Very low energy peak shifts in EDS spectra

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Abstract. The response function of energy-dispersive X-ray spectrometers (EDS) has been a topic for investigation as long as EDS has been used. This work systematically investigates soft X-ray peaks with energies below 150 eV in regard to the detector energy calibration linearity. It was found that Si-L (92 eV) and Al-L (73 eV) lines are not shifted in energy position in comparison to higher energy K-lines of boron, carbon and nitrogen. The reason is simply the silicon detector material has a large absorption jump at 99 eV (Si-L₂/Si-L₃), which causes much higher detection depths of photons with energies below 99 eV. There is also less shift than assumed with older approaches in the energy region 100 to 149 eV (Si-L₁). It is also expected that Li-K radiation will not be affected by an energy shift due to detector artefacts. The authors propose a modified shift-correction which corrects this detector artefact and linearizes the energy calibration of measured EDS spectrum below 600 eV. This energy shift effect of the measured X-ray lines is in principle with any silicon-based X-ray detector. But the shift value depends also on the front contact layer design and quality. The novelty with changed correction is that no shift is applied for X-ray peaks below 99 eV. Older applied correction procedures were found to produce a line energy misplacement in spectrum for this energy region.

1. Introduction
The response function of energy-dispersive X-ray spectrometers (EDS) was a topic of investigation for as long as EDS has been used. Heckel and Scholz [1] and Scholze and Procop [2] developed a full physics-based models, which allows the calculation of the detector response function dependent on detector construction parameters and on the measured X-ray energies. It is known [2] that the low-energy side of the detector response function (peak shapes) depends much on the detected photon energy. It is affected by how deep the X-rays interact with the detector material to create an electron-hole pairs cloud. If the interaction is near the detector surface, electrons can likely escape and then the total measured energy of the photon is with a loss due to different effects of incomplete charge collection (ICC) [2]. With photon energies below 500 eV, the typical low-energy tailing in peak shapes morphs into ‘all photons ICC’, resulting in a complete peak shift to lower measured energies than the predicted X-ray energy. Usually the photon interaction depth is reduced at lower energies, so the shift is increasing. In [2], the X-rays in the energy range from 100 eV to 10 keV were investigated for three spectrometer systems different in construction, including one being an SDD.
2. Method
An empirically measured numerical shift-correction algorithm is used with EDAX software as a fast processing spectrum correction with energies below 600 eV. Despite being empirical, this shift-correction is derived from principles with the detector physics. The goal of this approach is to correct a measured spectrum for the detector artefact, which results in a non-linear energy calibration due to the detector response. The corrected spectrum is then linear in energy calibration and the low-energy peak positions are correctly measured at their theoretical X-ray energy positions (Fig. 1). All further qualitative and quantitative spectrum analysis can be applied after the linearization of the spectrum energy-axis, including peak deconvolution algorithm with theoretical generated line-series shapes based on well-known X-ray data tables.

![Figure 1. Original measured X-ray spectra (blue lines) versus original shift-corrected spectrum (red bars) in comparison with line-markers which represent the tabulated X-ray energies of several low energy X-ray lines (4.98 eV/channel energy calibration with 10 eV offset).](image)

All peaks on the corrected spectra fit the expected X-ray line energy positions, except Be-K, which looks slightly overcorrected with 5 or 6 eV deviation instead of the expected 108 eV. This discrepancy was never investigated further.

3. Experimental
The more recent solid state detector (SDD) technology [3] and X-ray entrance windows [4] (Fig. 2) allow the investigation of X-ray energies below 100 eV.
Figure 2. X-ray attenuation of several 40 nm thick Si₃N₄ atmospheric windows measured with synchrotron [4]. The window is additionally coated with a thin Al-layer to protect against visible light.

Whereas the much thicker polymer windows (300 nm) are not, the new atmospheric window type is transparent to soft X-ray below 100 eV. The SDD detector has no metallic contact layer and has only a thin 40 nm thick SiO₂, ideally designed for low-energy detection. Therefore, the EDS spectrum contains X-rays with less energy than 100 eV, and Si-L (92 eV) and Al-L (73 eV) can be clearly detected (Figs. 3 and 4).

Figure 3. Original measured Si sample spectrum (blue line) versus original shift-corrected spectrum (red bars). The Si-L (92 eV) is with about 10 eV overcorrected with the original shift correction algorithm and misplaced in energy.

4. Theory
There was first a surprise as the X-ray peaks below 100 eV photon energy did not match the theoretical energies after the original shift correction (Figs. 3 and 4). Following the detector physics-based model understanding, the known peak-shift is based on a total incomplete charge collection; all detection events
with these photon-energies generated electrons are affected by ICC for the voltage jump in the charge-sensitive preamplifier. Therefore, it is required to investigate the excitation depth of photons energy below 100 eV in the detector material (Si).

There is little information about X-ray attenuation length (absorption) in material with energies below 100 eV but can be found at the ‘Berkeley Lab’ online sources [5] (Fig. 5). The X-ray attenuation length values with energies below 500 eV in silicon supports the original shift correction approach. The depth of photon excitation in SDD detector drops to 100 nm and less, which is the order of magnitude for the contact structures of the silicon detector surface. However, due to the Si-L jumps, the depth of excitation becomes much larger for photon energies below 100 eV than it is, for instance, for carbon Kα (277 eV).

Figure 4. Original measured Al sample spectrum (blue line) versus original shift-corrected spectrum (red bars). The Al-L (73 eV) is with about 11 eV overcorrected with the original shift correction algorithm and misplaced in energy.

Figure 5. X-ray attenuation length for Si [5], the detector material.
5. Results

Due to the Si-L absorption edge (Si L$_{2,3}$ at 99 eV and Si L$_1$ at 149 eV), the EDAX-used original shift-correction approach needs to be modified for photon energies below 149 eV. The attenuation length in silicon with photons of energies below 99 eV is like the photon energies above 500 eV (Fig. 5), therefore no peak-shifts are normally observed. This is an evidence for the shift effect being due to detector material and design properties, and not due to electronic effects or a non-linearity of the energy calibration.

The original empirical shift-correction applies a moderate linearly decreasing shift correction between 0 and 350 eV and a stronger decreasing correction until 550 eV. We propose a new shift-correction that is reduced below 149 eV to be consistent with the Si L$_1$ edge effects mentioned above, and which drops down to 0 shift below 99 eV (Fig. 6). With this new correction, the measured shifts of Al-L and Si-L are essentially zero, and the Be shift is less than with the original correction. The corrected spectrum with modified shift-correction have finally a perfect linearity in the energy axis (Fig. 7).

![Shift of Low-Energy X-rays](image)

Figure 6. Modified shift correction (blue line) in comparison to the former used curve (grey line). The change is with energies below 149 eV (Si L$_1$) and it drops down to zero shift with energies below 99 eV (Si-L$_2$/Si-L$_3$).

6. Conclusions

It is possible to describe the energy shift-effect of the detector response function with an empirical algorithm and to correct this artefact to get linear energy axis spectrum. The new algorithm proposed in this paper accurately corrects the shift effect also below 100 eV. Indeed, no shift-correction is needed with these X-ray energies. Thus, it is not required to modify the known soft X-ray line energies data, if the presented shift-correction modification is used (Fig. 6). The investigation of the low-energy peak shifts requires a clear view of the real zero-point of the energy calibration with the measured X-ray spectrum (the electronic setup of digital pulse processor). The used energy calibration for the linearized X-ray axis was with 4.98 eV/channel with an energy offset of 10 eV. The maximum shift we have
**Figure 7.** Original measured X-ray spectra (blue lines) versus shift-corrected spectra (red bars) by using the modified approach, in comparison with line-markers which represent the tabulated X-ray energies. The corrected peak positions are now no longer shifted in energy.

observed with boron-K was with about 2 channels. In consequence of this work, it is recommended to use Al-L and Si-L lines for calibration of detectors to determine the real offset (absolute part) of the linear energy calibration.

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**References**
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