Study of XAFS spectroscopic methods of speciation using mixtures of Cu(I) and Cu(II) chlorides

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Abstract. Speciation concerns determination of the chemical forms along with the relative quantities of the different species in a given sample. The aim of the present work is to make a comparative study of the different methods of speciation using X-ray absorption fine structure (XAFS) spectroscopy. For this purpose, mixtures have been prepared by mixing CuCl2 and CuCl in different proportions. The X-ray absorption spectra have been recorded at the copper K-edge in the mixtures and the two chlorides separately. The different characteristic features of the XANES spectra of the two chlorides, useful for speciation, have been identified. Firstly, Principal component analysis (PCA) and target transformation (TT) methods have been used to check the number and identity of components in the mixtures. After the identification of the components, the percentages of the species in the mixtures have been quantitatively determined by linear combination fitting (LCF) of XANES, derivative XANES, and EXAFS (k^3chi and k^2chi) spectra. The other methods of speciation which have been employed are normalized difference absorption edge spectra analysis (NDAES), methods based on derivative XANES spectra of species and the method based on the relative position of the absorption edge. Results obtained from these methods have been compared and their relative merits discussed. It is probably for the first time that such a study has been done. The first section in your paper

1. Introduction
X-ray absorption spectroscopy (XAS) is one of the best known structural techniques for speciation, i.e., for determination of the chemical forms along with the relative quantity of the different species in a given sample. For this purpose one usually models X-ray absorption fine structure (XAFS) spectra of the sample by using well-defined chemical species as standards. This can be done both in the X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. For speciation, several approaches for the analysis of XAFS data have been developed, the commonly used being: principal component analysis (PCA) along with target transformation method (TT) [1] and linear combination fitting (LCF) [2-4]. Other methods which can also be used are: derivative XANES spectra methods [5], normalized difference absorption edge analysis (NDAES) [6] and a method based on position of the edge. In earlier studies, we have applied these methods of speciation to only a single mixture of copper oxides and the LCF has been performed only in XANES spectra [7, 8]. In the present work, by taking five mixtures having specific percentages of Cu(I) and Cu(II) chlorides we have studied all of these methods of speciation and the LCF has been performed not only in XANES spectra but also in derivative XANES and EXAFS (k^3chi and k^2chi) spectra. The aim of the present work is to make a comparative study of these methods of speciation and to discuss their relative merits.
2. Experimental
Commercially available 99.99% pure CuCl and CuCl$_2$ powders were mixed in the specific ratios by weight to prepare five mixtures (numbered as M1, M2, M3, M4, and M5). The 'as prepared' percentages of CuCl and CuCl$_2$ in these mixtures are given in Table 1. Absorption screens were prepared of the finely powdered pure CuCl, CuCl$_2$ and their mixtures. The X-ray absorption spectra for these absorption screens were recorded at room temperature at the EXAFS beamline X-19A at National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Upton, New York, USA. The values of edge position, as determined from first inflection point, have been found to be to be 8979.0, 8981.9 and 8985.9 eV for Cu foil, CuCl and CuCl$_2$, respectively, representing the expected trend, i.e., increase in edge energy as the oxidation number increases. The positions of the K-absorption edge in the mixtures have been found to be in between those of CuCl and CuCl$_2$.

3. XANES features
Figure 1 shows the normalized K-edge XANES spectra of copper metal, cuprous chloride, cupric chloride and their mixtures. For the Cu(I) compound, a feature P at 8986 eV and in case of Cu(II) compound, a weak feature W at 8978 eV, absorption-edge shoulder S and an intense white line C at 8995 eV have been observed which have been taken as diagnostic features for speciation.

4. Data analysis, Results and Discussions:
In the present study, for PCA and target transformation, SIXPack data analysis software has been used. EXAFS data analysis software Athena has been used for performing LCF, for constructing the difference spectra and the derivative spectra and determining the position of the edge corresponding to the point having $\mu x = 0.5$ in the normalized spectrum. After confirming the number and identity of components in the five mixtures by using PCA and Target transformation (details of which are not given here), we have applied the following methods for determining the proportion of the CuCl$_2$ and CuCl in the mixtures and the results obtained are given in table 1.

| S. No | Method of speciation | max. % error | M1 | M2 | M3 | M4 | M5 |
|------|----------------------|--------------|----|----|----|----|----|
| 1.   | XANES LCF ± 3        | 13.6 86.4    | 34.7 65.3 | 47.3 52.7 | 52.9 47.1     | 76.0 24.0 |
| 2.   | Derivative XANES LCF ± 5 | 12.5 87.5 | 33.6 66.4 | 44.3 55.7 | 51.3 48.7       | 75.2 24.8 |
| 3.   | EXAFS LCF (k$^2$ chi) ± 7 | 12.7 87.3 | 41.2 58.8 | 52.1 47.9 | 58.3 41.7       | 75.8 24.2 |
| 4.   | EXAFS LCF (k' chi) ± 6  | 11.7 88.3 | 39.8 60.2 | 51.8 48.2 | 58.6 41.4       | 74.3 25.7 |
| 5.   | NDAES ± 5             | 13.8 86.2    | 34.2 65.8 | 46.7 53.3 | 51.3 48.7       | 75.2 24.8 |
| 6.   | Derivative Cu(I) spectra ± 3 | 18.0 82.0 | 36.5 63.5 | 47.0 53.0 | 53.0 47.0       | 77.0 23.0 |
| 7.   | Derivative Cu(II) spectra ± 5 | 15.2 84.8 | 39.4 60.6 | 54.5 45.5 | 60.6 39.4       | 75.6 24.4 |
| 8.   | Position of the edge ± 10 | 9.0 91.0 | 42.8 57.2 | 51.3 48.7 | 57.0 43.0       | 84.9 15.1 |
|      | As prepared           | 15.0 85.0    | 35.0 65.0 | 50.0 50.0 | 55.0 45.0       | 75.0 25.0 |

4.1 Methods based on derivative spectra: The derivative spectra of the five mixtures and the standards CuCl and CuCl$_2$ are shown in figure 2. The derivative spectra of a mixture has two distinct features: 'A' corresponding to the Cu (I) component and 'B' corresponding to the Cu(II) component. These two features have been used to determine the percentage of a species in the mixture in two ways one utilizing feature 'A' and another feature 'B'. The percentages of CuCl and CuCl$_2$ in the mixtures, as determined from these two ways, i.e., from derivative Cu(I) spectra and derivative Cu(II) spectra, are given in table 1.
4.2 Normalized Difference Absorption Edge Analysis (NDAES): Figure 3 shows the normalized difference edge absorption spectra for all the mixtures. The difference spectra show a positive peak $\alpha$ at 8983-8984 eV and a broad negative feature at 8990-9000 eV. The amount of cuprous ion present can be determined from the height of this positive peak $\alpha$. The height of this peak has been measured precisely in all the mixtures and the percentages of CuCl and CuCl$_2$ in the mixtures, as determined from this method are given in table 1.

4.3 Linear Combination Fitting (LCF): In the present work, LCF has been performed in the XANES spectra (over the range 8960-9040 eV), derivative XANES spectra (over the range 8960-9040 eV) and EXAFS spectra ($k^2\chi(k)$ and $k^3\chi(k)$) (over the range 2-12 Å$^{-1}$). The percentages of CuCl and CuCl$_2$ in the mixtures, as determined from LCF are given in table 1. The figures 4(a-d) show the results for mixture M3 (taken as a representative case). The results of XANES, derivative XANES LC fitting and EXAFS LC fitting ($k^3\chi(k)$ and $k^2\chi(k)$) are shown in figures 4(a), 4(b), 4(c) and 4(d) respectively. In case of...
XANES LC fitting, the figure 4(a) also shows the fractions of the CuCl and CuCl$_2$ making up the fitted spectra. In the case of M3, the R-factor and chi-square values are 0.00017 and 0.01537, 0.003003 and 0.00066, 0.020219 and 0.53792 and 30.04687, for the LCF performed in XANES, derivative XANES and EXAFS (k$^3$chi and k$^2$chi) spectra, respectively.

From table 1, it can be seen that the XANES methods give more accurate results as compared to the EXAFS (k$^3$chi) methods for estimating the percentages of components in the mixtures. This may be due to the fact that difference between the XANES spectra of the two copper chlorides is more significant than between their corresponding EXAFS spectra. Also, the absorption edge, which is the dominant feature in XANES spectra, occurs at significantly offset absorption edge energies for both the chlorides making XANES methods more reliable.

4.4 Method based on position of the edge: In this method, position of the edge is arbitrarily defined as the energy corresponding to normalized $\mu_{x} = 0.5$ [5]. The fraction $y_m$ of Cu(II) species in the mixture can be determined from relation $y_m = (E_m - E_{CuCl}) / (E_{CuCl2} - E_{CuCl})$, where $E_{CuCl}$, $E_{CuCl2}$ and $E_m$ are the energies of the position of the edge in the CuCl and CuCl$_2$ and the mixture respectively. The percentages of CuCl and CuCl$_2$ in the mixtures as determined from this method are given in table 1.

5. Conclusions:
The percentages of CuCl and CuCl$_2$ in the mixtures were estimated by different methods, namely, linear combination fitting (LCF) (in XANES, derivative XANES, and EXAFS (k$^3$chi and k$^2$chi) spectra), normalized difference absorption edge analysis (NDAES), two methods based on derivative spectra of Cu(I) and Cu(II) species and a method based on the relative position of the edge. A comparison of the results obtained from the different methods with the as prepared composition of the mixtures shows that LCF (in XANES spectra) appears to be the best method for speciation.

The methods of speciation described in the present work can be used for biologically or environmentally important systems, for example, which contain XAS-active metals in several oxidation states, each of which generates quite different fingerprint features in their XAFS spectra. The methods can also be utilized to solve the phase speciation problem of multi-component mixtures and to investigate the speciation of metal in the electrokinetic remediation (EKR) process [9]. Also these methods can be useful for molecular characterization of copper in soils [3]. The methods can also be used for the study of copper-based catalysts under in situ or in operando conditions [5].

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