



Detection of As, Cr and Cd in Walnut Trees by Extended X-Ray Absorption Fine Structure Spectroscopy, EXAFS

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Research Article

Received 21st June 2011
Accepted 17th July 2011
Online Ready 8th August 2011

ABSTRACT

Heavy metals are found naturally in the soil in small concentrations. These can be collected in bigger amounts by mining, agriculture, industry, and others. Also plants can process these in toxicity levels and if putted into the food chain, human physiologic integrity is affected. In this work, to determine which heavy metals are found in soil, plants and fruits sampling were carried out on two farms. Walnut crop specifically. For the analysis, samples of soil, plants and fruits were taken. The soil samples were treated with the quartering method and prepared for analysis by X-ray absorption spectroscopy (XAS). The results obtained by XAS show the presence of arsenic (V) in soil; Chromium (III) in soil, branch and fruit; Chromium (VI) in the branch; Cadmium (II) at the soil.

Keywords: Heavy metals; soil; walnut; X-ray absorption spectroscopy;

1. INTRODUCTION

Heavy metals are elements found naturally in the soil as small concentrations. However these concentrations can be enhanced by the natural activities such as erosion of the hills

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and volcanic eruptions and anthropogenic activities such as mining, agriculture, industry, among others. Plants grown in contaminated soils generally absorb more bio-elements or trace-elements and the concentration in their plant's tissues is often directly related to their abundance in soils. Excessive concentrations of metals in the soil could impact the quality of food, security crops and the health of the environment, because these concentrations move through the food chain via plant consumption (Kabata-Pendías and Pendías, 2001; Gulson et al., 1996; Puga et al., 2006).

An X-ray absorption spectroscopy (XAS) was used to determine the presence of heavy metals in soil and if they are absorbed by the walnut trees.

2. MATERIALS AND METHODS

2.1 Sampling

Systematic sampling was applied by a rectangular grid. It is to draw a grid on the ground with 10.5 m each square and selecting a starting point. Once at the sampling square first step was to remove organic matter and litter. A surface slice was taken with a spatula from top to bottom. The samples were of 500g with a depth of 15 to 20 cm. Then the samples were placed in sealed and labeled plastic bags. Also samples of the plants were taken and placed in plastic bags with a hermetic sealing, labeling and storage for further analysis.

2.2 Sample Preparation

Each sample was placed on a clean plastic. After lumps were crushed and mixed, quartering method was applied to obtain 5 grams samples. The samples were dried (both soil and plants) at 100° C. Samples of soil, branch and fruit without grinding were placed in plastic bags and labeled.

To prepare the sample for XAS analysis, plants were dried then were washed three times with deionized water and immersed in liquid nitrogen for 40 minutes (Gardea et al., 2004). Then the samples were placed in a dryer for 2 days for dehydration and eventually grind biomass in a homogeneous fine powder using a mortar. Wet soils have been kept in an Ar-atmosphere between the time of sampling and measuring (Hans-Rudolf et al., 2004)

2.3 XAS Analysis

XAS is a technique that has been used in recent years to examine the structure of the surroundings of a selected atom.

The samples were analyzed at the Stanford Synchrotron Radiation Laboratory (SSRL) for X-ray absorption spectroscopy, including XANES and EXAFS. This analysis was conducted to investigate the oxidation state, the interatomic distance and the number of nearest neighbor atoms to atoms. A current of 60 - 100 mA and energy of 3 GeV were the operation conditions. All samples were analyzed at a temperature near 15° K, using a helium cryostat to reduce the effects of Debye-Waller thermal disorder presenting in the samples.

The data obtained from the synchrotron were analyzed using the Win XAS software for atomic distances, disorder parameters and the coordination number around the scatter atom and the element chemical status.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-rays absorption spectra from samples of soil indicating the presence of As. All have a similar pattern with the edge of energy absorption located in the range of 11.865 to 11.869 keV. So is assumed that this is an As (V) as reported by Aldrich et al. (2007).

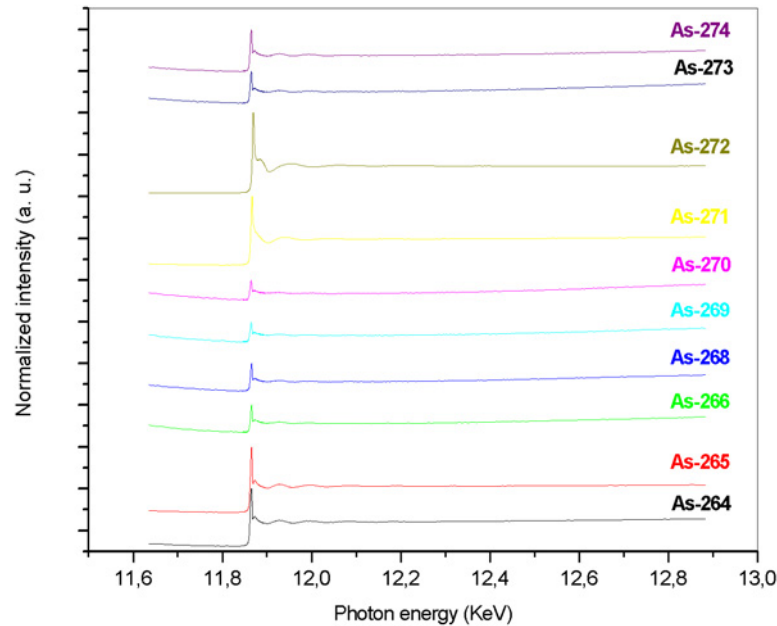


Fig. 1. Arsenic X ray absorption spectra

Figure 2 shows the radial distribution function $F(r)$ for each sample obtained after applying the Fast Fourier Transform to the absorption spectra of Figure 1. It clearly indicates the atomic distance to the first neighbor in each sample and in all of them, is in the range of $R=0.194$ nm to 0.201 nm and comparing them with the literature, these correspond to the distance As–O with $R= 0.179$ nm (Aldrich et al., 2007).

The difference in the atomic positions compared to the literature is mainly due to not have implemented any phase adjustment to the $F(r)$. Furthermore we note that although we found a spectrum of soil samples shifted to the left, remains as As-O, and the displacement can be explained in terms of number of neighbors surrounding the As but not necessarily has to be oxygen. In other words, arsenic is forming other compounds and it is using the same valence.

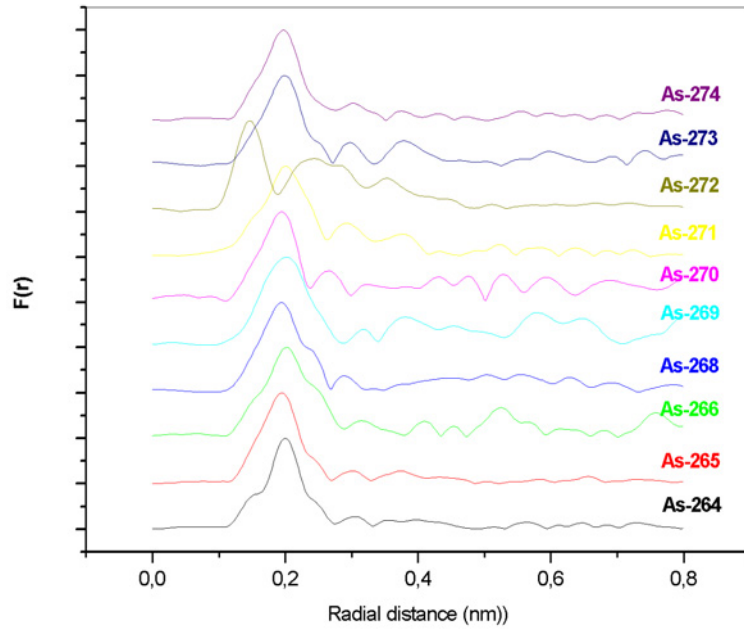


Fig. 2. Fast Fourier Transform of Arsenic XAS

In figure 3 all samples shown a similar pattern, with the edge of energy absorption at 26.71 keV. Compared with the literature, the edges of the samples are identical to the shape of the edge of cadmium nitrate and cadmium acetate. It indicates that it exists as Cd (II) (Rosa et al., 2004).

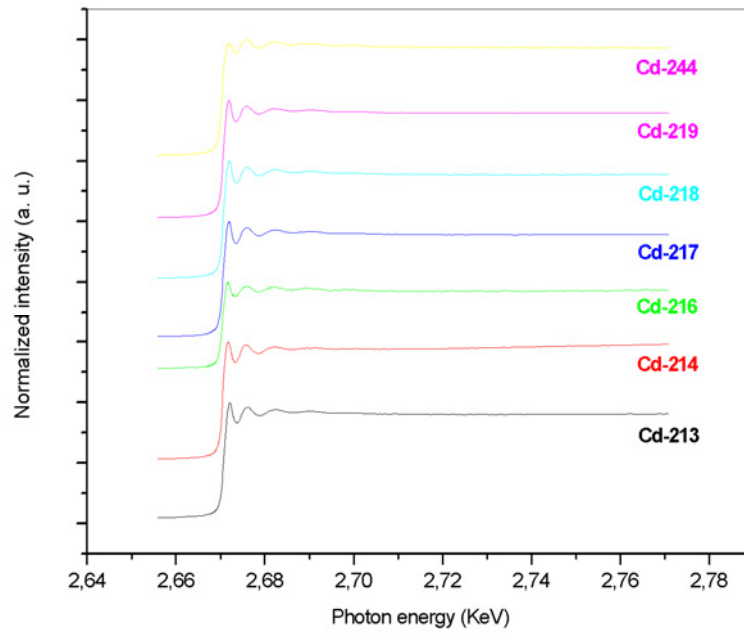


Fig. 3. Cadmium X ray absorption spectra

Figure 4 shows the radial distribution functions $F(r)$ obtained after applying the Fast Fourier transform of the absorption spectra shown in Figure 3. This $F(r)$ gives us the atomic first neighbor distance in each sample. The distance to first neighbors and with a slight variation is found at $R = 0.277$ nm so as reported in the literature for Cd-Cd $R = 0.304$ nm and 0.212 nm, corresponding to Cd-O with $R = 0.215$ nm. (Rosa et al., 2004).

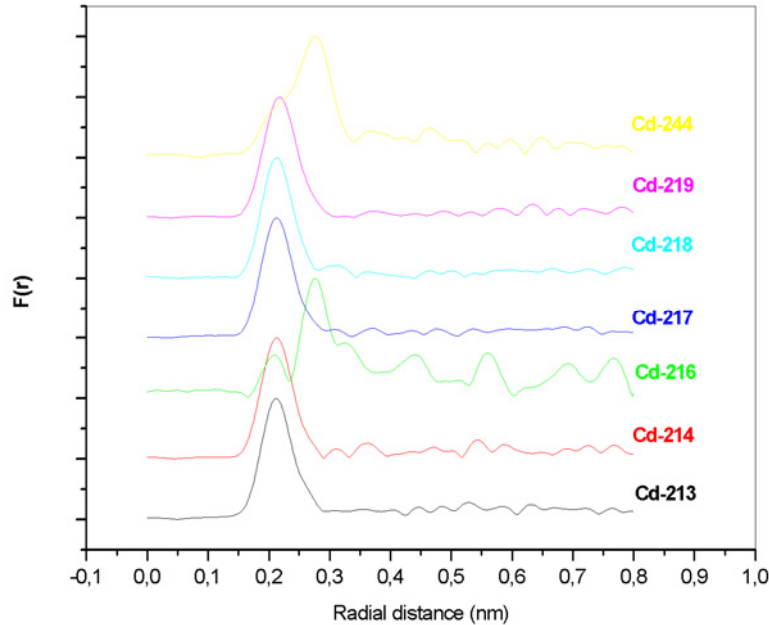


Fig. 4. Fast Fourier Transform of Cadmium X ray absorption spectra

In Figure 5 we see a similar trend in the X ray absorption spectrum and we can see a small peak in the pre-edge region which indicates the presence of Cr (III) as reported in the literature of studies on oat plants, where the absorption edge is at the energy of 5.99 keV.

Besides, can be seen in the spectrum which corresponds to a branch a larger peak located at the same energy. This indicates the presence of Cr (VI), a fact contrary to that already reported. In experiments on plants, these trend to reduce the Cr (VI) to Cr (III) (Gardea et al., 2000).

Figure 6 shows the $F(r)$'s Chromium. In this case the $F(r)$ is quite different between them due to that Cr in their valences III and VI have a different coordination. The way to know with precision what compound is present, is to fit from a model compound but this fit falls outside the context of this work. However it can be assumed that there is a contribution of oxygen because this is in the range of 0.16 nm and 0.24 nm. And to determine it, is necessary to do a series of adjustments but again, those are outside the context of this work.

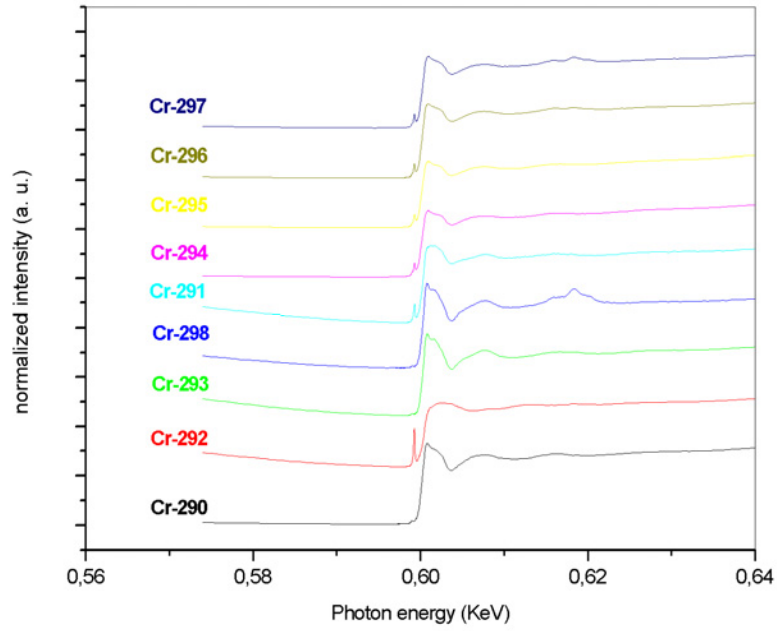


Fig. 5. Chromium X ray absorption spectra

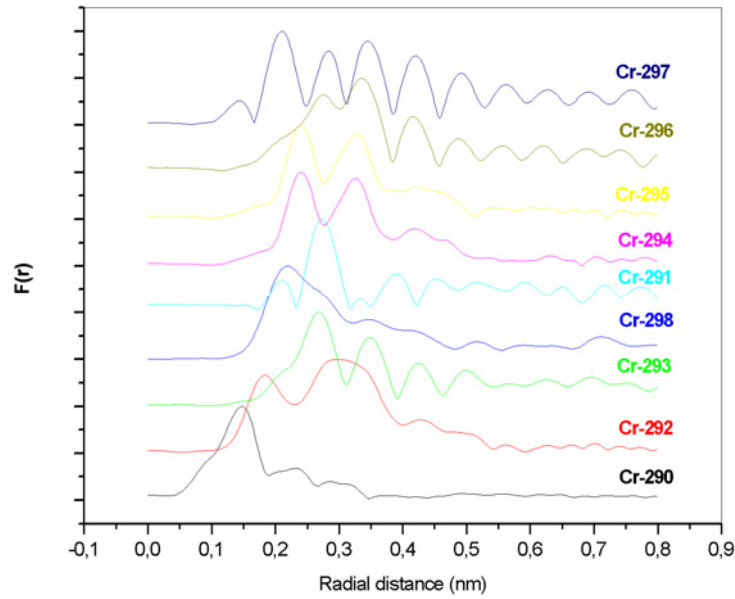


Fig. 6. Fast Fourier Transform of Chromium X ray absorption spectra

4. CONCLUSION

We note the presence of As in its valence V in samples of soil with oxygen contribution as As-O, Cadmium in valence II in the form of Cd-Cd and the contribution of oxygen as Cd-O and Chromium in its valence III in samples of soil, fruit and branch with the exception of one sample in which chromium is found in its valence VI.

ACKNOWLEDGEMENTS

The authors would thank to Centro de Investigación en Materiales Avanzados S.C. (CIMAV). E. Gallegos Loya gratefully acknowledges a grant provided by CONACYT (National Council of Science and Technology in México).

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