

## ChemiSEM: multimodal approach for faster quantitative elemental mapping.

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Scanning electron microscopy (SEM) combined with energy dispersive spectroscopy (EDS) has become one of the most frequent analytical techniques at the micro- and the nanometer scale, with extensive applications in material research, failure analysis and geology. Typically, SEM-EDS analysis provides the answers to three essential questions: (1) location of the investigated object on the sample, (2) the morphology and SEM contrast of the object and (3) the chemical, or elemental, composition of the object and its surroundings. Traditionally, analysis of the chemical composition with a decent analysis resolution was time consuming, even with the introduction of silicon drift detectors and large increases of their active area, elemental mapping with high spatial and chemical accuracy has remained a daunting task. Here, we present a novel method for real-time quantitative mapping in a tightly integrated SEM-EDS system which makes use of the simultaneous acquisition of data in both SEM and EDS modalities, and evaluate its performance against conventional EDS mapping approaches.

In SEM-EDS, secondary-electron (SE) or backscattered-electron (BSE) images can be acquired in real time at pixel dwell times down to 50 ns or less, and characteristic X-rays used to form the EDS chemical maps can be acquired simultaneously at the same high speeds. However, EDS data acquired at short dwell times are typically too sparse to deliver analytically relevant X-ray maps. This can be partially alleviated by improving detector solid angle and electronics at high system costs, but nonetheless forces many SEM users to sacrifice the quality of the resultant analysis by lowering the EDS resolution to speed up the acquisition.

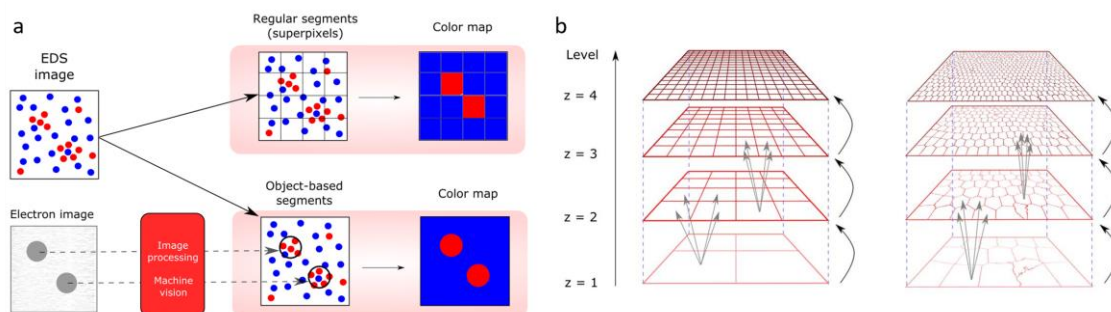
In ChemiSEM [1], the trade-off between acquisition speed and image resolution of the EDS maps is addressed by combining multiple signal modalities that are readily available in a tightly integrated SEM-EDS system. The key idea is that the BSE and SE images are acquired simultaneously with the X-ray data and used to register detected X-ray photons to the features seen in the electron images (see Figure 1). In contrast to conventional regular binning, machine vision algorithms are used to analyze the contrast and shape of the actual sample-defined features present in the SE and BSE images, and subsequently these are used to segment the area of interest into a hierarchy of object-based superpixels with variable spatial resolution over which the spectral analysis is done (see Figure 2).

Similar to conventional X-ray mapping routines, all X-ray photons assigned to an object-based superpixel are processed together using standard-less quantification to infer the chemical composition of the area. Optionally, a color is assigned to the respective area of the superpixel representing the relative concentration of chemical elements and plotted to the EDS map. A significant advantage is that the hierarchy of the superpixels can be used to dynamically increase the resolution based on the quality and availability of EDS data which vary for different materials and areas of the sample. As the data acquisition continues, the number of counts in each particular superpixel increases and upon reaching a threshold, the superpixel is broken down to smaller superpixels that are then re-processed and re-colored, independently of other superpixels. The continuous decrease of the superpixel size with increasing availability of data ensures that small compositional differences that were not identified in the initial SE or BSE image are

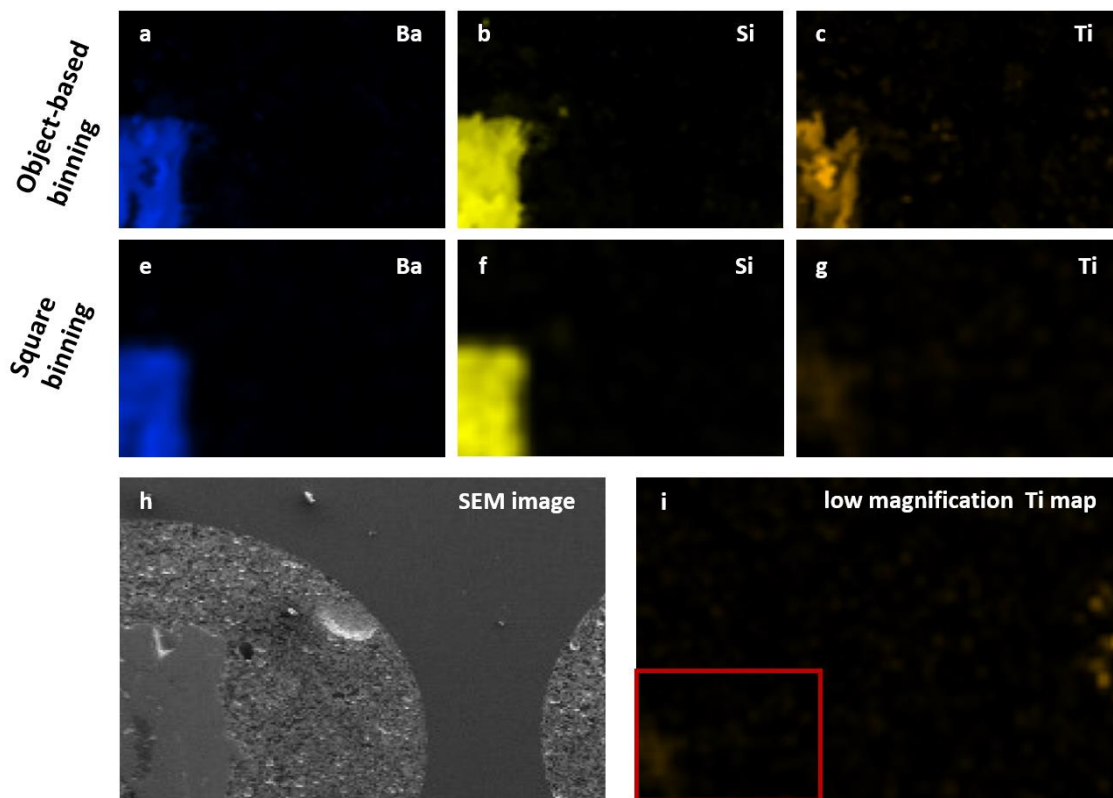
captured later. Processing of X-ray photons in each superpixel comprises on-the-fly standardless peak fitting with peak deconvolution by linear least squared fit, and Phi-rho-Z (PROZA) matrix corrections routines [2]. By doing so, overlapping peaks in the energy spectrum can be deconvolved, and even samples with complex composition can be analyzed in a timely fashion [3].

As a direct consequence of using the image-defined sample features for spectral analysis, the method described here enables a precise chemical analysis even at low numbers of acquired X-ray photons. Further, beam damage and charging of the sample can be significantly reduced, due to the significant reduction in achievable dwell time. We demonstrate this during the analysis of a benitoite mineral (see Figure 2). In the acquired data set, the benitoite phase only contains 65 thousand X-ray counts in total. Composition of the mineral comprises approximately 33 % of barium, 11 % of titanium, 20 % of silicon and 34 % of oxygen. While regular square pixel binning correctly assigned elements with higher concentration to the benitoite phase (Ba and Si in Figure 2d, 2e), titanium with lower concentration was allocated only poorly (Figure 2f) and majority of titanium was assigned to a wrong phase that in reality is titanium free (Figure 2i). This can only be avoided by enormous increase of the square bin size or by a significant increase of number of counts for square binning. In contrast, the method presented here used the fact that the benitoite phase could be identified in the SE image and all X-ray counts from that phase were processed together in object-defined superpixels (compare with Figure 2h). As a result, all elements including titanium were assigned to the correct phase (Figure 2a-c). Moreover, hierarchical processing of the superpixels resulted in sharper and better-defined quant maps.

In summary, we showed that combining multiple modalities available in an integrated SEM-EDS system enables the generation of accurate quantitative elemental maps from sparse EDS data and hence speeds up the acquisition of accurate EDS maps. On top of that, it can be synergistically combined with conventional EDS functionality such as Point and ID or Line Scan that complements the mapping results and ultimately leads to workflows requiring significantly shorter time to data.



**Figure 1.** Schematic representation of the difference between regular pixel binning and object-based segmentation (a) and their gradual decomposition into smaller segments (b).



**Figure 2.** Barium, silicon and titanium quant maps of a benitoite mineral obtained by objected based pixel binning (a-c) and traditional square pixel binning (e-g) together with corresponding SE image (h). Overview Ti map showing correct position of the Ti phase (red rectangle) indistinctly identified by square binning (i). The Benitoite phase contained 65 thousand x-ray counts only.

#### References

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