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Mapping Data with Heavily Overlapped Spectral Features

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It is well-accepted that multivariate methods for the analysis of spectrum image (SI) datasets present several advantages compared to peak integration or top-hat filtering methods, especially in presence of peak overlap or a low signal-to-noise ratio [1]. Multivariate curve resolution alternating least squares (MCR-ALS) have emerged as a blind method to segment SI. Compared to principal component analysis, MCR-ALS yields spectra and maps that are physically sound (positive pixel counts and components sum to unity). Another method, which considers log-likelihood maximization (MCR-LLM) based on the noise characteristics, has shown superior sensitivity and precision compared to MCR-ALS, especially for low-count data [2]. Here, using Monte Carlo simulations, we demonstrate that MCR-LLM is also able to segment SEM-EDS SI exhibiting strongly overlapping peaks much more reliably than MCR-ALS.

A $10\ \mu\text{m} \times 1.56\ \mu\text{m}$ sample (Fig. a) composed of three regions of Co in a Fe-Ni matrix (49.5Fe: 49.5Ni:1Co, 49Fe:49Ni:2Co and 47.5Fe:47.5Ni:5Co) was simulated to present severe peak overlap of the Co analyte (Fe K_β with Co K_α and Co K_β with Ni K_α) (reference spectra, Fig. b). The sample was made sufficiently thin (200 nm) to avoid non-linear matrix effects. The map data for various dwell times (50 ms, 100 ms, 500 ms, 1 s, 5 s, 10 s, 50 s, 100 s) were generated using MC X-ray [3] and a Python script. The Monte Carlo program first generated the emitted spectrum for each pixel without noise (beam current of 1 nA) and a nominal number of electrons was calculated. Three sources of noise were added: 1) Gaussian electron gun shot noise 2) Poisson noise on emitted X-rays (solid angle of 1.4 msr) 3) Gaussian electronic noise (50 eV) and detection noise. A typical spectrum for a dwell time of 5 s is shown in Fig. c. MCR-ALS and MCR-LLM were carried out using two components. The segmented spectra should in principle correspond to the end members of the map (49.5Fe:49.5Ni:1Co and 47.5Fe:47.5Ni:5Co).

A visual inspection confirmed that MCR-LLM was able to segment the three regions for dwell times down to 5 s (Fig. d) with calculated spectra corresponding to the expected end members (Fig. e). The Co K_α peak appears as a shoulder to the Fe K_β for the Co-rich component end member (Fig. e, red curve) and comes with a consistent decrease of the Fe and Ni peak intensity (Fig. e, insert). At this dose, MCR-ALS maps (Fig. f) and spectra (Fig. g) are inconsistent. With MCR-ALS algorithm, an acceptable segmentation becomes only possible at a dwell time of 50 s (10x that required by MCR-LLM).

Further work will focus on the precision and the detection limit of the spectral components and the maps computed using MCR-LLM. This will be accomplished by a combination of comprehensive simulated datasets and experimental references.

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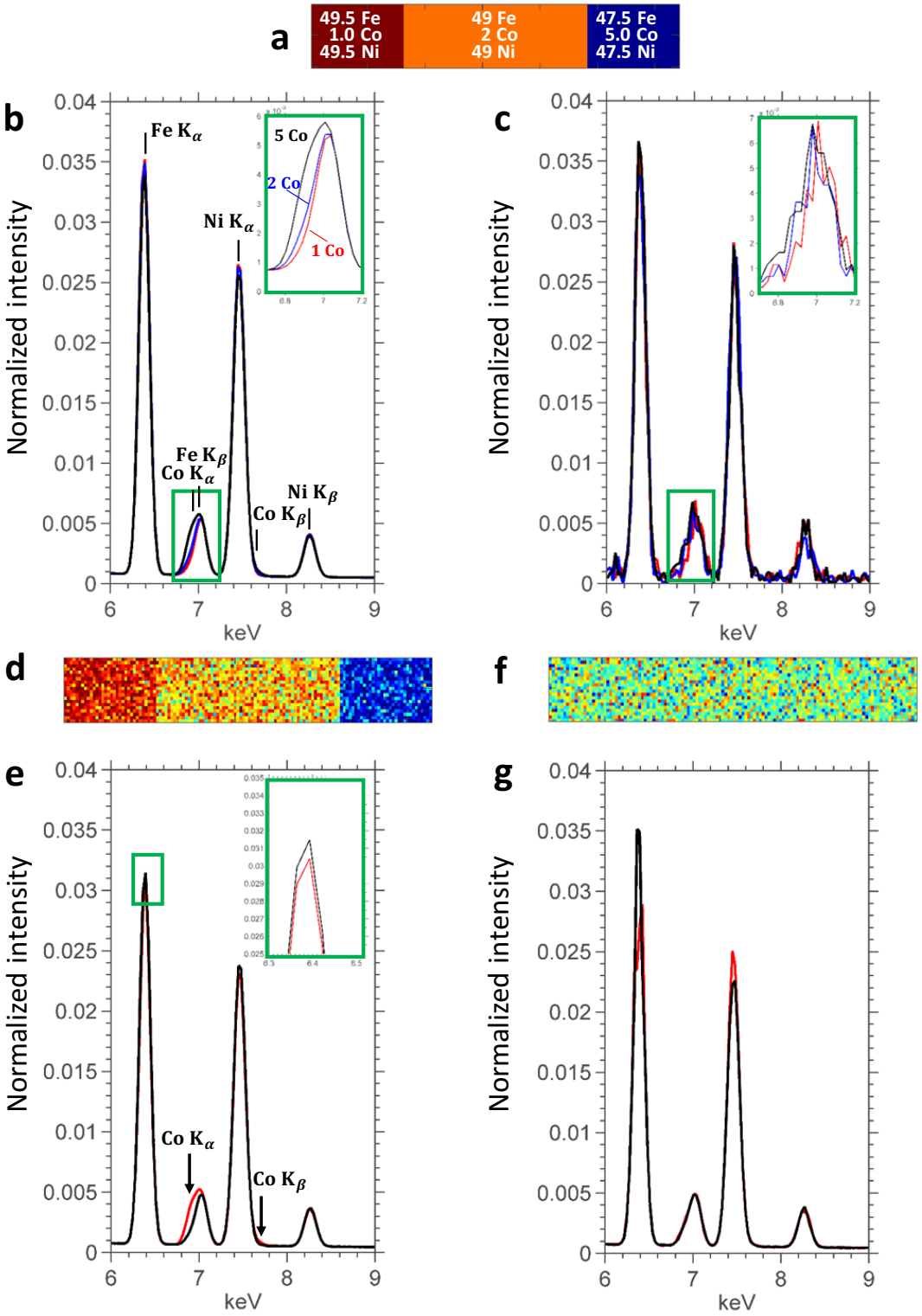

Figure 1. (a) Simulated sample with 3 separate compositions (128 pix X 20 pix). (b) Reference spectra: 49.5Fe:49.5Ni:1Co (red), 2Co (blue) and 5Co (black). (c) Same as (b), but for one relevant pixel taken from each zone (5 s dwell time). Insert shows details of the Fe K_β and Co K_α peaks overlap. (d) Calculated map using MCR-LLM (5 s dwell time) and corresponding end member spectra (e). Insert highlights the difference in Fe K_α peak intensity. (f) Calculated map using MCR-ALS (5 s dwell time) and corresponding end member spectra (g).

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