DIGITAL FILTERS FOR APPLICATION TO DATA ANALYSIS IN ELECTRON ENERGY-LOSS SPECTROMETRY

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One of the more difficult problems associated with data analysis in electron energy-loss spectroscopy (EELS) in the analytical electron microscope is related to detection of relatively small edges superimposed on large background signals. Although generic background modeling routines have been developed to simulate the shape of the background through least-squares fitting routines using either polynomial, log-polynomial, or power-law functions for the case of small edges located in the less than 300 eV, their operation is at best marginal. Digital filters have been used in X-ray energy-dispersive spectroscopy (XEDS) with some success during the last few years. However, their direct application to EELS has generally met with limited success due to the complexity of spectral shapes in EELS relative to XEDS. In this paper we shall review the limitations as well as the advantages of using digital filters in EELS, concentrating on their use for the low-energy-loss regime.

1. Introduction

One of the more difficult problems in electron energy-loss spectroscopy (EELS) is the detection of small characteristic edges superimposed upon relatively large background signals. For the case of edges having poor visibility owing to poor edge/background ratios the identification of the presence or absence of an element is virtually dedicated to some intuitive input on the part of the analyst. Once the decision is made that an edge is present, the experimentalist must decide upon a background model in order to attempt to show unambiguously the presence of the atomic species of interest by showing the existence of a signal above the general background level. Although various modeling routines have been developed to simulate the shape of the continuum EEL signal through polynominal, log-polynominal, or power law functions, they still require substantial operator input with respect to the identification of "background fitting" regions as well as a judgement as to the validity of extrapolation to regions · beyond the fitting window. In addition, there is the added complication that many of these models

tend to perform poorly in the energy-loss regions showing high curvature when extrapolated beyond their initially defined fitting regime. This is primarily due to the fact that the background shape in this region is rapidly changing due to the multiplicity of contributions to the signal: phonon, plasmon, inter- and intraband transitions, inner-shell losses, and multiple scattering effects.

Digital filtering is a well established procedure for removing background components from comlex spectra and has been used in X-ray energy-dispersive spectroscopy (XEDS) with reasonable success during the last few years. In general there are two types of digital filtering methods: the first relies on Fourier Transform techniques, while the second is more closely related to differentiation and/or averaging. The latter is more frequently associated with "zero-area top-hat filters" [1,2] or "difference filtering" [3] and is the type of digital filter which we will be considering in this text. This technique may also be compared to the separation of peaks from large background signals in Auger electron spectroscopy using lock-in amplifiers and suitable differentiation circuitry [4].

For the purposes of this manuscript we shall

consider background corrections as the process of removing from spectra the continum energy-loss signal and retaining some measure of the presence of a characteristic edge. Thus, we shall intentionally ignore the physics associated with the generation of this (background) signal and view it as an undesirable aspect of the spectrum which we would like to remove in the most expeditious and simple way possible. A method that does not rely on any explicit model and/or operator intervention would of course be ideal. The application of digital filters very nearly satisfies this criterion. The simplest way to visualize the result of digital filtering is that it is essentially a differentiation, sometimes combined with averaging, of the experimental spectrum. Low-frequency components (i.e. background) are suppressed, while the higher-frequency components (i.e. edge onsets) are highlighted.

2. Discussion

The algorithms which are employed to implement the various types of digital filters are extremely fast and simple. Difference filters are designed to average the contents of adjacent "windows" of channels in the spectrum and replace the contents of the centroid of one of the two windows by the resulting difference. One can diagrammatically sketch this process by envisioning a step-function filter having a single positive and a single negative amplitude lobe of equal width W as illustrated in fig. 1a. This filter is then simply sequentially incremented through the entire spectrum, processing each channel in succession. Top-hat digital filters, as illustrated in fig. 1b, replace the content of the centroid channel by a value equal to the average of the data in the symmetrically positioned window of width W about that point minus the average of L channels either side of the central window. If the total area under the positive amplitude lobe is equal to that of the two negative amplitude lobes (i.e. a zero-area filter), then the application of this variety of filter to any linear signal will yield a filtered spectrum having zero slope and amplitude. These filters can be considered as essentially equivalent to a smoothed first or second derivative of the spec-
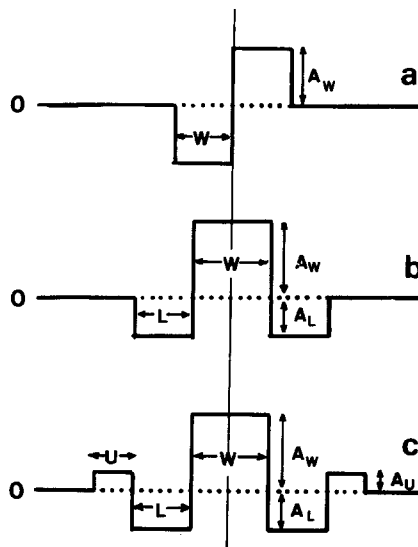

Fig. 1. Spectral weighting functions for (a) difference, (b) top-hat and (c) second-order top-hat digital filters. The parameters W, L and U correspond to the widths (in channels) of the filters, while A_W, A_L and A_U correspond to their respective amplitudes.

trum for the difference and top-hat filters respectively. During the course of this study, a third variation of digital filter was found necessary in situations of high background curvature. This second-order top-hat filter (fig. 1c) has an additional positive lobe and is operationally similar to calculating the fourth derivative of the spectrum.

The characteristics of the different filter types are controlled by the widths and amplitudes of the different lobes in the filter function. The parameters W, L, and U of fig. 1 refer to the respective channel widths of the lobes, and A_W, A_L, and A_U to their amplitudes. Due to the fact that energy-loss edges do not all have identical profiles, it is difficult to analytically determine the "best" filter function to use in all situations. This is in direct contrast to the X-ray spectroscopy case where the Gaussian nature of all the characteristic peaks allows one to establish an "optimal" filter width [1,2]. Increasing the width of the individual lobes reduces the apparent noise in the processed spectra; however, it also correspondingly reduces the effective resolution. For all the cases studied, difference filters performed poorly relative to the
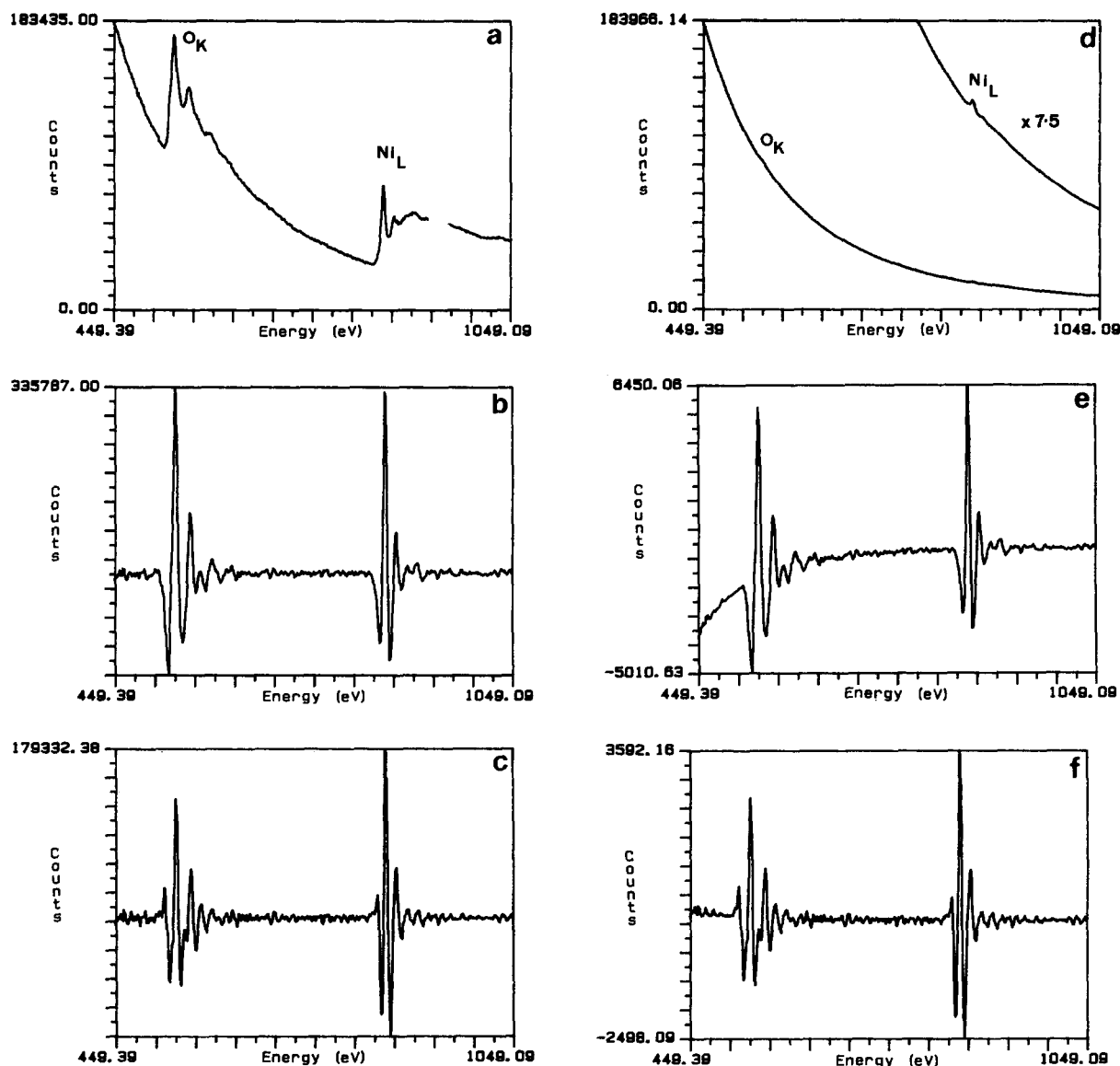
Fig. 2. Example of the application of top-hat digital filters to the O–K shell and Ni–L shell edges in NiO. (a) Original data; (b) asymmetric top-hat filter applied to data in (a); (c) asymmetric second-order top-hat filter applied to data in (a); (d) artificial spectra by dividing the characteristic edges in (a) by a factor of 50; (e) asymmetric top-hat filter applied to (d); (f) asymmetric second-order top-hat filter applied to (e). See text for filter parameters.

top-hat functions and as a result will not be discussed further. Symmetric zero-area top-hat filters ($W = L$, $A_W = 2A_L$) having central lobes less than 3 channels wide were found to be ineffective in that they tend to amplify the noise present in the data. On the other hand, symmetric top-hat filters having widths (W) greater than 7 channels, al-

though providing adequate noise and background suppression, result in unacceptable losses in resolution. As a compromise, it was found that asymmetric top-hat filters having the parameters $W = 3$, $A_W = 4$, $L = 6$, $A_L = 1$ and corresponding second-order top-hat filters with parameters $W = 3$, $A_W = 8/3$, $L = 6$, $A_L = 1$, $U = 2$, $A_U = 1$ per-

formed best for typical spectra acquired at ~ 2 eV energy resolution and recorded at 1 eV/channel. These filters tended to provided noise and background suppression roughly equivalent to a symmetric 5-channel top-hat filter, yet had resolutions only slightly worse than the symmetric 3-channel top-hat functions. These filter characteristics should scale with the inverse of the energy resolution and spectral dispersion (eV/channel) should one operate under different conditions than those given above.

In order to illustrate the usefulness of these filters in EELS, K and L edges in NiO and an M shell edge in molybdenum were processed using the latter two filters and are shown here as examples. All spectra were generated using a Philips EM400T electron microscope equipped with a Gatan Model 605 spectrometer. Spectra were recorded using an EDAX 9100/70 multichannel analyzer and subsequently analyzed on a DEC PDP 11/2 computer running the EELS data analysis program NELS (version 8410100018-NJZ).

Fig. 2 shows the results for the oxygen K and nickel L shells in NiO. The first half of this figure (figs. 2a–2c) presents the original data (fig. 2a), followed by the application of the previously defined asymmetric top-hat filters (figs. 2b and 2c). In all cases, the existence of a characteristic signal is well defined. The spectrum shown in fig. 2d is artificial, in that it was generated from the real spectrum of fig. 2a in the following manner. First, a conventional power law (AE^R) background was fitted to the pre-oxygen region of the data and extrapolated under the O–K and Ni–L edges and then subtracted. The remaining characteristic signal was then divided by a factor of 50 and then added back to the fitted background curve. This artificial spectrum (fig. 2d) was then processed using the identical filter functions, the results of which are shown in fig. 2e. Conventional top-hat filters (fig. 1b) when applied to EELS background signals which are highly non-linear tend to exhibit an undershoot of the vertical axis (i.e. a negative curvature) as is visible at the low-energy end of fig. 2e. This effect becomes more pronounced as the filter width decreases and/or the background curvature increases. This can be partially overcome through the use of the second-order filter

function (fig. 1c) and was the motivation for its implementation. The reduction in the curvature of the filtered spectrum is shown in fig. 2f, together with the additional oscillations introduced into the resulting characteristic edge profiles. It should be apparent that although the characteristic signal is present in fig. 2d, the poor edge/background ratio prohibits its direct observation; however, the application of the digital filters clearly indicates the existence of the characteristic features in the spectrum.

Fig. 3 illustrates a corresponding application of these filters to a less well defined spectral edge, the molybdenum M shell. As in the case of fig. 2, spectra 3b and 3c illustrate the effect of these filters on the original data (spectrum 3a). Spectra 3e and 3f result from the filtering of the artificial spectrum (3d) produced from spectrum 3a by subtracting the pre-edge background, scaling down the characteristic signal 50 fold and then adding back to the fitted background curve. In both these cases (NiO and Mo) the digital filters provide an unambiguous identification of the presence of a characteristic edge in the spectrum. Although this is already apparent without the application of the filters in both figs. 2a and 3a, one cannot draw the same conclusions from the situations represented by figs. 2d and 3d due to the poor edge/background ratios.

It is important to point out that, in these examples, we are operating with essentially noise-free spectra. In general, in order to apply any type of digital filtering to spectral analysis, it is a prerequisite that the characteristic edge signal level exceed the random noise (in contrast to background) in the experimental data. Using the artificial data as discussed above, it was possible to still identify the presence of an edge at characteristic signal reductions of factors of greater than 500 times the original peak/background levels; in an ideal situation this would indicate a dramatic improvement in the detectability limits of EELS. In day-to-day applications, however, insufficient statistics in the experimental data will become the limiting factor in the use of this type of data analysis, and substantial differences should be expected for statistically poor spectra.
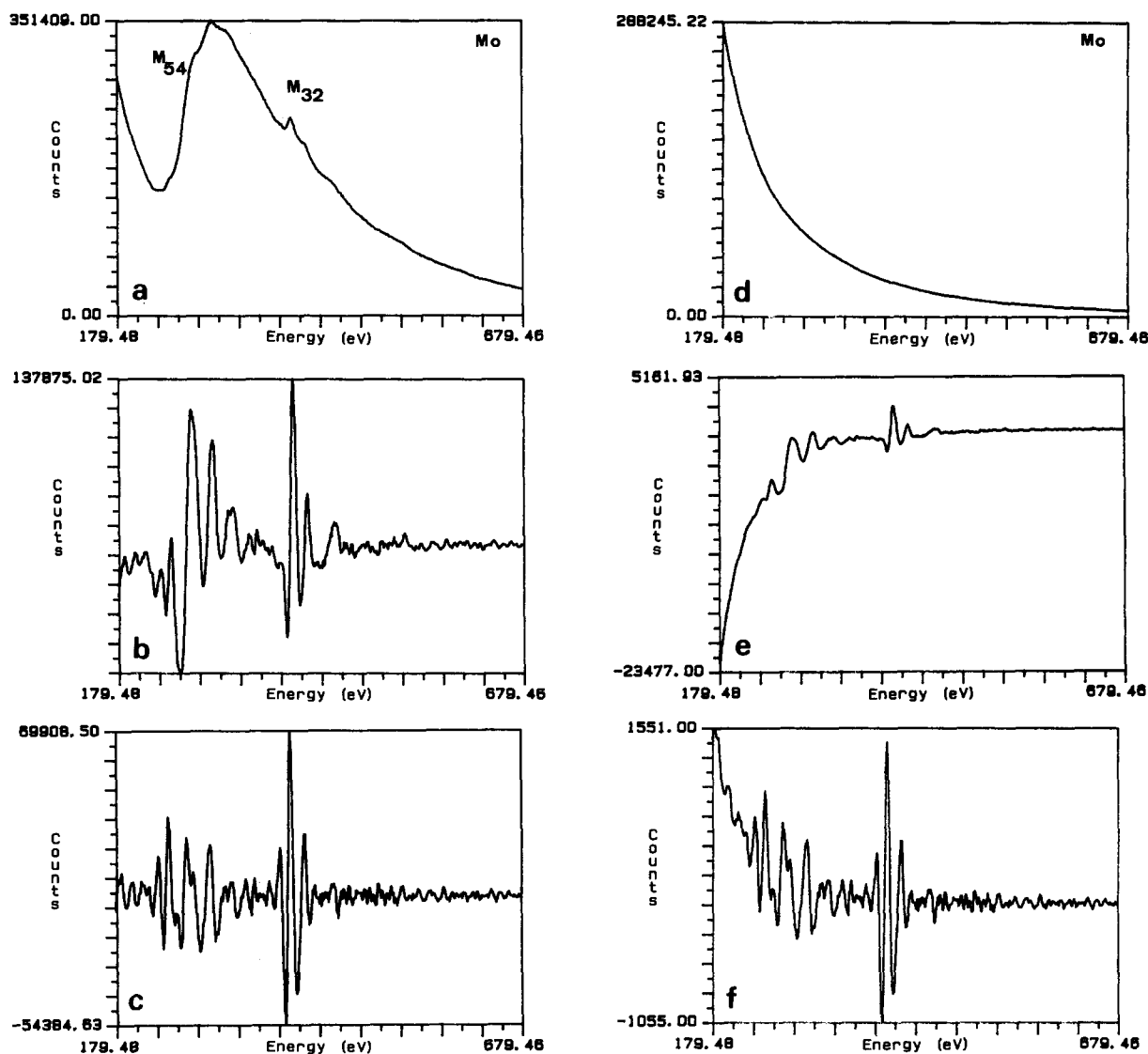
Fig. 3. Example of the application of top-hat digital filters to the Mo–M shell in pure molybdenum. (a) Original data; (b) asymmetric top-hat filter applied to data in (a); (c) asymmetric second-order top-hat filter applied to data in (a); (d) artificial spectra by dividing the characteristic edges in (a) by a factor of 50; (e) asymmetric top-hat filter applied to (d); (f) asymmetric second-order top-hat filter applied to (e). See text for filter parameters.

3. Conclusions

The versatility of digital filters, at the present, is limited to their ability to easily and rapidly point out the existence of small characteristic signals in the presence of large background levels. Further work is in progress in order to more fully exploit the application of digital filtering in EELS and determine its usefulness for improving the minimum detectable mass fraction in various material systems [5].

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