

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

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The chemical origins of our solar system are stored within meteorites and other planetary materials, the solid relics leftover from its birth 4.5 billion years ago. Energy-dispersive X-ray spectroscopy (EDS) has been central to compositional analysis of such materials. Coupled to an electron microscope, 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 in planetary science for identifying two-dimensional compositional variations, and ultimately, as an aid to phase identification. Quantitative analysis is particularly important for planetary materials 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 the early solar nebula. Quantitative EDS has and will continue to be important for analysis of planetary materials including those we currently have in our collections and those to be returned by sample-return missions, e.g., Hayabusa 2 [1], OSIRIS-REx [2], and CAESAR [3] over the coming two decades.

In the transmission electron microscope (TEM), there are several approaches to quantitative EDS. For well over four decades, the ‘Cliff-Lorimer (CL) approach’ [4] has arguably been the most widely used method for quantitative EDS. By assuming a ‘thin-foil criterion’, i.e., that the sample is sufficiently thin so as not to absorb or fluoresce X-rays, the intensity of characteristic peaks are proportional to the elemental concentration multiplied by a detector sensitivity ‘k’ factor, determined by measuring reference standards. With sufficient counting statistics, 1% relative error is achievable. The CL approach is perfectly suitable for thin specimens but becomes problematic for thicker samples, where absorption and fluorescence can become significant. In comparison, the ζ -factor method utilizes pure element thin-film standards to derive a ζ -factor assuming X-ray yield is proportional to mass thickness [5]. However, this approach requires measurement of beam current, which requires a sample holder with an integrated Faraday cup. Recently, [6] reported a new approach involving a single standard. Briefly, a thin film with known mass thickness serves as a reference without the need to measure 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 planetary 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. The beam measurement was measured over a large (>250 nm) area and acquired until a total of 600,000 counts. The measurement was repeated to verify beam-current

stability within 2% of the initial value. In addition to our Si_3N_4 reference, we measured a sample of [100] SrTiO_3 (purchased from Sigma Aldrich) prepared with an FEI Helios focused-ion-beam scanning-electron microscope (FIB-SEM) also at UA, using previously described techniques [7]. All spectra were acquired in scanning TEM (STEM) mode using a 35 μm STEM condenser aperture (330 pA probe current) with the sample tilted 10° clockwise about the sample-rod axis (α tilt) toward the right detector (the left detector was turned off).

Figure 1 shows a reference spectrum from the STO sample. The major (characteristic) peaks of Sr, Ti, and O occur together along 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. Table 1 shows the quantification, in atomic %, together with the deviation from ideal stoichiometry for both methods. 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 Si_3N_4 reference sample and the FIB section. We will discuss the implications of these differences at the meeting [8].

References:

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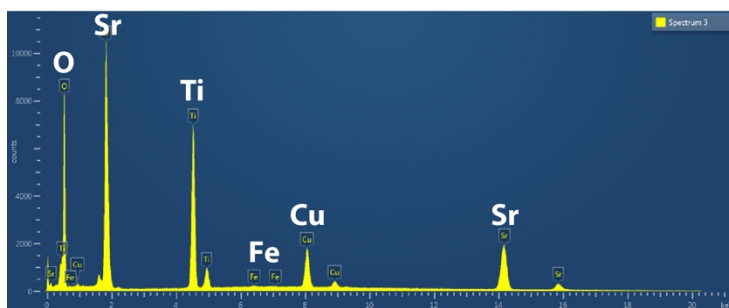


Figure 1 (left). EDS spectrum of STO. Cu and Fe are artifacts. **Table 1** (below). Quantification of STO spectrum using mass-thickness (MT) and CL approach. Difference (δ), relative to stoichiometry, shown in percent.

Table 1	Atomic %		δ (%) rel. to stoich.	
	MT	CL	MT	CL
O	60.07	52.65	0.1	12.3
Ti	20.74	24.51	3.7	22.6
Sr	19.19	22.84	4.0	14.2
Total	100	100		