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 µm×1.56 µm 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 Kα with Co Kα and Co Kβ with Ni Kα) (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 Kα peak appears as a shoulder to the Fe Kβ 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.

References:

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$_\alpha$ and Co K$_\alpha$ 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$_\alpha$ peak intensity. (f) Calculated map using MCR-ALS (5 s dwell time) and corresponding end member spectra (g).