

Determination of Compositional Variation of Bimetallic Nanoparticles by Direct Measurement of Mass Thickness Using EDS

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X-ray spectrometry in the transmission electron microscope (TEM) is widely used to characterise both the quantities and distribution of elements in nanoparticles. Understanding both these parameters and how they vary with particle size and shape is critical to the understanding of a particle's catalytic activity. Recently a number of techniques for determination of composition and volume to the atomic level have started to be used in this field. These include quantitative HAADF imaging [1], using atomically resolved energy dispersive X-ray spectrometry (EDS) or Electron energy loss spectrometry (EELS) as well as using combining all three of these techniques to generate quantifiable scattering cross-sections [2].

Typically using transmission mode EDS alone for quantification of these nanoparticles has proved inaccurate due to the difficulty of determining the local effects of X-ray absorption and fluorescence. This is essentially due to the difficulty of measuring the local thickness and density of a nanoparticle. These are parameters which control the accuracy of quantification using the Cliff-Lorimer k-factor method. Here, we have used a new method for quantification of EDS spectra that directly determines specimen mass thickness [3,4]. As a result of this, the mass thickness is automatically incorporated into the corrections for specimen absorption. The intensity of a characteristic X-ray for a given element A is defined as:

$$I_A = (\rho t)_{sp} \cdot C_A \cdot [N_0/A_A \cdot (Q_A \cdot f_A)] \cdot f(\chi)_A \cdot D_{sp} \cdot (\Omega/(4\pi)) \cdot \epsilon_A$$

By using a specially characterised Si₃N₄ thin film standard of known mass thickness and an EDS detector with known conversion efficiency, ϵ_A , microscope conditions, such as solid angle, Ω , and dose at the specimen, D_{sp} can be calibrated to allow quantitative measurement of mass thickness $(\rho t)_{sp}$ and composition C_A .

We compare this new x-ray method with the aforementioned quantitative imaging methods when used on the same needle shaped pure element standards. The method is then applied to pure element nanoparticles and bimetallic particles comprising these previously measured pure elements. Finally we show automation of this acquisition of these quantified EDS spectra to allow determination of variation in elemental ratio over a range of particles sizes.

[1] A.M. Varambhia et al, Particle & Particle systems characterization (2016), 33, 438-444

[2] K. E. Macarthur et al, Microsc. Microanal (2016), 22, 71.

[3] P. Statham et al, Microsc. Microanal (2016), 22, 38.

[4] P. Statham et al, IOP Conf. Ser.: Mater. Sci. Eng. 304 (2017), 012017