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# Improving Sensitivity in Soft X-Ray STXM Using Low Energy X-Ray Fluorescence

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Scanning transmission X-ray microscopy (STXM) provides chemical identification and quantitation of samples with ~30 nm spatial resolution. It has been used to quantitatively examine many different types of samples and physical phenomena, including picosecond magnetic dynamics [1], biological magnetism [2], wet biomaterials samples [3] and 3-d chemical mapping by spectro-tomography [4]. However, since signals are detected in transmission, the detection limit is relatively modest – typically 0.1%. It is well known that yield techniques offer a simple way to increase sensitivity and reach lower detection limits, since the signal of interest is detected directly rather than by evaluation of the difference of two large numbers, as is the case with deriving absorbance from transmission measurements. Recently Alberti et al [5] have shown that silicon drift detectors (SDD) can be implemented in STXM to detect low energy X-ray fluorescence, providing greater sensitivity and thus the potential to detect components present at much lower concentration. Here we report implementation of such a system in a STXM at the Advanced Light Source (ALS) and demonstrate that XRF-detection in STXM does indeed provide improved sensitivity.

A compact Peltier-cooled SDD system (Amptek model X-123SDD) was installed in the STXM at ALS beamline 11.0.2 with the detector chip sufficiently close to the sample to obtain a large solid angle of collection. The detector was mounted orthogonal to the X-ray beam, so that Rayleigh scattering was minimum. Several samples were examined including a natural mixed species river biofilm exposed to 1 μg/mL Ni for 24 hours, and Acidovorax, strain BoFeN1, an anoxic Fe(II) oxidizing, nitrate-reducing bacterium isolated from Lake Constance which was cultured in 10 mM Fe(II) with 1 mM $As^{2+}$ added to the culture medium. The Ni-biofilm sample was prepared by solvent casting onto a silicon nitride window while the BoFeN1 sample was also solvent cast, but then gently washed to remove salts deposited from the culture medium. The samples were measured dry, under low vacuum.

Fig. 1 is an image of the sample recorded with transmission detection at 1342 eV, showing a number of BoFeN1 bacteria and associated biomineral deposits. Fig. 2a presents X-ray fluorescence spectra each recorded for 10 minutes with the incident beam of ~$10^8$ ph/s in a sub-50 nm spot centered on an As hot spot (white circle in Fig. 1). Two incident photon energies were used – 1315 eV, just above the onset of the Mg K edge, and 1340 eV, above the As $L_3$ edge. The XRF spectra show strong signals from O and Fe, a weak Na signal, and a peak at 1.3 keV which, subsequent XRF-yield spectroscopy showed is a composite of signals from the As Lα line at 1.28 keV and the Mg Kα line at 1.25 keV. The difference in intensity of the Fe peak in the two XRF spectra probably reflects a rapidly changing concentration (iron is known to be concentrated at the membrane of the bacteria [6] and small shifts in the position of the incident X-ray beam. A sequence of images was recorded from 1308 to 1356 eV, covering the Mg K and As $L_3$ edges while simultaneously recording the transmitted X-rays and the full XRF spectrum at each pixel. Fig. 3 shows the absorption spectrum of

the hot spot extracted from the transmission signal (and converted to OD using the Io off the bacteria). Signals at the Mg or As edges are not seen, yet these elements are known from the XRF spectrum to be present at this point in the sample. However, when the yield signal from the combined Mg Kα and As Lα lines was extracted from the XRF spectra at the region of the hot spot, very clear Mg K and As $L_3$ spectral features were observed, with near edge fine structure reflecting the chemical environment of these elements. This is clear evidence of a significant sensitivity enhancement by detection using X-ray fluorescence rather than transmission. Elemental distribution maps, derived by windowing selected lines in the XRF spectrum, are presented in Fig. 4. The Fe and As signals are strongly spatial correlated. Quantization of these results is presently being developed. XRF detection is also being implemented in the STXM at the Canadian Light Source (CLS); it is anticipated that first results from the CLS XRF-STXM will be presented at this meeting. [7]

References

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[7] Supported by NSERC. STXM carried out at ALS BL 11.0.2 (supported by BES-DoE)

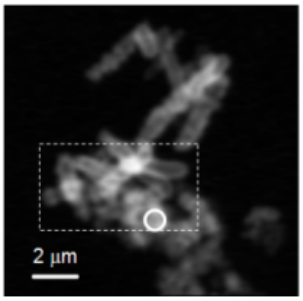


**Fig. 1** STXM absorption image (1342 eV) recorded with 1 ms/pixel from BoFeN1 bacterial sample. Dotted lines = location of image sequence, circle = location of spot XRF.

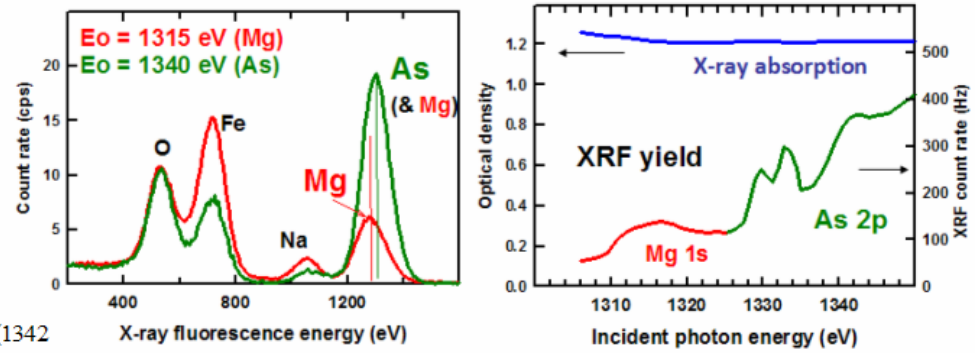


**Fig. 2** (a) X-ray fluorescence spectra (600 s), recorded with SDD with 1315 and 1340 eV incident energy. (b) (blue) X-ray absorption signal from hot spot area extracted from transmission signal of an image sequence (1308-1356 eV) compared to XRF-yield signal from the overlapping Mk Kα and As Lα peak. Dwell per pixel was 180 ms for the sequence.

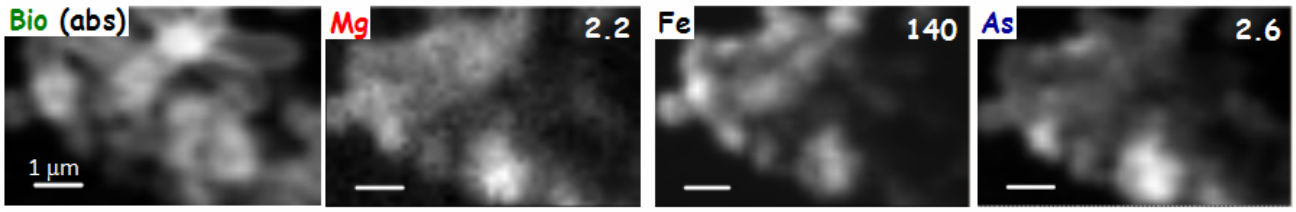


**Fig. 3** Component maps derived from transmission (Bio-abs) and X-ray fluorescence yield (Mg, Fe and As). The numbers indicate the peak counts detected in each map.

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