

EDS Mass-Thickness Measurements in the TEM: A New Approach to Quantitative Chemical Analysis of (Planetary) Materials?

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Coupled to an electron microscope, energy-dispersive X-ray spectroscopy (EDS) can provide both qualitative and quantitative information in the form of false-color maps and as (normalized) elemental abundances, respectively. Both kinds of information are critical for identifying two-dimensional compositional variations, and ultimately, as an aid to phase identification. Quantitative analysis is particularly important in planetary science because it allows for comparison to equilibrium thermodynamic predictions and therefore constraining fundamental parameters, e.g., pressure and temperature, that are central to chemical models of solar-system formation.

There are several approaches to quantitative EDS in the transmission electron microscope (TEM). Recently, a new approach was reported that involves a thin-film standard with known mass thickness but does not require measurement of beam current. This mass-thickness approach potentially offers a robust means of quantitative analysis without prior knowledge of beam current, and an alternative method to EELS for determination of sample thickness. Here we explore the mass-thickness approach to the analysis of SrTiO₃ (STO) with the goal of applying it more broadly to heterogeneous materials.

A Si₃N₄ mass-thickness standard was used for the beam measurement, which establishes the expected X-ray yield under a standard set of optical and detector conditions. Our Si₃N₄ sample was measured using a 200 kV aberration-corrected Hitachi HF5000 S/TEM, recently installed at the University of Arizona (UA), and equipped with an Oxford Instruments X-Max^N 100 TLE EDS system with dual 100 mm² windowless silicon-drift detectors. In addition to our Si₃N₄ reference, we measured a sample of [100] SrTiO₃ (purchased from Sigma Aldrich). All spectra were acquired in scanning TEM (STEM) mode with the sample tilted 10° clockwise about the sample-rod axis (α tilt) toward the right detector (the left detector was turned off).

The reference spectrum from the STO sample contains major (characteristic) peaks of Sr, Ti, and O together with Cu and minor Fe. The Cu peak originates from the support grid that holds the FIB section, and the Fe is an artifact peak likely from the pole piece, but both were deconvoluted prior to quantitative analysis. We quantified the spectra using both the CL and mass-thickness approaches. We find that the mass-thickness approach quantifies the STO sample to within 0.1%, 3.7%, and 4.0% of ideal stoichiometry for O, Ti, and Sr, respectively. In comparison, the CL approach indicates significant deviations from stoichiometry. The STO sample was probed further using the mass-thickness approach, and we find that spatial variation in detector occlusion can be observed using this methodology which would have been overlooked using either CL or the ζ -factor method. We hypothesize that this occlusion is due to differences in sample geometry between the Si₃N₄ reference sample and the FIB section. We will discuss the implications of these differences at the meeting.

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