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A Readily-automated Scheme for Estimating the Critical Dose of Beam-Sensitive Materials

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The probe used to measure a sample will often modify it in some way. The relative rates of data collection and sample modification become critical to understanding and validating an analysis. This is a common concern for electron microscopy of organic materials. A "critical dose" at which a signal has changed by a factor $1/e$ is used as a metric, following the assumption that features will evolve with electron dose (used interchangeably with fluence to mean electrons per unit area) as $f(x) = Ae^{-x/\tau}$, with a critical dose of τ [1]. This assumption is largely phenomenological—there is nothing inherently special about the value of τ—but it has become a useful metric for comparison amongst different materials.

For spectra or diffraction patterns, particularly those with multiple features that diminish or appear at different rates as a function of dose, estimating the critical dose is not always straightforward. Two common approaches are integration over a user-selected subset of the data, or a fit to a series of model features. There are relatively robust schemes for automatically generating models to fit peaks and backgrounds for simpler, mature cases like x-ray diffraction and energy dispersive spectroscopy (EDS). Cases like electron energy loss spectroscopy (EELS) and soft x-ray spectroscopies with heavily overlapping features and backgrounds still require manual creation of a fitting model. For EELS, the models are then both element and chemistry specific. This can lead to ambiguous reporting of critical dose or discourage reporting of critical dose altogether.

A readily-automated scheme for estimating an ensemble value of $\bar{\tau}$ would be useful, even at the expense of accuracy or a clear physical interpretation. To that end: as a first order approximation, the critical dose can be estimated by fitting each spectrum in a dose series to a linear combination of the initial spectrum and the final spectrum. This removes effectively all user input and works for an arbitrary set of signals with arbitrary dimensions, requiring only that features change monotonically with dose and that the reference spectra have sufficient signal to noise. For this work, the fitting has been scripted in Python with Hyperspy [2].

This abridged scheme can be compared to a manually generated model for an archetypal core-loss EELS series from a beam-sensitive polycarbonate thin film, collected at -170°C, at 200 kV, with an energy resolution of ~0.4 eV at *fwhm* (Fig. 1). Spectra were fit to a series of Gaussians, a power-law background, and an arctangent for the ionization edge. The components' fits variously yield critical doses of $\tau_{285.5\ eV} \approx 7800$ e/nm^2, $\tau_{287.3\ eV} \approx 6300$ e/nm^2, $\tau_{287.6\ eV} \approx 5700$ e/nm^2, and $\tau_{290.7\ eV} \approx 5300$ e/nm^2. A naïve average is $\bar{\tau} \approx 6300$ e/nm^2. Heavily overlapping shrinking/growing signals, like those at ~287.3 eV and ~287.6 eV, can artificially skew the analysis. The feature at ~290.7 eV, for instance, may also be better modeled by a pair of overlapping shrinking/growing features: not obvious without knowledge of the probable radiolysis products.

For the same dose series, a least squares fit to the initial and final spectra yields $\bar{\tau} \approx 6200$ e/nm^2 (Fig. 2). The value varies by < 500 e/nm^2 when the series is truncated by up to two spectra at either end of the

series, for this particular example. The error of the exponential fit is comparable to the fits of Gaussian components. In general, this self-referencing approach seems to bias slightly towards the most rapidly evolving features. It is not clear whether this should be more or less "correct" than alternative fitting models: the intent is rather an approach to measuring $\bar{\tau}$ that is sufficiently simple and reproducible that it might increase consistent measurement and reporting.

This approach can be applied to other spectra and patterns, including 2D patterns. It will be used to compare critical dose measurements for a semi-crystalline polymer using EELS and electron diffraction, approaches that have often been found to give inconsistent results.

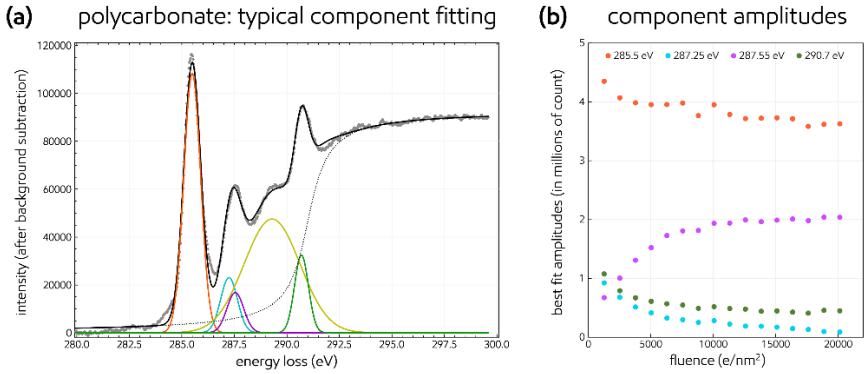

Figure 1. (a) Typical fitting of the carbon K-edge of polycarbonate to a series of Gaussians, a power law background, and an arctangent model for the ionization edge. The positions of the Gaussians are inputted manually, and constrained to a narrow range of mean energy and widths to successfully fit the dose dependence. (b) The dose dependence of the prominent features: most decay, at least one grows, and the rates of change differ slightly by feature.

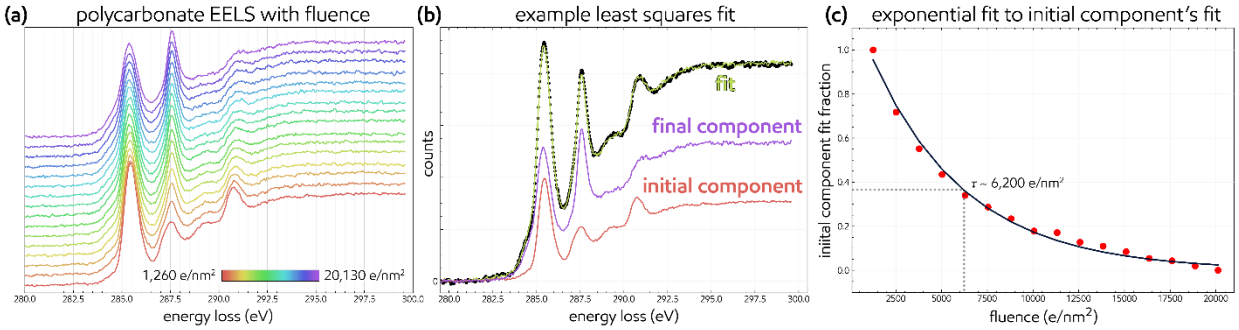

Figure 2. (a) Dose-dependent spectra of polycarbonate at 200 kV and -170°C. (b) In the simplified approximation scheme, a linear combination of the initial and final states is used to fit the entire dose range. (c) The result is typically very similar to an average of the individual fits.

References:

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