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Evaluation of Sensitivity of Multivariate Statistical Analysis on STEM Spectrum-Imaging Datasets and its Improvement

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Aberration-corrected scanning transmission electron microscopy (STEM) is the essential approach for atomic-scale characterization towards advanced materials developments. Not only atomic-scale imaging but also chemical analysis via electron energy-loss spectrometry (EELS) and X-ray energy dispersive spectrometry (XEDS) can be performed routinely by using the latest aberration-corrected STEM instruments [e.g. 1]. It would no longer be a dream to apply chemical analysis at atomic scales with single-atom detection sensitivity. In combination with the latest hardware, the advances in the recent software developments allow us to acquire large-scale datasets such as multidimensional image series and spectrum images (SIs). Although the trend to acquire large-scale datasets is desired, it is more challenging to deal with the large-scale datasets, e.g. extraction of unknown features and estimation of dominant trends. If the datasets are relatively noisy, which is very common for atomic-resolution EELS/XEDS SIs, data analysis would be much harder tasks. Multivariate statistical analysis (MSA) is one of efficient approaches to analyse the large-scale datasets in terms of feature identification and extraction [2, 3]. Since a use of MSA is relatively straightforward, various MSA approaches have been applied to SIs as data-mining and noise-reduction tools [e.g. 4]. Despite that the MSA approach is very efficient and useful, it may create unexpected artifacts especially in higher noise conditions [5]. Since these artifacts might mislead results, it is essential to explore the sensitivity of MSA. In this study, the MSA sensitivity will be evaluated by using SIs simulated to match atomic-resolution analysis conditions. Then, procedures to improve the MSA sensitivity will be proposed.

In order to evaluate the MSA sensitivity, first X-ray spectra were simulated for 40-nm-thick Cu-Mn alloys using NIST Desktop Spectrum Analyzer package [6]. In the simulation, the acquisition time and the beam current were set as 0.2 s and 0.2 nA, which are typical for the atomic resolution XEDS analysis. Once X-ray spectra were simulated, Poisson noise was applied and SIs with 10x10 pixels were synthesized. As shown in Fig. 1, an X-ray spectrum of Cu- x wt%Mn alloys (x = 20, 10, 5 and 2) is placed at only one pixel out of 100 pixels (rest is pure Cu) in the synthesized SIs. It should be noted that the Mn Kα peak height is higher than random noise at 20 and 10 wt%Mn, almost same at 5 wt%Mn and lower at 2 wt%Mn. By applying principal component analysis (PCA), the single pixel variation was detected for SIs with 20 and 10 wt%Mn spectra. However, when the peak variation is in the noise level or below, PCA does not detect the single-pixel feature. After the PCA application, noise-reduced SIs were reconstructed with two dominant components. Then, the integrated intensity of Mn Kα line in reconstructed SIs is quantitatively compared from that in the original clean and noised spectra. Figure 2(a) compares those three spectra for 10 wt%Mn and the summary of comparison is shown in Fig. 2(b). There is no difference in the measured intensity above 10 wt%Mn. However, significant intensity reduction can be seen in reconstructed spectra below 5 wt%Mn. This result indicates that the PCA reconstruction process may modify absolute signals when the signal variation is in the random noise level or below.

There are two approaches to improve the MSA sensitivity: (1) reduction of random noise and (2) enhancement of true variations. The former requires modifications in experimental conditions (higher currents and longer acquisitions). Conversely, the latter can be achieved by PCA analysis to divided small segments within a SI, which is called the local PCA approach. The division can be made (a) spatially and (b) spectrally. Especially the spectrally local PCA is useful for EELS SIs since the background intensity varies significantly. Advantages of the local PCA approach will be addressed.

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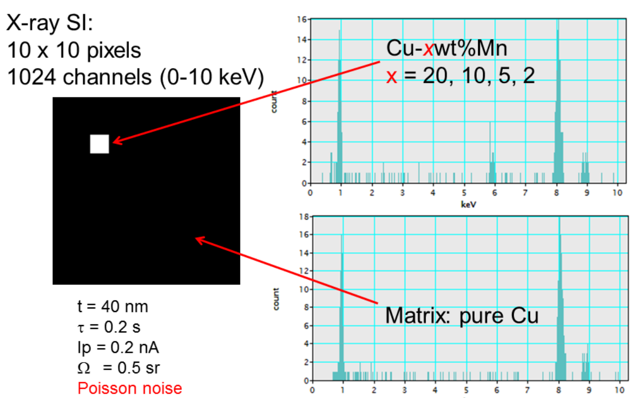

Figure 1: A schematic model of simulated SI and summary of conditions.

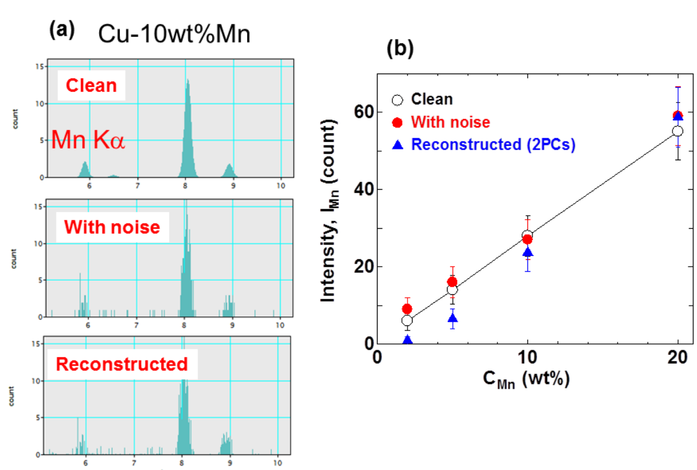

Figure 2: Comparisons of (a) the original (clean and noised) and reconstructed spectra from Cu-10wt%Mn, and of (b) the measured Mn Kα intensity, plotted against the Mn composition.

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