Microscopy AND
Microanalysis

Letter to the Editor: Comments on "Compositional Averaging of Backscatter Intensities in Compounds"

The electron backscatter coefficient (η) and the related correction factor for X-ray intensity (R) are both strongly dependent on atomic number and although quite good data are available for pure elements, the derivation of values for compounds is problematic. This issue is addressed by Donovan, Pingitore, and Westphal (*Microscopy and Microanalysis*, Vol. 9, No. 3, June 2003, pp. 202–215), in which an "electron fraction" averaging method is advocated as an improvement on "traditional" mass fraction averaging, which is known to be only an approximation. (The difference, according to Table 3, is only significant, however, for samples containing heavy elements such as Pb and Th.) New thinking on this topic is welcome, but I believe this proposal should be treated with caution pending more rigorous testing.

Both η and R are determined by geometrical considerations, in which electron stopping power must also be taken into account. Furthermore, R (but not η) depends on the energy distribution of the backscattered electrons (which affects the X-ray intensity they would have contributed had they not been backscattered), and it is necessary to know the form of the distribution for a compound. The theoretical considerations offered in support of the proposed averaging method are, therefore, incomplete. Likewise, the experimental η data are of limited value, and the observations on isotopes are not only unsurprising but fail to illuminate the question of R averaging for compounds.

Direct experimental determination of R is difficult, and adjusting the R averaging method to obtain "correct" analytical results is a dubious procedure, given the uncertainties in the other corrections. Therefore the best prospect for improvement in this area is, in principle, to apply Monte Carlo modeling. However, the model needs to be rigorous in its treatment of scattering and energy loss, where it is usual to make simplifying approximations. It should in any case be noted that there is no *a priori* reason why any single R averaging method should be strictly applicable to all combinations of different elements.

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Response to Reed's "Comments on 'Compositional Averaging of Backscatter Intensities in Compounds'"

We agree with many of Stephen Reed's comments, particularly his suggestion that our proposal should be treated with caution and subjected to rigorous evaluation. This is generically true of any hypothesis in science.

Reed states at the outset that η and R are both strongly dependent on atomic number and we agree with this statement. Therefore we advocate the atomic number based electron fraction approach (itself an approximation), in part because it contains one less faulty assumption—that mass affects elastic scattering of electrons in solids.

The difficulty with the latter assumption can be demonstrated by considering that the maximum energy transfer to a recoiling nucleus actually occurs in the case of perfectly elastic scattering with a scattering angle of 180°. (For inelastic scattering, the effect is smaller.) The kinetic energy of the recoiling nucleus of mass M is

$$dE = 2M \frac{m_e^2}{(m_e + M)^2} v^2$$

where m_e is the mass of the electron and v is the initial velocity of the electron. Since m_e is much smaller than M, $m_e + M$ equals M to a very good approximation, so we can express this as

$$dE \approx 4 \frac{m_e}{M} E$$

where E is the initial kinetic energy of the electron and dE is the energy taken from the electron and carried off by the recoiling nucleus. The largest energy loss is for hydrogen where $m_e/M \sim 1/2000$. So for each purely elastic collision with protons in pure hydrogen, the electron loses a maximum 0.2% of its kinetic energy. For the vast majority of collisions, with small scattering angles, the energy loss is much less than this. For heavier nuclei, such as iron, it is smaller still (by a factor of A). The *difference* in this quantity, for two isotopes of the same element, is even smaller than this (e.g., for ^{56}Fe and ^{57}Fe the difference in fractional energy loss per nuclear collision is, at most, 6×10^{-7}).

The point is, for electrons slowing in solids, *nuclear* stopping power—the stopping power due to collisions with nuclei—is completely negligible compared with *electronic*
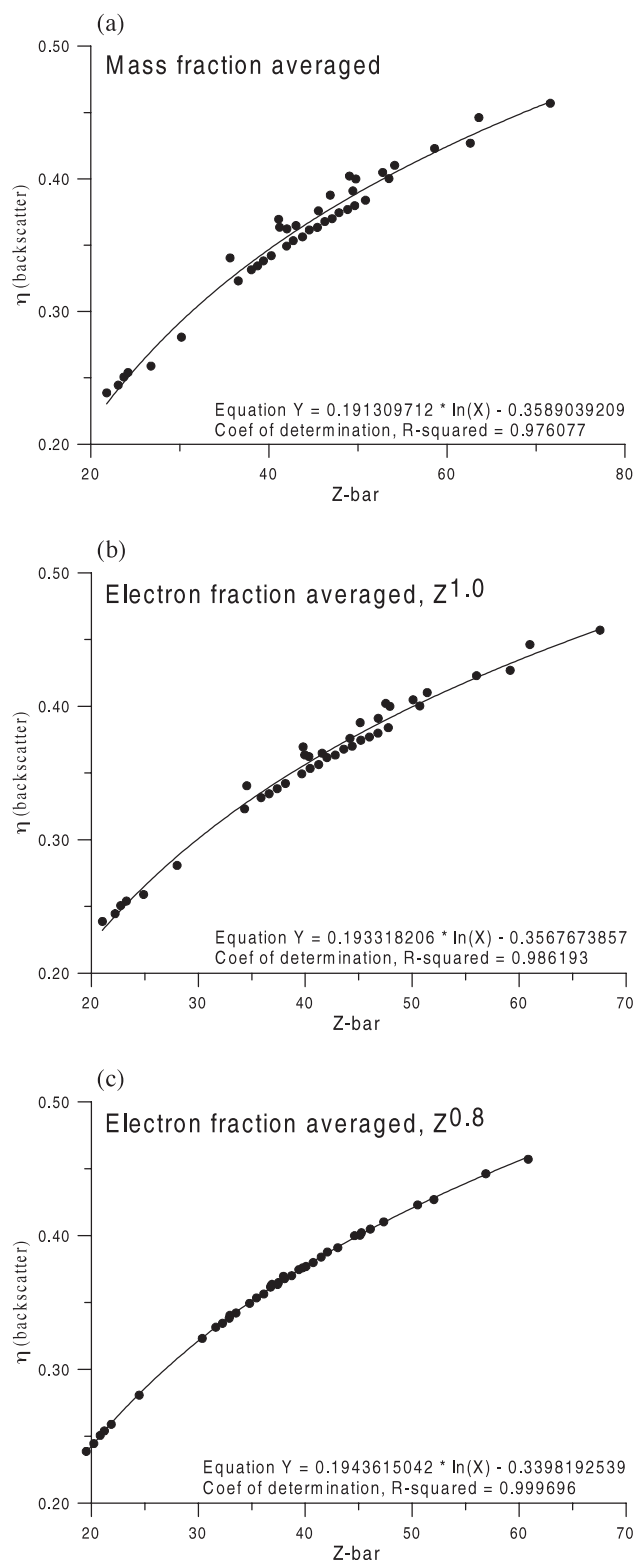
(a)

Mass fraction averaged

Equation Y = 0.191309712 * ln(X) - 0.3589039209
Coef of determination, R-squared = 0.976077

(b)

Electron fraction averaged, $Z^{1.0}$

Equation Y = 0.193318206 * ln(X) - 0.3567673857
Coef of determination, R-squared = 0.986193

(c)

Electron fraction averaged, $Z^{0.8}$

Equation Y = 0.1943615042 * ln(X) - 0.3398192539
Coef of determination, R-squared = 0.999696

Figure 1. Backscatter intensity calculations using NIST MQ software (1,000,000 trajectories for each data point at 20 keV) for a number of compounds containing elements with moderate to large differences in A/Z. Average Z calculated using mass averaging (**a**), "simple" electron fraction averaging (**b**), and electron fraction adjusted for nuclear screening by inner orbital electrons (**c**).

stopping power, that is, the stopping power due to collisions with electrons. For this reason, we agree with Reed that the isotope measurements are unsurprising. However, several researchers in the field have publicly expressed surprise and skepticism at this result, so we felt compelled to make the point explicitly in our paper—that these measurements provide empirical evidence of what is known from fundamental principles of physics.

We further agree, as stated in the paper, that stopping power is involved in R loss, and that the average of this power loss can be correctly calculated using mass fractions but only because mass-based units are utilized in its calculation. It should be clear, as noted above, that the introduction of mass in the stopping power calculation is arbitrary and that these mass-based units eventually cancel out, leaving the electron column density as the determining factor in both stopping power and backscatter averaging. In any case, our paper focuses on the elastic scattering portion of the backscatter correction, which, as we have shown, is negligibly affected by mass.

We concur with Reed that a fast Monte Carlo method, which incorporates detailed physics of electron scattering and energy loss, would be a useful tool, especially for "on-line" microanalysis, but for the moment we must live with simplifying approximations. We did perform many high-precision calculations to model backscatter averaging in compounds using the NIST MQ software but did not include them in the paper. These calculations show that, for various compounds ($BaTiSi_3O_9$, Sb_2S_3, $PbSiO_3$, etc.) containing elements with moderate to large differences in A/Z, mass fraction averaging (Fig. 1a) does not perform as well, even when compared to the "simple" electron fraction model (Fig. 1b), where the only difference is the substitution of Z for A in the calculation of average Z. After adjusting the "simple" electron fraction model, using $Z^{0.8}$ to compensate for nuclear screening by inner orbital electrons in higher atomic number atoms (based on experimental backscatter measurements of the Cu-Ag-Au alloys), our model performs surprisingly well (Fig. 1c).

We are not making the claim that this model is completely rigorous in its treatment of electron scattering and energy loss. It is yet another semi-empirical approximation that may offer some benefit to the analyst in situations where a large atomic number correction is required and problems have been observed with current methods.

While we are encouraged by these results and others described in our paper, we know that this approximation can be significantly improved. We therefore hope that other researchers, including Stephen Reed, will work to quantitatively evaluate this approximation.

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