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A New Method for the XEDS ζ-factor Measurement Through Modulation of Beam Current.

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Despite the introduction of the ζ-factor method over 20 years ago X-ray energy dispersive spectroscopy (XEDS) is often used in the Transmission Electron Microscope (TEM) in a qualitative or "semi"-quantitative manor using vendor supplied Cliff Lorimer k-factors [1]. While these offer ease of use to the analytical microscopist, inaccuracies due to absorption and microscope, detector and specimen geometries may result in systematic errors > 10 at.% [1,2]. ζ-factors for an element *i*, are measured from the XEDS Intensity (I_i) from standards of known composition (C_i) density (ρ) and thickness (t) for electron dose ($D_e = e\ i_0\ \tau$; number of electrons, probe current and acquisition time, respectively) and are quantified using the following relation [1]:

$$C_i = \zeta_i \frac{I_i}{(\rho t D_e)} \tag{1}$$

And the associated error is calculated using:

$$\Delta\zeta_i = \zeta_i \sqrt{\left(\frac{\Delta I_i}{I_i}\right)^2 + \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta i_0}{i_0}\right)^2 + \left(\frac{\Delta \tau}{\tau}\right)^2} \tag{2}$$

These microscope dependent ζ-factors for a particular element may be quantified using a single spectrum from a material of known composition, specimen thickness and electron dose are known [1]. Alternatively, one may fabricate wedge shaped samples using focused ion beam or mechanical polishing and determine the zeta factor by linear regression from thickness vs XEDS intensity [3] or even by sample volume vs XEDS intensity using electron tomography [4].

This work introduces two new methods (3 and 4 below) for ζ-factor measurement which seek to reduce systematic errors by measuring the ζ-factors as a function of beam current. Using beam current modulation has the following advantages over other thickness based techniques: (1) the probe current may be changed quickly and easily over 3 orders of magnitude whereas thickness measurements are limited ranges < 100 nm (due to absorption) (2) the probe current is independent of sample geometry whereas thickness based measurements require careful sample preparation to generate wedge-shaped samples, (3) using a faraday cage stochastic error from beam current measurements may be brought below 1% and the using method 3 as here removes any systematic or instrumental error.

Table 1: Comparison of the 4 measurement methods and associated errors

Mode of Measurement	**ζ-Factor (kg m^{-2} electron/photon)**	**Absolute Error (kg m^{-2} electron/photon)**	**% Error**
1: Individual point Spectrum	251	14.5	5.8
2: from a line scan (thickness modulation, fixed beam current)	231	13	5.7
3: from multiple point spectra using different probe currents	178	5.85	3.3
4: from multiple thickness line scans at different probe currents	223	10.7	4.8

Table 1 compares four measurement methods used to determine the Ga Kα ζ-factor from a GaAs standard. For all methods used the specimen was tilted 20° towards the detector, close to a 2-beam condition to allow thickness measurements to be made using convergent beam electron diffraction (CBED). In method 1 the ζ-factor is calculated from the Ga Kα intensity measured from a single spectrum using equation (1). Method 2 uses a line scan on a wedge-shaped sample, the line scan 'distance' is correlated to the sample thickness using a thickness map determined by CBED and HAADF intensity and the ζ-factor determined using linear regression. Method 3 uses multiple point spectra acquired at different probe currents and the Ga Ka intensity is normalized to thickness measured using CBED (figure 1a) and the linear regression is used to determine the ζ-factor. Finally, method 4 repeats method 2 for a range of probe currents (figure 1b), the ζ-factor is measured independently for each probe current with the mean and standard deviation are used as the ζ-factor and error respectively. Initial results and errors for each method are summarized in table 1, method 3 shows the lowest relative error.

This work introduces two new methods for the measurement of XEDS ζ-factors using probe current modulation. Probe current modulation (method 3) is demonstrated to reduce the measurement error by a factor of almost 2 and this is expected to improve using a larger range of probe currents in the future. These results will be repeated and verified on a double aberration corrected JEOL ARM300F2 with a dual XEDS detector configuration currently being installed at UNSW.

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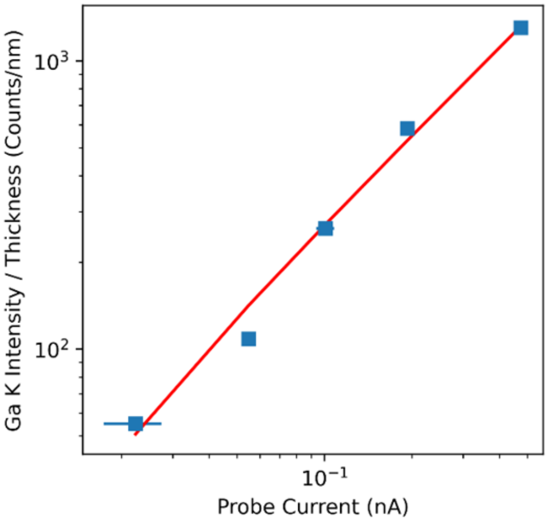

Figure 1. Demonstration of the ζ-factors determination by modulating the probe current measured using method 3

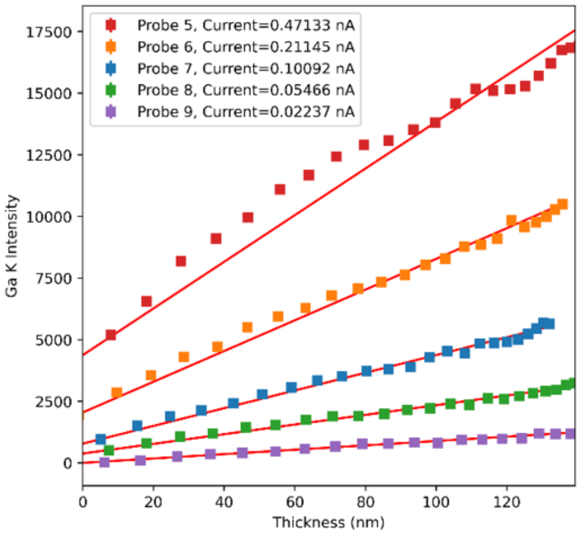

Figure 2. Demonstration of ζ-factors determination using method 4, Ga Kα intensity plotted against thickness for 5 probe currents.

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