

Quick X-ray absorption spectroscopy for determining metal speciation in environmental samples

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We present a method for determining the chemical speciation of metals in environmental particles based on Quick-X-ray Absorption Spectroscopy. The approach can be applied to either the extended or the near edge fine structure, and consists in the decomposition of the XAS spectrum of an unknown sample on a reference set of standards' spectra using quadratic linear programming. The analysis accounts for the statistical experimental errors generated during the acquisition of X-ray absorption data, and leads to error estimates on the various fractions determined via a Monte Carlo procedure. An application example is presented for the speciation of inorganic Zn in a contaminated sediment sample.

Keywords: Environmental; Metal Speciation; Q-XAS; Spectral Decomposition.

1. Introduction

The determination of the chemical speciation of metals in environmental samples is key for assessing the toxicity, bioavailability, and fate of these elements in aquatic systems. It has been shown that total metal concentration is a poor predictor of toxicity, but that, instead, the free ion concentration, the labile fraction, or some specific species are responsible for deleterious ecological effects. Although present environmental regulations still rely primarily on total metal concentrations, there is a critical need to address speciation issues in more details (Renner, 1997). Traditionally, the chemical speciation of metals in aquatic systems is either appraised using chemical models based on equilibrium reactions (Allison *et al.*, 1989) or determined using wet chemical methods relying on the sequential extraction of various phases (Tessier *et al.*, 1979; Tessier & Campbell, 1988). However, these two approaches present serious limitations. On the one hand, thermodynamical equilibrium is rarely achieved in natural systems and consequently the predictive power of these speciations codes remains poor. On the other hand, sequential extraction protocols are prone to artefacts (Tipping *et al.*, 1985) and require careful evaluation and calibration before being used on a specific sample (Tessier & Campbell, 1988). Hence, these methods are often considered as operational procedures, and have been openly criticized without any proposal for viable alternatives (Nirel & Morel, 1990). The task of defining the speciation of metals in environmental samples remains an open-ended and important problem.

Within the last decade, the construction of various synchrotron radiation rings has provided the community with intense X-ray photon sources that can be used to probe the local coordination environment of most of the metals of environmental importance.

The application of X-Ray Absorption Spectroscopy (XAS), since the establishment of the theoretical foundation for the interpretation of its spectra (Sayers *et al.*, 1971; Teo, 1986) has flourished in environmental sciences, (*e.g.*, Manceau *et al.*, 1996; Hesterberg *et al.*, 1997; Kemner *et al.*, 1997; O'Day *et al.*, 1998; Kim *et al.*, 1999; Ostergren *et al.*, 1999; Manceau *et al.*, 2000). The first paper to mention the use of this spectroscopic tool to probe the speciation of metals in environmental samples was published about 20 years ago (Jaklevic *et al.*, 1980). The approach was to use linear combinations of XAS spectra to quantify the different fractions of metal compounds present in air particles. Since then, quite a few investigations have relied on this technique to determine the speciation of metals in a wide variety of environmental samples, using either the XANES or the EXAFS region (*e.g.*, Bajt *et al.*, 1993; Manceau *et al.*, 1996; Peterson *et al.*, 1997; Kim *et al.*, 1999; Ostergren *et al.*, 1999; Welter *et al.*, 1999; Manceau *et al.*, 2000, and others). This method is attractive since it is element specific, it can be applied to crystalline or amorphous samples, and it is thought to be non-destructive. However, the use of ionizing radiation can lead to beam damage that will affect the chemical integrity of the sample. Therefore, to minimize the exposure of the sample to the X-ray beam, and verify the spectra do not change during the experiments, we have used Quick X-Ray Absorption Spectroscopy (Frahm, 1989). This experimental set-up presents additional advantages: (1) the associated statistical errors can be extracted directly from the signal, (2) the precision of the measurements is increased significantly because the fluctuations of the beam are reduced compared to longer time scale scans, and (3) the averaging of multiple spectra improves statistics (Murphy *et al.*, 1995).

2. Methods and Data Analysis

X-ray absorption measurements were performed at the Advanced Photon Source, Argonne National Laboratory (IL) on the bending magnet beamline of the Dupont-Northwestern-Dow Collaborative Access Team (DND-CAT). The storage ring was operating at 7.0 GeV, using electrons, with a beam current ranging between 100–60 mA. The beamline was equipped with a Si(111) double crystal monochromator that was used to vary the X-ray energy from 200 eV below to 750 eV above the absorption K edge of Zn (9659 eV). The monochromator was detuned to approximately 75% of the maximum intensity to avoid the interference produced by higher harmonics. The incident intensity, I_0 , and transmitted intensity, I_T , were measured using ionization chambers designed at DND-CAT that are characterized by a high linearity, and that also behave well under high x-ray photon fluxes delivered at the APS. The fluorescence signal, I_F , was measured with a Stern-Heald "Lytle" detector equipped with a Z-1 filter. Kr or Ar were used as fill gases depending on the concentration of Zn present in the samples. All the detectors were connected to Stanford Research System SRS 570 current amplifiers, and the signals were continuously recorded at 12.5 kHz using a sixteen-bit analog to digital converter (Bornebusch *et al.*, 1999; Quintana, 2000). Data were collected while the monochromator was continuously slewed between the beginning and ending energies. Nine successive scans, of 75 seconds each, were recorded for every sample. The data were binned and averaged over 1 eV for the pre-edge and the near edge regions, and over $k = 0.05 \text{ \AA}^{-1}$ in the EXAFS. Assuming that the error of each individual channel is the same and Gaussian, the experimental uncertainty for each channel in a bin is given by $\sigma_x = [\sum_{i=1}^N (x_i - \bar{x})^2 / (N - 1)]^{1/2}$ where x_i is the measurement of a single channel in the bin, \bar{x} is the average of the binned channels, and N is the number of points in the bin.

The uncertainty in the average value of the bin is $\sigma_{\bar{x}} = \sigma_x / \sqrt{N}$ (Mandel, 1984). This reflects the actual experimental error that arises from counting statistics and electronic noise in the system. To improve the signal to noise ratio, multiple scans of the same sample were averaged, and the errors were carried through using the standard propagation of errors theorem. The fluorescence and transmittance signals, μ_F and μ_T respectively, can then be computed together with their attached experimental errors. Since the normalization and extraction of the EXAFS signal involve non-linear steps, the errors for these properties were calculated using a pseudo-Monte Carlo method. For the normalization process, randomly generated Gaussian errors based on experimentally determined uncertainties ($\pm\sigma_{\bar{x}}$) were added to the original data. The error-induced signal was fitted to a line in the pre-edge region and to a quadratic polynomial expression in the EXAFS region. This process was repeated 1000 times, and the coefficients for each fit were stored. The average value of the coefficients was then used to remove the background signal. The error of the signal was determined by the standard deviation of each of the fitting coefficients. A similar process was used in the isolation of the EXAFS $\chi(k)$. Again, a randomly generated Gaussian error using $\pm\sigma$ was added to the original signal. AUTOBK (Newville *et al.*, 1993) was then used independently to remove the background signal and isolate $\chi(k)$ and store the array of data values. This was repeated 1000 times, and the final $\chi(k)$ was determined by the average of the 1000 replicates. Errors for these values were estimated by calculating the standard deviation of the replicates.

The composition of mixtures was determined by spectral decomposition based on a quadratic linear programming (QLP) fit of the EXAFS signals of samples to standards (Vandenberghe & Boyd, 1996). It consists in minimizing an objective function with an augmented langrangian, to solve the dual problem:

$$\sum_{i=1}^{n=m} (k^3 \chi_{\text{sample}}(k) - \phi_i \cdot (k^3 \chi_{\text{standard}_i}(k)))^2 = 0$$

subject to:

$$\forall i, \phi_i \geq 0; \text{ and } \sum_{i=1}^{n=m} \phi_i = 1$$

where ϕ_i is the fraction of the standard i in the analyzed spectrum. To obtain the uncertainties on the ϕ_i values we use as before a Monte Carlo process, whereby about 1000 QLP fits are performed using randomly sampled spectra within the error bars calculated previously.

Standards were chosen after a careful geochemical analysis of the sediments investigated (Webb *et al.*, 2000; Webb & Gaillard, 2000). Standards included sphalerite: ZnS; zincite: ZnO; amorphous zinc hydroxide: Zn(OH)₂; smithsonite: ZnCO₃; zinc phosphate (Zn₃(PO₄)₂); and zinc carbonate hydroxide (ZnCO₃·2Zn(OH)₂) (Aldrich - Hesterberg *et al.*, 1997). All EXAFS signals were k^3 -weighted to better emphasize the structure at large k values.

3. Results

A typical averaged spectrum, representing a series of nine scans lasting 75 seconds, is shown in Figure 1. The insert details the structure of the experimental errors associated with the experiment. In the EXAFS region, the experimental errors ($\frac{2\sigma}{\mu_F}$) are less than approximately 10^{-3} , and decrease with increasing energy.

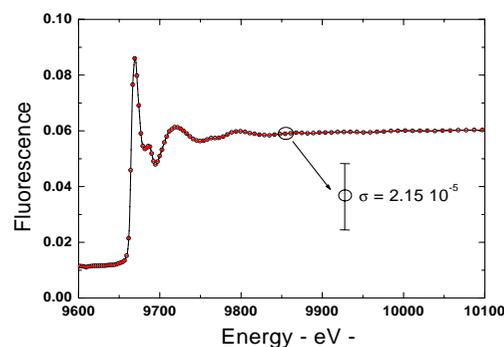


Figure 1

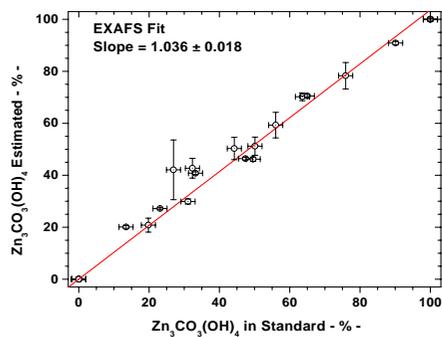
Average Q-XAS spectrum from a typical environmental sample resulting from 9 consecutive scans of 75 seconds each. The insert provides an enlargement of the variation of μ_F with energy showing the error bars corresponding to the final signal.

To test the accuracy of the fitting procedure and calibrate the speciation method, we prepared a series of mixtures of known standards and performed the spectral decomposition as detailed above. Mechanical mixtures of fine powdered standard material were prepared in various proportions, and were then spread directly, as a very thin films, on Kapton tape to minimize self-absorption effects. It was found, using pure standard materials, that this preparatory technique provided good spectroscopic information for fluorescence studies. The low concentration of metals usually found in environmental systems impinged on us to use fluorescence, since one cannot acquire representative data in absorption.

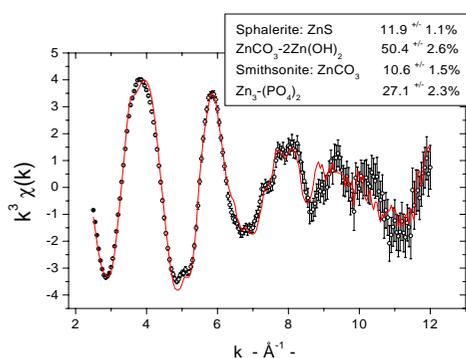
The results of a calibration study, for mixtures of zinc carbonate hydroxide with other standard compounds, are presented in Figure 2. Overall, the trend observed between the fractions estimated by QLP and the calibration standards is acceptable, although departures from a pure 1:1 relationship can be significant. We attribute these departures primarily to our ability of preparing accurate calibration standards, *i.e.*, it is quite difficult to mix and spread evenly fine dispersed solids. Consequently, one can note in Figure 2 that a few calibration points carry large error bars that reflect these difficulties. Nonetheless, multiple calibrations experiments confirmed that this analytical scheme was quite robust.

The analysis of an environmental sample collected from the sediments of Lake DePue (IL), a lake contaminated by the operation of a zinc smelter (Webb *et al.*, 2000) is presented in Figure 3. This sample was retrieved using a hand-held piston core, and a thin sediment section (about 1 mm thick) was preserved under two stripes of Kapton tape at cryogenic temperature - Liquid N₂. The total zinc concentration in the sample analyzed was about 2%, on a dry weight basis.

The spectral decomposition by QLP establishes that the only significant compounds present in the sample are: sphalerite, smithsonite, zinc carbonate hydroxide, and zinc phosphate. All the other standard compounds are characterized either by negligible proportions, or by proportions that are associated with error bars that make them indistinguishable from zero. Hence, for the final fit reported here, only the significant zinc coordination environments


Figure 2

Calibration line for zinc carbonate hydroxide. The error bars for the calibration standards were arbitrarily set to 5 %, a rather optimistic estimate, whereas the error bars for the estimated fractions result from both Monte Carlo calculations and repeated analyses through the prepared surface of the thin film of standard material. One can note, in some instances that some heterogeneity exists within a particular sample, as reflected by the length of the error bars.


Figure 3

Zn K-edge EXAFS signal - open circles - with associated error bars for a thin slice of Lake DePue sediment. The solid line corresponds to the fitted spectrum using the various proportions of the standards indicated in the insert.

were considered for the spectral decomposition. The various fractions of the different ligation environment found are consistent with the geochemical and analytical electron microscopy study of these sediments (Webb *et al.*, 2000). The errors associated to the different fractions, that have been estimated by the Monte Carlo procedure, indicate that the speciation of Zn is relatively well constrained. The goodness of fit shows that most of the structure of the signal is reproduced quite successfully. Some discrepancies are however present for $8 < k < 10 \text{ \AA}^{-1}$. These can be attributed to potential systematic errors that could be in part related to the

incompleteness of the data base of reference spectra.

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