



	Experiment title: HERDF-XANES at the Zn K edge : a way to improve sensitivity and accuracy of XANES in natural and very complex matrices	Experiment number:
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Shifts: 15	Local contact(s): Mauro Rovezzi	<i>Received at ESRF:</i>
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Report:

Aims of the experiment and scientific background

Metal speciation in natural systems is a crucial information to determine their fate and toxicity. It can be identified with X-ray absorption spectroscopy (XAS) techniques, such as XANES. Sometimes, reference compounds XANES spectra don't show specific characteristics that allows a clear distinction to determine metal speciation in natural sample with accuracy. The recent development of High-Energy Resolution Fluorescence Detectors (HERFD) for XAS can help to fill this technical gap. For example, the lower energy resolution (~1eV) of these detectors compared with conventional SSD detector (150-300eV) allowed a clear discrimination of Hg reference compounds¹. Our aim was to determine to which extent HERFD-XANES at Zn K-edge can enhance the accuracy of XANES to identify Zn speciation in natural samples. Briefly, the objectives were (I) to scan a set a references compounds to identify specific XANES features, (II) to compare Zn speciation determined by conventional and HERFD detection modes on natural samples with low Zn concentration, (III) evaluate the sensitivity of HERDF detection mode for Zn K-edge XANES measurement.

Experimental

17 Zn reference compounds and 2 soils XANES spectra were measured with filtered K α fluorescence emission line and with total fluorescence /or transmission detection mode, for comparison. HERFD-XANES were also measured with filtered K β and K_{satellites} emission lines to determine the impact on XANES features of reference compounds. Reference compounds include representative compounds found in soils and environmental samples such as Zn sorbed on clays and oxy-hydroxides (ferrihydrite, goethite, HIM 20), Zn bound to organic compounds (cysteine, malate, oxalate) or Zn precipitated as mineral (hopeite, sphalerite (nanostructured and bulk)). Soils samples are from a demonstration field in Southern Brazil, mainly composed of clays and silt (68 and 31%) and sampled on the control zone (control soil) and organic waste-amended zone². A Nitisol was sampled in the 0-25 cm horizon on an experimental field on the island of Réunion (France)³. The initial Zn concentration is 170 mg/kg and it was diluted in ultrapure water to reach 6, 2 and 0.6 mg/kg in order in evaluate the sensitivity of HERDF-XANES at Zn K-edge in a natural sample.

Samples were cooled at the He temperature for XANES measurement at Zn K-edge (9659 eV) on FAME-UHD beamline. Linear Combination Fitting were performed on Athena Software between 9643.5 and 9743.5 eV using the 17 available references to determine Zn speciation in the soil samples.

Results

1) Zn references characterisation: XANES features as function on the detection mode

A first test was performed on the ZnS reference compounds. The HERFD-XANES were scanned using the $K\alpha$, $K\beta$ and $K_{\text{satellites}}$ emission lines. The main difficulty was related to the decrease in intensity from the $K\alpha$ (not shown), $K\beta$ and $K_{\text{satellites}}$ emission lines as seen in the following figure 1A.

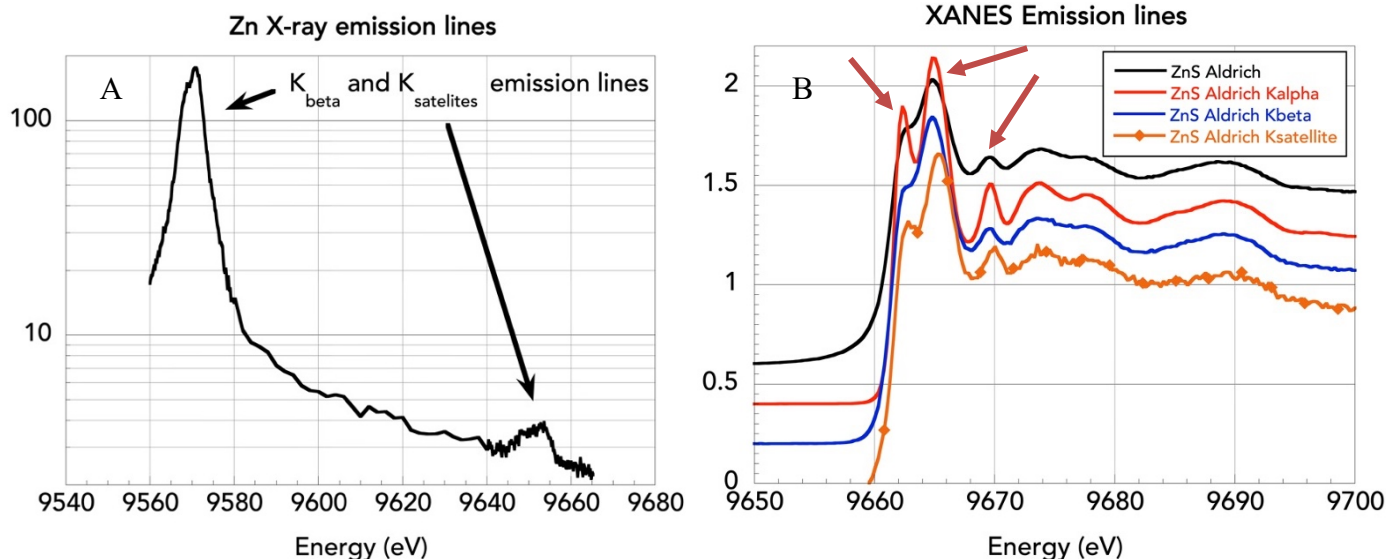


Figure 1: A) Zn $K\beta$ and $K_{\text{satellites}}$ emission lines. B) comparison of conventional and HERFD-XANES of the ZnS reference compound

The XANES spectra measured in transmission and with the $K\beta$ emission line exhibit very similar shapes (figure 1B). Indeed, the various features did not differ in position as well as in intensity. The features at 9661.2 eV, 9665 (white line) as well as 9669.4 eV appeared more intense in the case of HERFD-XANES $K_{\text{satellites}}$ emission lines than in transmission. However, the low intensity of the $K_{\text{satellites}}$ emission lines lead to very noisy XANES spectra and can only be used for concentrated samples.

Interestingly, the HERFD-XANES using the $K\alpha$ emission line has the most pronounced structures and due to the high intensity of the emission line, is the less noisy. The intensity and sharpness of the 9661.2 eV, 9665 (white line) as well as 9669.4 eV features can be seen for bulk and nano-ZnS (figure 2).

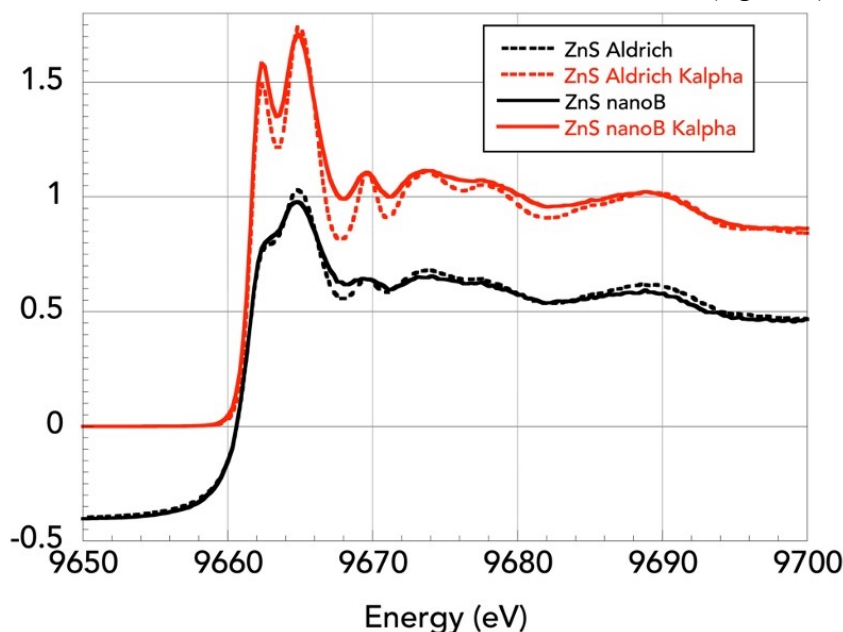


Figure 2: Zn $K\alpha$ emission line HERFD-XANES (red curves) compared with transmission XANES (black curves) for bulk (dotted lines) and nano-ZnS (plain lines).

While the differences between the nano and bulk ZnS remain very limited in transmission mode, the intensity of the features at 9661.2, 9665 and 9669.4 eV with $K\alpha$ emission line detection can help to distinguish both references (Figure 2).

For all other reference compounds as well as soil samples the $K\alpha$ emission line detection was used. It is worth noting that for all samples, As for ZnS, the $K\alpha$ emission line HERFD-XANES spectra of the reference compounds exhibit more intense features than the transmission/fluorescence spectra, as it can be seen in the following figure.

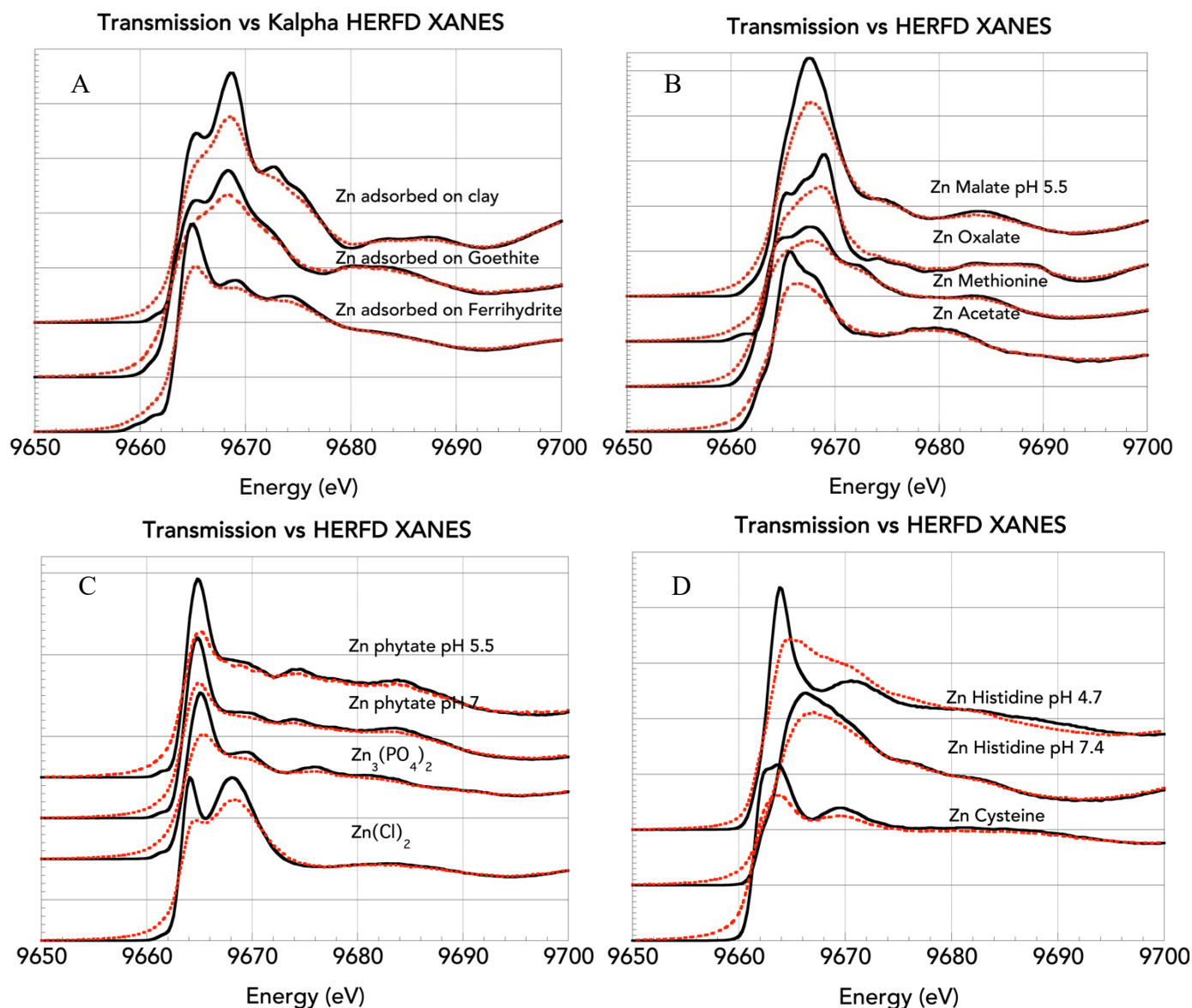


Figure 3: Zn $K\alpha$ emission line HERFD-XANES (black plain lines) compared with transmission XANES (red dotted lines) for A) Zn adsorbed on various minerals B-C-D) Zn chloride, phosphate and organic reference compound).

The effect is more or less pronounced as function of the compound. For instance, in the case of some organic Zn references like Zn-cysteine, Zn-histidine, Zn-malate the difference between HERFD and conventional XANES are limited. However, regarding Zn-oxalate, Zn-methionine, Zn-acetate HERFD spectra exhibit features that are not distinguishable in the transmission spectra. These features can help better identifying unknown compounds. It is particularly true when Zn is bound to organics for which the complex is often time challenging to identify because of the poor retro-diffusion of low-Z elements in the second coordination shell.

2) HERDF and conventional detection modes for Zn speciation characterisation in a soil

Control soil XANES obtained with $K\alpha$ emission line exhibit a more structured spectrum compared with the total fluorescence mode (Figure 5). However, the Linear combination Fitting (LCF) results in the same speciation: 56 % Zn sorbed on clays minerals, 32 % Zn-phosphate and 12 % Zn bound to organic matter. For the organic-waste-amended soil, LCF results were also similar with the 2 detection modes. Therefore, for this soil (clayey soil with [Zn] = 100 and 188 ppm), the HERDF detection with $K\alpha$ emission line doesn't improve accuracy of

XANES for Zn speciation determination. However, for a natural sample containing Zn bound to sulfur compounds (nano-ZnS, sphalerite, Zn-cysteine...), K α emission line detection could improve XANES accuracy to better discriminate sulfur containing references.

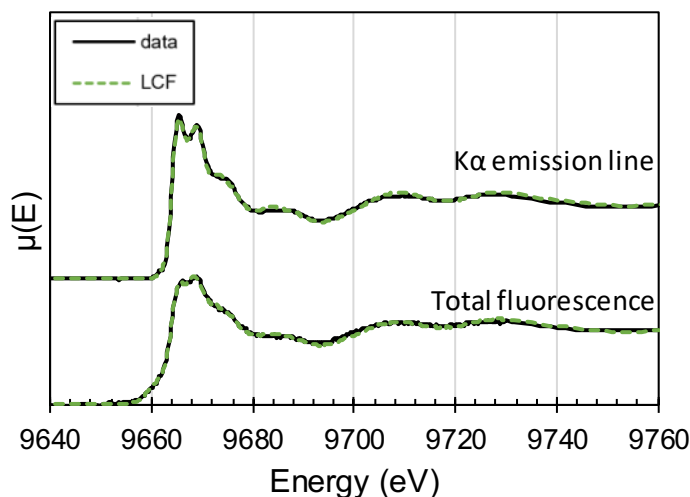


Figure 4: Zn K-edge XANES spectra of the control soil (in black) obtained with total fluorescence mode (bottom) and with K α emission line detection mode (top) and their respective Linear Combination Fitting (LCF) results (dashed green lines).

Another example illustrating the adding value of HERFD is shown below: In total fluorescence detection mode, a natural sample with Zn bound to cysteine (simulated by adding 0.1 level noise on Zn-cysteine reference on Athena software) can be considered as nano-ZnS as their XANES spectra have common oscillations (Figure 5 bottom). However, in K α emission detection mode, the sharp feature of nano-ZnS spectra leads to an unambiguous reject of nano-ZnS speciation in this sample (Figure 5 top).

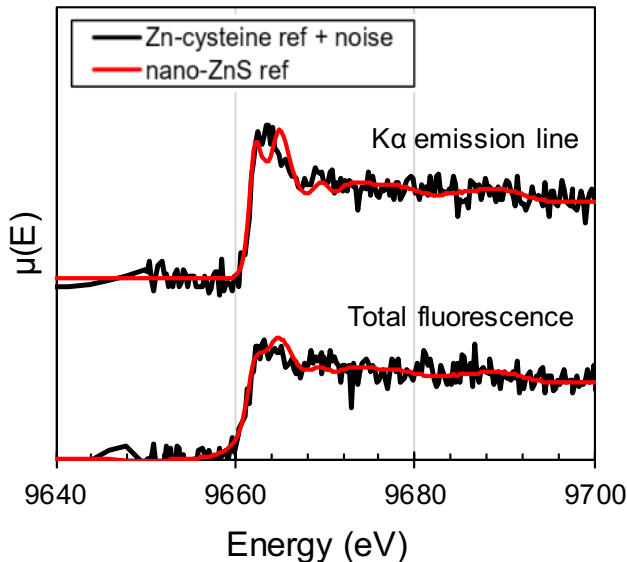


Figure 5: Zn K-edge XANES spectra of (Zn-cysteine reference with numerically added noise compared with nano-ZnS reference in both total fluorescence detection (bottom) and K- α emission line detection (top).

3) Sensitivity of HERDF detection mode for Zn K-edge XANES

Zn K-edge XANES spectra of the sampled Nitisol at [Zn] = 170 ppm and diluted to reach 6, 2 and 0.6 ppm are shown on Figure 6. Sharp oscillations are observed for the Nitisol at 9665.6, 9669.6 and 9674.8 eV for the non-diluted and diluted to 6 ppm soils. LCF results in the same speciation: 87% Zn adsorbed on clay minerals and 13 % Zn bound to organic matter. At 2 ppm, we notice the same oscillations that are less sharp. LCF results are slightly similar at this concentration: 85 % Zn adsorbed on clay minerals and 15 % Zn-phytate. However, at 0.6 ppm, the previously observed features are wider. Therefore, LCF results in a different Zn speciation: 23 % of Zn adsorbed on clays and 77 % of Zn bound to organic matter. From these results, we can conclude that the minimal concentration to accurately determine Zn speciation in this type of sample is higher than 2 ppm.

Therefore, HERDF detection mode improves sensitivity for XANES measurement compared with the conventional total fluorescence detection that requires dozens of ppm.

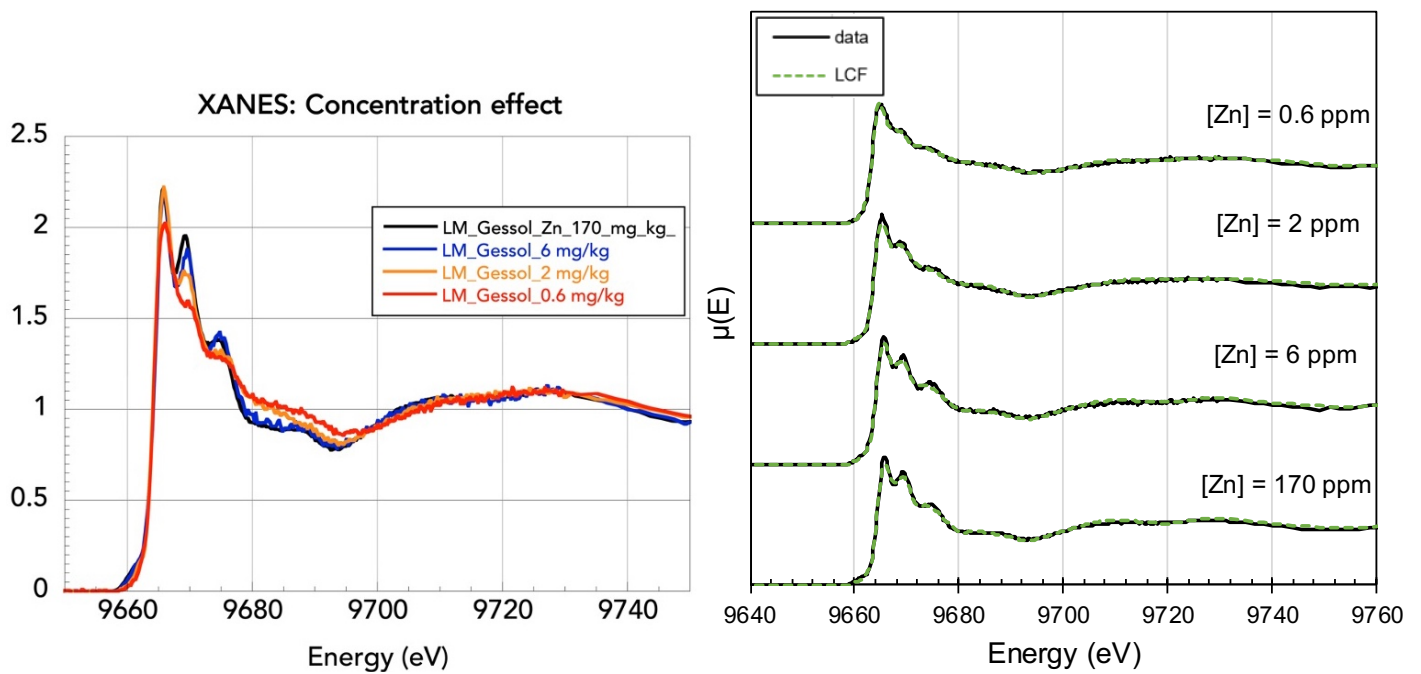


Figure 6: Zn K-edge XANES spectra obtained with $K\alpha$ emission detection for the Nitisol ($[Zn] = 170$ ppm) (bottom) and the diluted Nitisol with Zn concentrations of 6, 2 and 0.6 ppm (top).

Conclusion

From this study, we can conclude that HERDF detection mode results in sharper features for Zn references, more or less pronounced as function of the compound. This could help to discriminate sulfur compounds in a natural sample with low Zn concentration. However, for a soil containing Zn associated to clays, phosphate and organic matter, HERDF detection mode doesn't improve accuracy for Zn speciation determination. The major input of HERDF detection mode for Zn K-edge XANES measurement is the increased sensitivity, since Zn speciation can be assessed for concentrations higher than 2 ppm.

References

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