

## On the Detection Limits of Li K X-rays Using Windowless Energy Dispersive Spectrometer (EDS)

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With the advent of commercially available EDS detector compatible with the detection of Li K X-ray (54 eV) it is very important to know the detection limits in order to determine if Li is present or if it can be detected (higher than the detection limits) For the K X-ray lines of higher atomic number this value is often easy to determine, or calculate and is around 0.1 wt%. However, several problems can be found for Li K X-ray; very low and unknown electronic efficiency (very low signal, absorption at the top surface layer of the detector), very high absorption of the top surface layer (contamination, surface oxide and roughness), emission function of chemical bonding, very few knowledge of the fundamental emission parameters (elastic cross-section, mass absorption coefficient, fluorescence yields, etc.). This work will present some of the parameters that could affect the Li K detection limits.

We present in Fig 1 EDS spectra from metallic Li acquired using two windowless detectors. One detector has the optimized electronics for very low energy and the other a more standard electronics. This figure is clearly showing that the optimized electronics detector is showing more than 250% more signal in the Li K peaks. This electronic efficiency is not taken account in any detection limit calculation and could vary from one detector to the other or even over time. In addition, contamination at the crystal surface, which can greatly absorb very low-energy X-rays, should be avoided and monitored since these detectors are running in the same environment as the microscope (windowless detector).

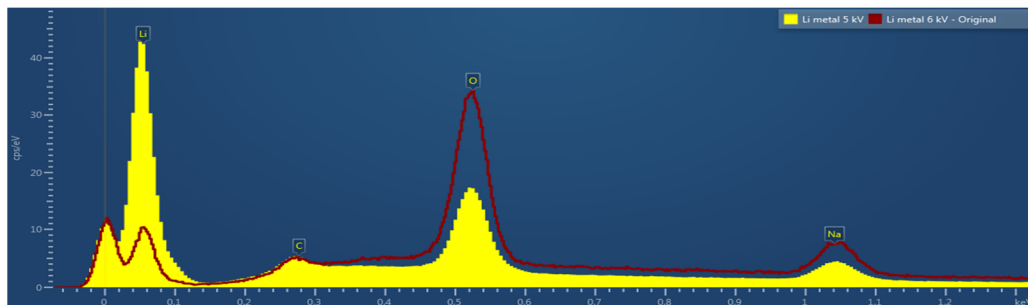
In order to calculate a composition or detection limit, the detected X-ray intensity must vary linearly with the beam current. In Fig 2 we are showing a spectrum on LiF taken using a spot mode compared to a spectrum taken in the image mode. All spectra were taken at 2 kV using the same beam current (1nA) and the same live time (30 sec). We clearly see that the spectrum taken in a spot mode contains a much higher Li K signal and a much lower F K peak than the one taken using the area mode. Fig 2 also shows severe beam damage after the spot mode acquisition (30 secs). During acquisition in spot mode, we also noted that the increase of Li intensity with time is always accompanied by a decrease of F. This change in intensity with time and beam current will greatly affect the detection limit. It is also important to note that pure Li and Li<sub>2</sub>S are showing constant X-ray emission with time.

It is also important for the calculation of the Li K detection limits to gain an insight into the physical origin of the significant differences of Li K intensities for different lithium compounds, since the electrons responsible for the X-ray emission are also involved in chemical bonding. Hence, it is possible that transitions responsible for Li K emission in some compounds can be changed and even decrease to an undetectable amount. Therefore we performed first-principles theoretical simulations of X-ray emission spectra (XES) for a series of Li-based systems. Fig 3 shows calculated XES spectra for metallic Li (BCC lattice), LiF, and LiCl crystals. The energy position in eV is relative to Li K in metallic Li. Assuming the Li atom has been ionized by an incident electron, the plots show the relative theoretical X-ray emission of a single Li atom in different chemical environments. This shows that there is a large variation in effective emitted X-ray intensity for different Li compounds and the intensity and peak position is affected by chemical composition. Those variations are not taken into account in the entire traditional model of quantification.

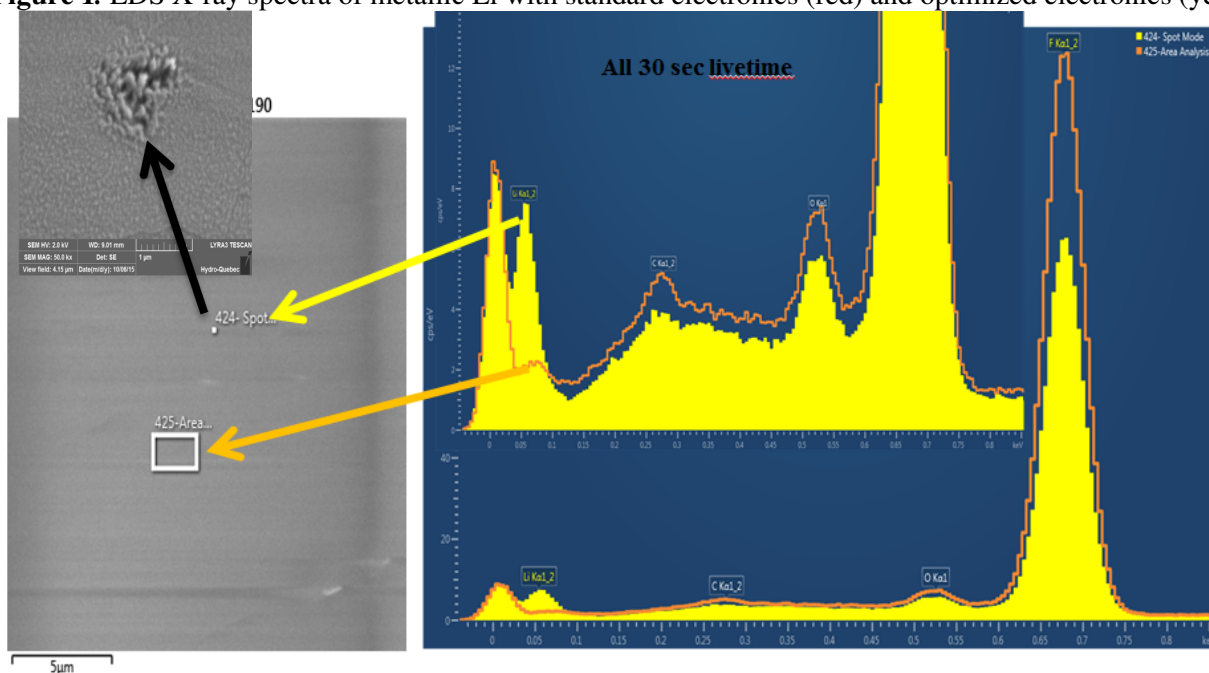
In conclusion, the determination of the detection limits for one element and a given analytical method is of key importance. However, for the Li K using 'Li-compatible EDS' it is strongly dependent on the detector condition, sample analyzed, condition used and samples chemical bonding structure. Several other parameters will be presented and other techniques to carry out Li detection and quantification at high spatial resolution will be discussed.

### References

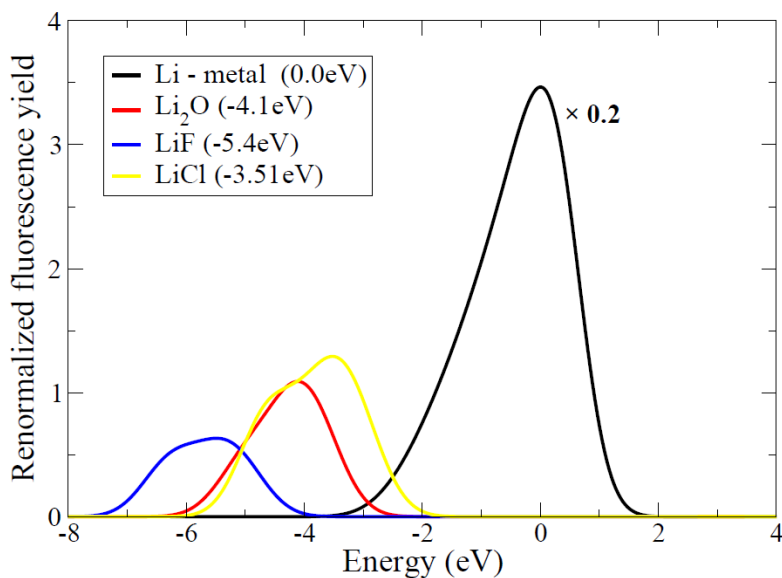
[1] P. Hovington *et al*, Scanning, Vol. 38, Nov/Dec 2016, pp. 571-8



**Figure 1.** EDS X-ray spectra of metallic Li with standard electronics (red) and optimized electronics (yellow)



**Figure 2.** EDS X-ray spectra from LiF taken at 2 kV (1 nA) in spot and area mode. Also shown, a higher magnification micrograph of the region after acquisition in spot mode showing severe beam damage.



**Figure 3.** Calculated X-ray emission spectra for metallic Li (BCC lattice),  $\text{Li}_2\text{O}$ , LiF, and  $\text{Li}_2\text{S}$  crystals. The energy position in eV is relative to Li K in metallic Li. Assuming the Li atom has been ionized by an incident electron, the plots show the relative theoretical X-ray emission of a single Li atom in different chemical environments. This shows that there is a large variation in effective emitted X-ray intensity for different Li compounds and the intensity and peak position is affected by chemical composition.