

Use of Partial Scattering EDX Cross-Sections to Quantify Light Elements in the STEM

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Energy dispersive X-ray spectroscopy (EDX) is a versatile tool within the scanning transmission electron microscope (STEM). Qualitative chemical maps may be obtained with good spatial resolution and relatively little effort for many samples, in contrast with the more labour-intensive data processing required to produce elemental maps using e.g. electron energy loss spectroscopy (EELS).

However, accurate quantification of EDX data remains challenging. The most common route to quantitative data is via the Cliff-Lorimer method, in which EDX peak counts are correlated with elemental concentration via a library of instrument-specific k -factors [1]. For reliable quantification, these k -factors must be carefully measured from standard compound samples of known concentrations, for every element present in the sample of interest. However, difficulties in obtaining thin-film standards with homogenous composition at the nanoscale mean full characterisation of a complex multi-element sample in this manner is a daunting task [2-4].

More recently, the ζ -factor method proposed by Watanabe and Williams has been shown capable of providing absolute measurements of a given element, in atoms per volume, by linking peak counts with mass-thickness via use of single-element reference standards [4]. Quantitative results depend on measuring this sample thickness, usually by analysis of the low-loss EEL spectrum. However, many (S)TEMs (especially those without aberration correction) are not equipped with an EEL spectrometer, and are therefore unsuited to use of the ζ -factor method.

In this paper, we will discuss our recent work developing the quantification of light elements using EDX partial scattering cross-sections, σ_{EDX} . Measurements of σ_{EDX} have previously been obtained for heavy elements such as platinum (Pt) and cobalt (Co) by measurement of single-element standards such as nanoparticles [5,6]. These measurements have subsequently been shown to be robust for quantification of e.g. bimetallic catalytic nanoparticles when compared with EELS. Recently, we have adapted this method to allow σ_{EDX} values to be measured without the need for any direct thickness measurement (**Figure 1**). Instead, quantitative annular dark field (ADF) imaging is used to estimate the number of atoms of particular species present at a particular site. Simultaneously collected EDX data may subsequently be processed to extract total peak counts. By considering electron dose, it is then possible to deduce σ_{EDX} values directly for any atomic species, without the requirement to obtain a single-element or thin-film reference sample. Elements in samples of interest may then be robustly quantified in units of *atoms nm*⁻².

We demonstrate measurement of σ_{EDX} for several elements with $8 \leq Z \leq 20$ (**Figure 2**), obtained using powder samples and with minimal sample preparation. We show that these values provide quantification results consistent with those obtained by EELS and ADF imaging, and discuss the potential applications of EDX partial scattering cross-sections to the characterisation of battery materials, biological structures and catalysts [7].

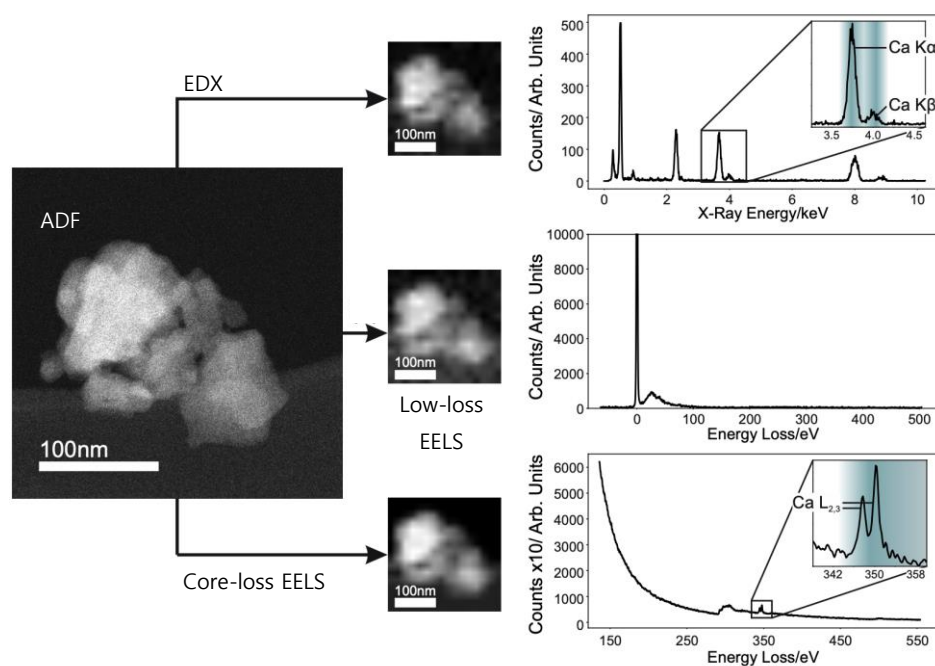


Figure 1: Schematic of data acquisition for measurement of σ_{EDX} from a calcium sulphate nano-cluster. Quantitative high-angle ADF imaging is used to estimate the number of calcium, sulphur and oxygen atoms within the cluster. Extraction of e.g. calcium $K\alpha$ and $K\beta$ x-rays may then be scaled by a factor determined by the experimental probe current and used to calculate σ_{EDX} . EELS data was also used for some elements to calculate experimental cross-sections for comparison with Hartree-Slater values and/or σ_{EDX} .

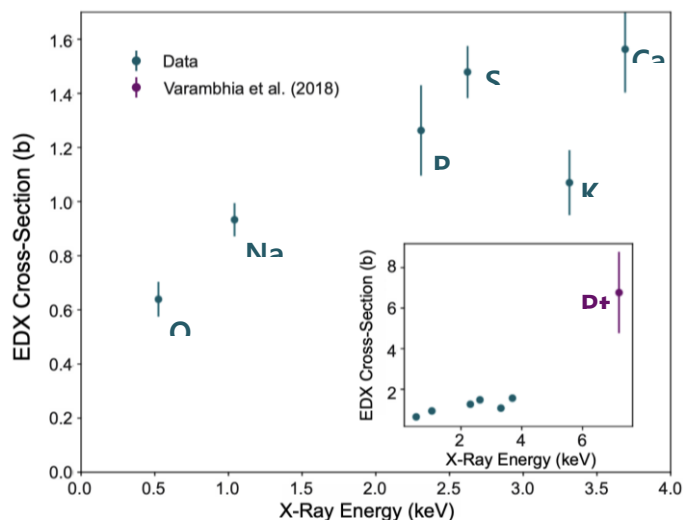


Figure 2: Values of σ_{EDX} for oxygen, sodium, sulphur, chlorine, potassium and calcium, measured from nanopowders of various compounds on the Oxford JEOL ARM200F. These values may then be used for any other quantitative EDX experiment on the same instrument.

References:

- [1] G. Cliff and G. W. Lorimer, *Journal of Microscopy* **103**(2) (1975), p. 203–207.
- [2] N. J. Zaluzec in “Introduction to Analytical Electron Microscopy”, eds. J. Hren, J. Goldstein, and D. Joy, (Springer, New York City) p. 129–168.
- [3] D. M. Longo, J. M. Howe, and W. C. Johnson, *Ultramicroscopy*, **80**(2) (1999), p. 85–97.
- [4] M. Watanabe and D. B. Williams, *Journal of Microscopy*, **221**(2) (2006), p. 89–109.
- [5] K. E. MacArthur et al., *Microscopy and Microanalysis*, **22**(1) (2016), p. 71–81.
- [6] A. M. Varambhia et al., *Micron*, **113** (2018), p. 69–82.
- [7] The authors acknowledge use of characterization facilities within the David Cockayne Centre for Electron Microscopy, Department of Materials, University of Oxford and in particular the Faraday Institution (FIRG007, FIRG008), the EPSRC (EP/K040375/1 “South of England Analytical Electron Microscope”) and additional instrument provision from the Henry Royce Institute (Grant reference EP/R010145/1).