What Can You Do With a Million X-rays?

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Energy-dispersive X-ray spectroscopy (EDS) is a widely adopted characterization technique used for qualitative and quantitative chemical analysis in a broad range of scientific and industrial applications. Advances in detector design and digital pulse processing in recent years have enabled EDS analysis at high throughputs and with excellent spectral resolution. Throughputs in the order of 100,000 stored counts/s are now routine, allowing for a point-mode analysis with precision down to 1% of weight concentration to be completed in a few seconds. However, X-ray throughput remains a significant bottleneck to high-speed EDS analysis, especially for spectral imaging. For example, even with 1 million X-rays collected (that is, after 10 seconds of acquisition time with the above throughput), a conventional spectral image with a spatial resolution of 768 x 512 pixels contains only 2.5 counts per pixel on average. To enable an accurate analysis of such a sparse data set, we argue that advanced computational methods can be combined to significantly shorten the time needed to achieve high-quality outputs. In this work, we demonstrate and compare the efficiency of three fundamentally different yet complementary computational methods for spectral imaging: (1) gross count mapping as a reference method, (2) standardless quantitative mapping, and (3) phase analysis based on multivariate statistical analysis.

For comparison (see Fig. 1), we present all three methods with a spectral data cube of 1 million X-rays, collected over a sample containing four different phases, namely Zinc sulfite, Galena, Tetrahedrite, and Quartz. In Fig. 1, the first column shows the conventional spectral maps obtained with gross count mapping. Here, every pixel represents the number of counts corresponding to a specific element line which is the simplest approach algorithmically. However, the resulting map clearly does not account for peak overlaps, background effects, and geometric artifacts.

This can be solved by the method of quantitative mapping, as shown in the second column of Fig. 1. Unlike gross count mapping, here the pixels are grouped into (traditionally square-shaped) segments to increase the counting statistics, and subsequently, each region is processed using the same quantitative approaches that would be used in the conventional point-mode analysis. In particular, we used standardless peak fitting with peak deconvolution by linear least squared fit, and Phi-rho-Z (PROZA) [1] matrix corrections routines to infer the concentrations with high accuracy. To further increase the spatial accuracy of the spectral map, we employed a feature-based segmentation algorithm based on [2] in which individual features in the electron image are detected through computer vision and the spectra were analyzed over the sample-dependent regions rather than square-shaped regions. Multiple layers of these feature-based regions with increasingly finer resolution create a hierarchy where segments from one layer break down to finer segments in a lower layer as more counts are collected to achieve the highest possible spatial resolution without compromising the overall spatial or spectroscopic resolution. While the spatial accuracy and detection of individual chemically significant regions were greatly

improved, the results may be ambiguous in the case of complex samples containing multiple phases with similar elements. The algorithm will then produce quantitative maps where each elemental map can spread over multiple phases. In Fig. 1, only the Cu and Sb maps (Sb is not displayed in Fig. 1) clearly show the small Tetrahedrite phase separated from Zinc sulfide (because Tetrahedrite contains both Zn and S), making it more demanding for an operator to reach the correct conclusion.

In the third approach, we break the implicit assumption of the independence of individual pixels or sample regions by performing component-based phase mapping using multivariate statistical analysis. Here, the dominant components within the entire spectral data cube are computed and used to define the elementally unique phases [3]. The components are calculated by determining the variance-covariance of the data and then creating a matrix of the variances, from which matrix transformation calculations eigenvectors and eigenvalues are determined. Such an approach performs particularly well on sparse data sets, as it is less susceptible to noise despite no prior knowledge of the elemental constituents or their relationships within the data set. As the third column of Fig. 1 shows, the phase mapping algorithm correctly finds four phases where the discrimination of Tetrahedrite from Zinc sulfite was clear along with the accurate isolation of the Galena phase, without trading off the spectral or spatial resolution.

In this paper, we demonstrated that computational methods including feature-based quantitative mapping and multivariate phase analysis can greatly improve the accuracy and information content of spectral maps, thereby reducing the time to data and accelerating EDS workflows in science and industry. Due to recent advances in computational power and algorithmic techniques, the presented approach applies to both offline and live EDS use cases, and thereby positions EDS even stronger as a ubiquitous and fast analysis technique.

References:

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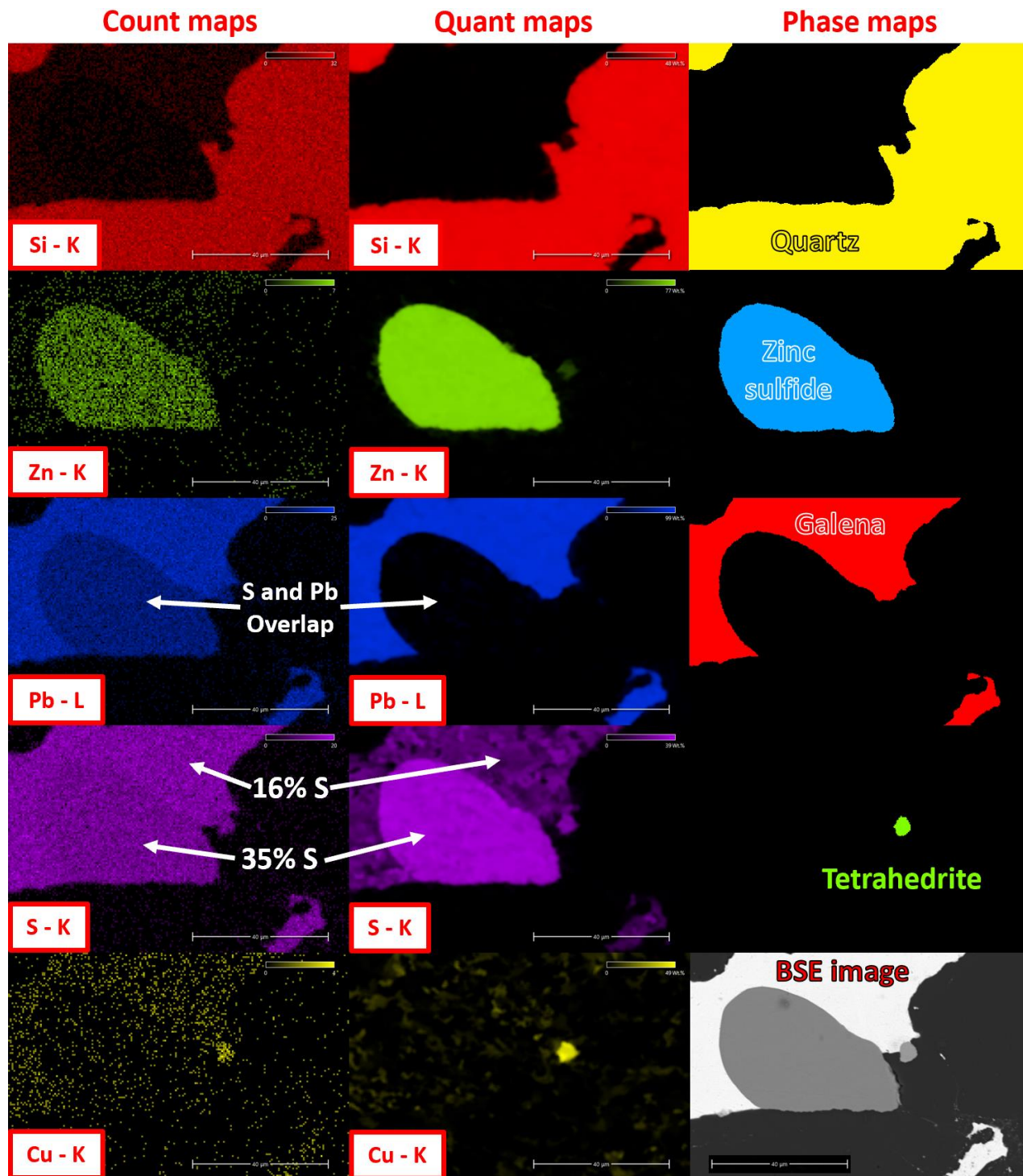[3] Kotula, P., Keenan, M., and Michael, J., Microscopy and Microanalysis **9** (2003), p. 1.

Fig. 1: EDS mapping of a sample containing four phases: Zinc sulfide (ZnS), Quartz (SiO_2), Galena (PbS), and Tetrahedrite [$(Cu,Zn,Ag)_{12}Sb_4S_{13}$]. The left column of images shows count maps (4x4 segmentation) of the individual elements that can be compared to the quant maps (object segmentation) in the middle column. S overlaps with Pb, and the quant maps show the deconvolved elemental layout while the count maps do not show Pb and S correctly and cannot distinguish between the two S concentrations in Zinc sulfide and Galena. The right column shows the phase map images correctly recognizing the four phases that can be consecutively quantified or matched to a database. BSE image is provided as a reference. The EDS dataset contains 1 million integral counts (2.5 counts per pixel) and was acquired using HV=15 kV. O, Sb, and Ag count/quant maps are not displayed.