent with the state Mo(V) with at least one sulfur bond in assumed hexacoordinate bonding.

Many elements, particularly among the transition elements, show considerable structure in the preionization region because of many available transitions to unoccupied molecular states. In these cases it is not possible to reliably establish the position of the absorption edge, but much can be deduced from the observed transitions. Hu, et al. (8) studied the edge structure in the oxidized and reduced states of copper in cytochrome c oxidase. Transitions of K electrons to four bound states were observed for both reduced and oxidized compounds. Both showed a transition at 8983 eV with that of the reduced compound having twice the intensity of that of the oxidized compound. These results were compared with model Cu compounds of oxidation states I, II, and III. The Cu(I) model

compounds showed the 1s to 4s transitions to fall in a range including 8983 eV, whereas no Cu(II) or Cu(III) compounds showed any transitions near 8983 eV. The conclusion is that of the two Cu atoms in the oxidized form of the oxidase, one Cu atom is in the +1 oxidation state and upon reduction, both Cu atoms are +1. This conclusion is at variance with a previous report that the oxidized form has two Cu(II) atoms, based on coulometric titrations.

Maylotte, et al. (9) investigated the speciation of vanadium in coal at the 1000 ppm concentration level. After grinding the coal, two fractions were obtained by mixing with water. One was the floating fraction, the other was the sinking fraction. A sample was also liquefied under pressure at high temperature. The model compounds used were V_2O_3 , an octahedrally coordinated compound; Roscoelite, a vanadium mineral with octahedral symmetry around the vanadium; NH_4VO_3 , a tetrahedrally coordinated compound; V_2O_4 , square pyramid coordination; and vanadium porphyrin, a +4 oxidation state with nitrogen ligands. For all the model compounds other than the octahedrally coordinated, there is a strong pre-edge peak caused by dipole transition from the 1s orbital to the t_2 orbital which contains considerable metal 3d character. This transition is forbidden for structures with centers of symmetry, as is the case in octahedral coordination. All coal samples had a pre-edge peak at 4.5 ± 0.2 eV (compared to a vanadium metal feature defined as zero). The float fraction showed an increase in the height of the pre-edge peak and the heavy fraction showed a decrease, indicating at least two environments

for vanadium in coal. V(V) as in V_4O_{15} , NH_4VO_3 is eliminated from consideration because their pre-edge peaks are in the 5- to 6 eV range. The 4.5 eV value is in good agreement with V(IV) in oxygen coordination. The data would seem to exclude V(IV) compounds with nitrogen ligands where the peak occurs at 3.5- to 4.0 eV. The liquefied sample shows a spectrum with essentially no peak and is similar to that of V_2O_3 , indicating a reduction in the liquefaction process.

Jaklevic, et al. (10) separated coarse aerosol particles (2.4 to 20 μm) from fine particles (less than 2.4 μm) at an urban sampling site. They compared the whole zinc x-ray absorption spectrum, including the EXAFS region, with those of $(NH_4)_2Zn(SO_4)_2$, $ZnSO_4$ and ZnO model compounds. They were able to show a preponderance of ZnO in the coarse particles and $(NH_4)_2Zn(SO_4)_2$ in the fine particle fraction. Using mathematical fitting routine, they quantitatively determined the distribution of the zinc compounds in the various fractions with an absolute accuracy of about 3 percentage points.

SUMMARY

The application of synchrotron radiation to XANES studies of the metal sites in biologically active compounds promises a new avenue to the chemical speciation of those metals. The high brightness of synchrotron radiation and new detection techniques sources provides the capability of obtaining absorption spectra of metals at trace concentrations levels. A number of examples of such studies were

described with the intent of illustrating the method of analyzing the data and relating the observations with those of model compounds. Other examples, not described, include studies of biological compounds involving Ca (11), Co(12), Ni(13), Mn(14) and others. The field of speciation is still in its infancy because of the newness of synchrotron radiation and the very limited facilities that have been available. With the construction of new dedicated sources and their availability to the whole research community, the number of applications to chemical speciation should grow at a great rate.

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Figure Caption

Fig. 1. X-ray absorption spectra of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$. The absorption is plotted relative to the continuum absorption at higher energy, α_a . From ref (1).

