Fluorescence X-ray microscopy on hydrated tributyltin-clay mineral suspensions

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Abstract. Using the scanning transmission X-ray microscope at ID21 beamline of the ESRF in fluorescence mode, we mapped tin at a bulk concentration of 1000 µg(Sn)/ml within hydrated tributyltin (TBT) - clay mineral (Kaolinite) dispersion with sub-300 nm spatial resolution. Using the L absorption edges of tin at 3929, 4156 and 4465 eV fluorescence radiation was excited in tin atoms with incident photon energies of 4 and 4.5 keV. When using 4 keV X-ray radiation, only tin fluorescence is excited. For 4.5 keV X rays, both the fluorescence of tin and calcium (which is present in the solid phase) can be measured. Methodologically, we were interested in assessing and proving the possibilities and limitations of fluorescence mapping using the L absorption edges of tin, where the fluorescence yield is significantly lower compared to other elements with their K edges in the same energy range.

Scientifically, organotin-clay mineral interactions are of environmental concern because this factor influences significantly the distribution of toxic TBT in the aquatic system. On one hand, the half-life of TBT deposited to the sediment phase increases, and consequently the time of its bioavailability. On the other hand, the adsorption process is reversible, which means that contaminated sediments can act as a source of pollution. The adsorption and desorption effects can be studied directly with high spatial resolution and brought into connection to the surface properties of the clay mineral under study as well as to other experimental parameters, like pH or salinity.

1. INTRODUCTION
Due to their widespread use in numerous areas of human activity, butyltin compounds have been introduced to various ecosystems. Thus, contamination of these pollutants can be detected in nearly all compartments of the aquatic environment: water, suspended matter, sediment and biomass. One example for introducing organotins into the environment is the former usage of highly toxic tributyltin (TBT) in anti-fouling paints on wooden harbor piers and ships.

The persistence of butyltins in polluted ecosystems is a function of physical, chemical and biological removal mechanisms [1]. Adsorption to suspended matter and its deposition is an important mechanism in controlling the distribution and fate of organotin compounds in aquatic systems [2]. Research of organotins is mainly restricted to the high toxic TBT. Systematic laboratory experiments had shown that adsorption of TBT to clay-rich sediments is a reversible process depending on pH values or salinity [3]. But also the less alkylated and less toxic derivatives monobutyltin (MBT) and dibutyltin (DBT) should be of high environmental concern [4]. A better knowledge of the adsorption and desorption behavior of organotin compounds are necessary to assess the bioavailability and the ecological risk of these toxic contaminants in natural systems.

So far, results describing the distribution of organotins on single mineral grains and aggregates are not available. To study the surface covering and the interaction between clay mineral surfaces and the organotin molecules, we used for the first experiments a well characterized aqueous suspension of a clay mineral (kaolinite KGa-1) and tributyltin at a bulk concentration of 1000 µg(Sn)/ml and successfully mapped tin within these samples by detecting the 3 respectively 5 fluorescence lines of tin when exciting with 4 respectively 4.5 keV photon energy X rays.

2. SCANNING X-RAY MICROSCOPY IN FLUORESCENCE MODE

2.1 Experimental Setup at the ID21 beamline of the ESRF

The ID21 scanning X-ray microscope (SXM), operating in the 2 – 8 keV energy range is a unique tool for elemental mapping and near-edge spectroscopy of many K edge (Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co) elements in low concentrations and at high spatial resolution detecting the fluorescence
radiation created in the atomic species mentioned using an energy-dispersive Germanium detector (Princeton Gamma Tech). L and M edge elements are also accessible, however, at a higher detection limit due to the reduced fluorescence yield compared to K absorption edges. The experimental setup of the ID21 SXM consists of an undulator source, providing an illumination with a high degree of coherence on typical Fresnel zone plate diameter transverse lengthscales, allowing to create a (in an ideal case) diffraction limited focal spot. A double crystal silicon monochromator ensures focusing free of chromatic aberrations as well as a high energy resolution for near-edge spectroscopy. An overview is shown in figure 1 and the setup is described in more detail elsewhere [5].

The Fresnel zone plate optics (diameter 227 μm, outermost zone width 100 nm) used in this experiment were made of Tungsten by P. Charalambous, King’s College, London [6]. For a reasonable working distance between order sorting aperture (OSA) and sample at a focal length of 73.25 mm (4 keV), an OSA diameter of 50 μm was chosen in combination with a center stop diameter of 80 μm. The measurements were made with the hydrated sample at atmospheric pressure, which is possible due to the acceptable transmission for X rays of the approximately 10 cm air path at photon energies around 4 keV. The sample was prepared in sealed wet cell sandwiched between two 7 μm thick Kapton membranes, following a shim-based design for soft X-ray microscopy [7] adapted to the setup here.

### 2.2 Fluorescence X-ray microscopy on tin

A variety of fluorescence radiation transitions have been observed experimentally at 4 and 4.5 keV photon energy for the tin-\(L_{\text{env}}\)-absorption edges at 4465, 4156 and 3929 eV as listed in the table below.

<table>
<thead>
<tr>
<th>Incident energy</th>
<th>Fluorescence radiation</th>
<th>remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Both at 4.0 &amp; 4.5 keV</td>
<td>Cl Kα(_{1/2}) 2622 / 2620</td>
<td>Cl Kβ(_{1}) at 2815 eV too weak for detection</td>
</tr>
<tr>
<td></td>
<td>Ar Kα(_{1/2}) 2958 / 2956</td>
<td>Approx. 1% Ar gas in air, side effect</td>
</tr>
<tr>
<td></td>
<td>Sn Lα(_{1/2}) 3444 / 3435</td>
<td>Largest Sn peak, no influence of other elements</td>
</tr>
<tr>
<td></td>
<td>Sn Lβ(_{2}) 3905</td>
<td>At 4.5 keV some influence of Ca Kβ(_{1})</td>
</tr>
<tr>
<td>Only at 4.5 keV</td>
<td>Ca Kα(_{1/2}) 3692 / 3688</td>
<td>Peaks overlapping, however Ca dominating</td>
</tr>
<tr>
<td></td>
<td>Sn Lγ(_{1}) 3663</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ca Kβ(_{1}) 4013</td>
<td>Weaker than Ca Kα(_{1/2})</td>
</tr>
<tr>
<td></td>
<td>Sn Lγ(_{1}) 4131</td>
<td></td>
</tr>
</tbody>
</table>

**Table 1:** Table listing the different fluorescence transitions that were measured in the TBT-clay mineral sample. Experimental results are shown in figures 2 and 3.
3. EXPERIMENTAL RESULTS

3.1 Tin-Mapping in Kaolinite-tributyltin samples at 4 keV photon energy

When the energy is chosen to be 4 keV, the energy is too low to excite a fluorescence signal in Calcium, which can be found in the Kaolinite clay mineral, and only tin can be mapped. Elemental maps of chlorine, argon and tin were calculated by selecting appropriate energy intervals of the multi-channel-analyzer (MCA) fluorescence spectrum data available for each individual image pixel (acquired with 120 msec dwell time) using the ARTEMIS software [8]. The fluorescence spectrum is obtained by integrating the MCA-spectra of all pixels and represent all elements in the whole image field.

![Image](image.png)

**Figure 2:** Fluorescence spectrum (center), acquired by integrating the fluorescence spectra of all image pixels. Figures 2 a / b / c / d show elemental maps for Chlorine / Argon (1 % in air, homogeneous, side effect, cross check for homogeneity) / Tin (with good photon statistics) / Tin (with reduced photon statistics), calculated from the spatially resolved fluorescence data available [8]. The energy of the incident X-ray beam was 4 keV, permitting to excite fluorescence radiation (Sn Lα1/2 and Sn Lβ2) of the Ln tin absorption edge at 3929 eV.

3.2 Tin- and Calcium-Mapping in Kaolinite-tributyltin samples at 4.5 keV photon energy

When using 4.5 keV radiation, additional tin transitions occur compared to 4 keV (see also table 1) and furthermore, the fluorescence of Calcium will be excited (figure 3). The Ca Kα1,2 transition overlaps with the Sn Lβ1 transition and gives a mixed Calcium-tin map, see figure 3d. Furthermore, the Ca Kβ1 fluorescence line is just between the Sn Lβ2 and the Sn Lγ1 line and overlapping with them, so also in these cases, mixed Sn/Ca-maps are obtained (see figure 3e. and f.). However, there are still transitions for tin (Sn Lα1/2) being uninfluenced of Calcium, which deliver pure Sn maps and can be used as a reference for the Sn distribution to calculate the Ca distribution by normalization (see figure 3g.). Therefore, it is preferable to run the experiments at 4.5 keV to obtain as a by-product the Calcium distribution as well. The cross section for generating fluorescence radiation for tin absorption edges below 4 keV does not decrease strongly when comparing the possible excitation energies of 4 and 4.5 keV. In addition to the fluorescence signal, the transmitted signal can be detected and gives information on the total optical density of the material probed.

4. CONCLUSIONS AND OUTLOOK

The feasibility of high resolution X-ray fluorescence elemental mapping using the L-absorption edges of tin (where the fluorescence yield is relatively low compared to K-edges of other elements in the same energy range) has been demonstrated on an aqueous tributyltin (1000 μg(Sn/ml) Kaolinite-clay mineral suspension [9].

To link this new technique to other measurements of organotin-systems and to draw scientific conclusions, further comparative studies are necessary: The dependencies of the spatial distribution of the absorption and desorption of organotins on clay mineral surfaces need to be studied for

- organotin compounds with different numbers of organic substituents (e.g. monobutyltin/tributyltin)
Figure 3: Fluorescence spectrum (center), acquired by integrating the fluorescence spectra of all image pixels and elemental maps (left and right), calculated from the spatially resolved fluorescence data available [9]. The energy of the incident X-ray beam was 4.5 keV, allowing to excite also the $L_{mm}$ absorption edges of Tin at 4465 and 4156 eV besides the $L_{sp}$ edge at 3929 eV thus having more fluorescence transitions than at 4 keV (see figure 2 and table 1). The Calcium map (g.) was obtained by dividing the mixed Ca/Sn-map (d.) by the Sn-map (c.) for normalization.

- different concentrations of organotin, down to environmentally relevant concentrations, since even very low amounts might cause toxicological effects to sensitive organisms
- different types of clay minerals varying in their physico-chemical surface properties (e.g. Kaolinite and Montmorillonite).

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References