X-Ray Absorption Near Edge Structure Spectra as a Basis for the Speciation of Lead

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Abstract. For this study several inorganic lead (II) compounds were measured at the Pb-L\textsubscript{1}- (13035 eV), L\textsubscript{3}-(15860 eV) and M\textsubscript{5}-(2484 eV) edge using X-Ray Absorption Near Edge Structure Spectroscopy (XANES) to determine experimentally which edge is most sensitive to the coordination environment. Each edge probes a different electronic configuration because of the selection rules and has a different resolution because of life-time broadening. Pb-L\textsubscript{1}-XANES spectra are only sensitive to the first coordination shell. Pb-M\textsubscript{5}-XANES spectra show a better energy resolution which is due to decreased lifetime broadening, but the pure lead spectra are also sensitive only to the first coordination shell. Spectra at the Pb-L\textsubscript{3}-edge show the highest sensitivity: differences in coordination out to the third shell could be distinguished. Therefore, even though Pb-L\textsubscript{1}- and M\textsubscript{5}-edges have some advantages, because of physical conditions compared to the L\textsubscript{3}-edge, these advantages do not result in increased sensitivity.

1. Introduction

X-Ray Absorption Fine Structure (XAFS) Spectroscopy has proven to be an important tool for the speciation of the chemical environment of specific elements and thus for applications to biological systems. Parsons et al. [1], for example, review the applications and point out the advantages of both Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES). We concentrate on XANES because it gives a more representative picture of the element under investigation [1]. Since lead is a widely spread biological hazard lead speciation using XANES is frequently reported. Because the energy of Pb-K-edge at 88 KeV is much too high for most XAFS beamlines and also has a natural line width of 60.6 eV due to lifetime broadening [2] it is not an option for XANES measurements. The Pb-L\textsubscript{1}-edge shows the same features as the Pb-K-edge because of the
same dipole-allowed transitions and would be the first choice, however, the difference of the photoabsorption cross sections, which defines the absorption edge, before and after the edge (at L$_{1}$-edge: 131.1 cm$^2$/g to 149.9 cm$^2$/g) is higher at the Pb-L$_{3}$-edge (64.0 cm$^2$/g to 159.2 cm$^2$/g) [3]. Because of the low energy of the Pb-M$_{5}$-edge (2484 eV) and hence significant absorption in air at ambient pressure, measurements at reduced pressure are required and only one publication reports Pb-M$_{5}$-edge XANES measurements [4]. Therefore, the Pb-L$_{3}$-edge is usually used for XANES measurements. Previously the sensitivity of the Pb-L$_{3}$-edge was determined to be limited to the first coordination shell [5]. In this study we present a thorough sensitivity analysis of the L$_{1}$-, L$_{3}$- and M$_{5}$-edges of lead to understand how lifetime broadening and different dipole-allowed transitions affect the sensitivity and which one of these edges is more sensitive beyond the first coordination shell. Lifetime broadening affects the line width, for core-levels that are further away from the nucleus lifetimes increase, therefore, line widths decrease. Line widths at the K- (60.6 eV), L$_{1}$- (11.8 eV), L$_{2}$- (6.1 eV) and M$_{5}$- (2.48 eV) edges of lead are reported by Campbell and Papp [2] and confirm this effect.

2. Materials and Methods

The Pb-L$_{3}$- (13035 eV) and L$_{1}$-edge (15860 eV) experiments were carried out at the INE beamline of the synchrotron radiation source ANKA, Karlsruhe, Germany, with an energy of 2.5 GeV using Ge(422) crystals for the Double-Crystal-Monochromator (DCM) and the M$_{5}$-edge (2584 eV) measurements at the DCM Beamline of the CAMD, Baton Rouge, Louisiana, USA using InSb(111) crystals. All spectra were recorded in transmission mode using ion chamber detectors. At the Pb-L-edges ion chambers were filled with argon at atmospheric pressure, at the Pb-M$_{5}$-edge ion chambers were filled with nitrogen at 44 Torr. Parameters for the XANES spectra at the specific edges are summarized in Table 1.

| Edge (step size in eV) | Pb-L$_{1}$ | Pb-L$_{3}$ | S-K/Pb-M$_{5}$ |
|------------------------|-----------|-----------|----------------|
| Pre-edge region I      | 15710 – 15810 (5) | 12885 – 12985 (5) | 2440 – 2460 (1) |
| Pre-edge region II     | 15810 – 15830 (1) | 12985 – 13005 (1) | 2460 – 2465 (0.5) |
| Main-edge region       | 15830 – 15910 (0.5) | 13005 – 13085 (0.5) | 2465 – 2520 (0.1) |
| Post-edge region       | 15910 – 16100 (0.8 incr.) | 13085 – 13275 (0.8 incr.) | 2520 – 2580 (0.3) |

For this sensitivity comparison at the various edges the inorganic lead (II) compounds lead β-monoxide, lead nitrate, lead carbonate, lead citrate tri-hydrate, lead sulfate, lead sulfide, lead hexadecyl mercaptide and phthalocyanine lead were purchased in high purity from Sigma Aldrich and Alfa Aesar (lead sulfide). Data were normalized and analyzed using the ATHENA program of the IFEFIT package [6].

To determine the sensitivity of the spectra at an edge to different coordination environments first a qualitative analysis of the reproducibility of spectra of the same compound was made (not shown). Differences between spectra were calculated subtracting normalized spectra from each other and taking the root mean square (RMS difference) of all points. Spectra of the same compound, measured several times, showed a RMS difference of 0.01 for spectra with a good signal to noise ratio at Pb-L-edges and 0.02 at Pb-M$_{5}$-edge. The next step was the calculation of differences between spectra of compounds with different coordination. The spectra shown in Figures 1, 2 and 3 are examples of lead in various coordinations: different first shell (e.g. Pb-S vs. Pb-O in lead monoxide versus lead sulfide which have a similar tetrahedron like coordination [7],[8] different second shell (e.g. Pb-S-Pb vs. Pb-S-C in lead sulfide vs. lead hexadecyl mercaptide [9] Pb-O-Pb vs. Pb-O-N or Pb-O-C in lead monoxide, lead nitrate and lead carbonate and Pb-O-S vs. Pb-O-N in lead sulfate vs. lead nitrate which
also have a very similar coordination only differing in sulfur atoms instead of nitrate atoms in the second shell \([10], [11]\) and different coordination in third shell (e.g. lead carbonate vs. lead citrate tri-hydrate \([12], [13]\)).

### 3. Results and Discussion

Figures 1-3 show the XANES spectra at the three edges. The differences for spectra differing in the first coordination shell (namely lead sulfide vs. lead monoxide), in the second coordination shell (namely lead sulfate vs. lead nitrate, lead sulfide vs. lead hexadecyl mercaptide, lead nitrate vs. lead carbonate) and in the third coordination shell (namely lead carbonate vs. lead citrate tri-hydrate) are summarized for all three edges in Table 2.

![Figure 1: Pb-L\(_1\)-edge XANES Spectra of a) lead hexadecyl mercaptide, b) lead sulfide, c) lead sulfate, d) lead nitrate, e) lead carbonate, f) lead citrate tri-hydrate, g) lead monoxide](image1)

![Figure 2: Pb-L\(_3\)-edge XANES Spectra of a) lead hexadecyl mercaptide, b) lead sulfide, c) lead sulfate, d) lead nitrate, e) lead carbonate, f) lead citrate tri-hydrate, g) lead monoxide, h) lead phthalocyanine](image2)

Since for the pair of lead sulfate/lead nitrate the RMS difference of Pb-L\(_1\)-edge XANES spectra is about 0.01 these compounds cannot be distinguished with certainty through Pb-L\(_1\)-edge XANES spectra. Therefore, at the Pb-L\(_1\)-edge the sensitivity of XANES spectra does not extend beyond the first coordination shell.

At the Pb-L\(_3\)-edge lead sulfate and lead nitrate can be distinguished as the RMS difference is 0.02 which is beyond the calculated experimental uncertainty of 0.01. Additionally, lead carbonate and lead citrate tri-hydrate are very similar at the L\(_3\)-edge, but the RMS difference of 0.016 is just beyond the just beyond the uncertainty. Therefore, the sensitivity of Pb-L\(_3\)-edge XANES spectra is extended to the third coordination shell.

Pb-M\(_5\)-edge XANES spectra of the lead compounds have a decreased signal-to-noise ratio which leads to a larger uncertainty of 0.02. Due to the close proximity to S-K-edge (2469 eV) Pb-M\(_5\)-edge XANES spectra of sulfur-containing lead compounds are partially masked through an overlap of the two edges. Therefore, the RMS difference for Pb-M\(_5\)-edge XANES spectra was calculated in the range of 2510 eV to 2580 eV. From this point of view the Pb-M\(_5\)-edge XANES spectra for lead sulfide/lead hexadecyl mercaptide are not different (RMS difference of 0.02). Henceforth, Pb-M\(_5\)-edge XANES spectra are only sensitive to the first coordination shell. If S-K-edge is taken into account sulfur containing compounds are easy to distinguish from pure lead compounds and thus the spectra are also sensitive to the second coordination shell.

Contrary to the Pb-M\(_5\)-edge, Pb-L\(_1\)-and L\(_3\)-edge XANES spectra have relatively pronounced White Lines which, in the case of Pb-L\(_3\)-edge, results in higher sensitivity. Pronounced White Line features at Pb-L\(_1\)-edge, which probes transitions into unoccupied final states of p-character arise from molecular
Figure 3: S-K-/Pb-M5-edge XANES Spectra of a) lead hexadecyl mercaptide, b) lead sulfide, c) lead sulfate, d) lead nitrate, e) lead carbonate, f) lead citrate tri-hydrate, g) lead monoxide, h) lead phthalocyanine

Table 2. RMS differences of the XANES spectra at the specific edges.

| Pair of Compounds | RMS Difference |
|-------------------|----------------|
|                   | L1  | L3  | M5  |
| Pb-O/Pb-S         | 0.025 | 0.037 | 0.090 |
| Pb-S-Pb/Pb-S-C    | 0.017 | 0.020 | 0.020 |
| Pb-O-S/Pb-O-N     | 0.011 | 0.026 | 0.051 |
| Pb-O-N/Pb-O-C     | 0.031 | 0.035 | 0.037 |
| Pb-O-C/O-Pb-O-C-Pb| 0.010 | 0.016 | 0.023 |

orбиталы, о.е. свинцовый оксид, которые являются межядерного сп-дуэрупции при коалентном соединении свинцового оксида и это приводит к расширенной линии. Атомные снимки свинцового оксида по сравнению с ионными соединениями позволяют более узким характеристическим признакам быть разрешены, но х5-XANES спектры еще более структурированы, чем L3. We conclude that Pb-L3-edge XANES spectra have the highest sensitivity and therefore should be preferred for the speciation of lead.

Acknowledgements
The authors would like to thank ANKA-ISS and CAMD for provision of beam time and the staff of INE and DCM beamline for their support.

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