On the use of ionization cross sections in analytical electron microscopy


KEY WORDS. Ionization cross section $Q$, $k_{AB}$ factors, experimental and theoretical comparisons of $Q$, analytical electron microscopy, microanalysis, ionization edge.

SUMMARY
There are two approaches to the utilization of the ionization cross section, $Q$, for use in the determination of $k_{AB}$ factors for quantitative microanalysis in the analytical electron microscope. The first approach is to interpolate a value of $Q$ from experimentally determined $k_{AB}$ factors at a fixed accelerating voltage (kV). The second approach uses a theoretical parameterization of $Q$ generated by fitting the fundamental Bethe expression to selected experimental values of $Q$ over a wide range of kV. This paper discusses the relative merits of the two approaches.

INTRODUCTION
The cross section for inner shell ionization ($Q$) is an important parameter for X-ray microanalysis in the analytical electron microscope (AEM). It is used in the calculation of the $k_{AB}$ factors (Cliff & Lorimer, 1975) which relate the composition ratio ($C_A/C_B$) of elements A and B to their characteristic intensity ratio ($I_A/I_B$). The $k_{AB}$ factors can either be determined experimentally by using standards or calculated with an equation of the form (Goldstein et al., 1977):

$$k_{AB} = \frac{Q_{wa}/A_B}{Q_{wa}/A_A} \cdot \varepsilon_B$$

where $\omega$ is the fluorescence yield, $a$ is the relative transition probability $[K_a/(K_a + K_B)]$, $A$ is the atomic weight and $\varepsilon$ is the efficiency of detection of X-rays from the element A or B.

There have been two approaches described in the literature concerning the calculation of $k_{AB}$ factors by means of equation (1) and the purpose of this paper is to discuss the relative merits of these two approaches. In order to follow the discussion in detail, it is necessary to present some background information concerning the historical development of each method.

BACKGROUND
The first approach, originally proposed by Goldstein et al. (1977), assumes that experimental values of $k_{AB}$ will generally be more accurate than calculated values because of uncertainties in the terms in equation (1), particularly $Q$. Using this microanalysis strategy, calculated $k_{AB}$ factors are used only in the rare cases when suitable thin film homogeneous standards for a particular system cannot be generated. Under these circumstances, Goldstein et al. (1977) compared experimental $k_{AB}$ factors with a range of calculated $k_{AB}$ factors using different values
of \( Q \), and determined which value of \( Q \) in equation (1) generated the best fit at a fixed operating voltage. This approach makes no assumptions about the absolute accuracy of the cross section data, or the experimental conditions under which these data were obtained. The aim is to determine, at a fixed operating voltage of the AEM, which existing cross section model can best be used to generate a \( k_{AB} \) factor for elemental pairs. If \( k_{AB} \) factor data are obtained at a different operating voltage then, using this method, it is essential to re-determine what model best fits the new data. There is no guarantee using this strategy that one model will work over a range of kVs and indeed this is not observed in practice. For example, in Goldstein et al. (1977) it was concluded that the cross section expression of Green & Cosslett (1961) based on the Bethe (1930) model gave the best fit to the experimental data at 100 kV. Similarly, Wood et al. (1984), using this same approach in a more detailed experimental study of \( k_{AB} \) factors, concluded that the Bethe (1930) cross section formulation as reviewed by Powell (1976a) using the fitting parameters of Brown (1974) gave a better fit at 120 kV. (We will refer to this hereafter as the Bethe–Brown cross section.) From the point of view of interpolating other \( k_{AB} \) factors it is not important that, for example, the Brown (1974) data were obtained at electron accelerating voltages of \(<50\) kV, substantially less than typical AEM operating voltages. This only becomes important if one is attempting to determine absolute cross section values. It is not significant when a ratio of values of \( Q \) is used, as in equation (1).

The second approach to the determination of \( k_{AB} \) factors in the AEM that has been proposed (Zaluzec, 1979a, b; Zaluzec et al., 1983), is based on the use of a theoretical cross section expression and tabulated cross section data. The theoretical expression for the ionization cross section, described originally by Bethe (1930), has the form:

\[
Q = \frac{b_{n1}\pi e^4 Z_{n1}}{(m_0\nu^2/2)E_c} \log \left[ \frac{c_{n1}(m_0\nu^2/2)}{E_c} \right]
\] (2)

where \( e \) is the electron charge, \( Z_{n1} \) is the number of electrons in the shell which has ionization energy \( E_c \), and \( b_{n1} \) and \( c_{n1} \) are constants for a particular shell. Bethe notes that \( m_0 \) is the rest mass of the electron and \( \nu \) is the velocity. At low beam energies, e.g. 10 keV, relativistic effects can be ignored and the term \((m_0\nu^2/2)\) can be set equal to the kinetic energy, which in turn is equal to the electron charge multiplied by the accelerating potential, \( V \) (Hall, 1953):

\[
(m_0\nu^2/2) = eV = E
\] (3)

where \( E \) is the beam energy. The Bethe expression using the nomenclature of Powell (1976b) can be written:

\[
Q = \frac{\pi e^4}{E E_{n1}} Z_{n1}b_{n1} \ln \left[ \frac{c_{n1}E}{E_{n1}} \right]
\] (4)

where \( E \) is the electron energy, \( E_{n1} = E_c \), \( Z_{n1} \) is the number of electrons in the \( nl \) shell, and \( b_{n1} \) \( c_{n1} \), which were physically defined in the original Bethe approach, are used by Powell as fitting parameters, which are independent of atomic number.

At high beam energies, the electron mass deviates substantially from the rest mass due to relativistic effects, and thus equation (2) must be modified to account for this effect. Williams (1933) derived a relativistically-corrected Bethe cross section for ‘light’ collisions in which the momentum imparted to the ‘knocked’ electron is small compared to the momentum of the incident electron. The Bethe cross section, with Williams’ relativistic correction has the form:

\[
Q = \frac{b_{n1}\pi e^4 Z_{n1}}{(m_0\nu^2/2)E_c} \left\{ \ln \left[ \frac{c_{n1}(m_0\nu^2/2)}{E_c} \right] - \ln (1 - \beta^2) - \beta^2 \right\}
\] (5)

where \( \beta \) is the ratio of the electron velocity (\( \nu \)) to the velocity of light (\( c \)) and \( 1/2 \ m_0\nu^2 = 1/2 \ m_0c^2\beta^2 \).

Zaluzec (1979a, b) proposed an expression for \( Q \) identical in form to the relativistically-corrected Bethe expression (equation 5), except that \( E_0 \) was defined as the beam energy,
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rather than \( \frac{1}{2} m_0 v^2 \). The Zaluzec expression (which was proposed as valid over a range of voltages from 2 kV to 2000 kV) may be written as:

\[
Q = \frac{ab_s}{E_c E_0} \left[ \ln \left( c_s \frac{E_0}{E_c} \right) - \ln \left( 1 - \beta^2 \right) - \beta^2 \right] \tag{6}
\]

In this expression \( a \) is a constant \((ne^4\), where \( e \) is the electronic charge\) and \( b_s \) and \( c_s \) are fitting parameters appropriate to the ionized shells. What was original about Zaluzec's approach was the determination of new values for the fitting parameters. For the K shell (Zaluzec, 1979b) determined these parameters by fitting equation (6) to selected cross section data to give:

\[
b_s = 0.35 \tag{7}
\]

\[
c_s = \frac{0.2}{U_0 \left[ 1 - \exp \left( -\frac{\gamma}{\delta} \right) \right] \left[ 1 - \exp \left( -\frac{\delta}{\gamma} \right) \right]} \tag{8}
\]

where \( U_0 = \frac{E_0}{E_c} \tag{9} \)

\[
\delta = 0.5E_c \tag{10}
\]

\[
\gamma = 1250 \langle E_c, U_0^2 \rangle^* \tag{11}
\]

Equation (6) has been referred to as the 'cross section formulation proposed by Zaluzec' (Zaluzec et al., 1983), or alternatively the 'Zaluzec cross section' in independent work (Ogilvie, 1983). More precisely, it is a restatement of the relativistically-corrected Bethe expression with \( E_0 \) defined as the beam energy, and new fitting constants, \( b_s, c_s \), parameterized by Zaluzec; i.e. equation (6) is a Zaluzec parameterization of the Bethe cross section.

Recently, Zaluzec et al. (1983) modified equation (6) by substituting the expression \( \frac{1}{2} m_0 c^2 \beta^2 \) for \( E_0 \). In this form the modified equation (6) is a return to the original formulation due to Bethe (1930) and Williams (1933) (equation 5). However, despite the change in definition of \( E_0 \), Zaluzec et al. (1983) did not modify the fitting parameters of Zaluzec (1979a, b) as defined in equations (7) and (8).

The discrepancy between the Zaluzec parameterization approach and the Goldstein et al. (1977) curve-fitting approach arises when Zaluzec et al. (1983) draw a comparison between the modified equation (6) and the Bethe–Brown cross section (with Dupouy's relativistic correction (1968) applied) as used by Wood et al. (1984). The latter cross section is criticized as 'erroneously modelling the functional dependence (of \( Q \)) at higher energies and is simply incorrect', despite the fact that the Wood et al. (1984) approach did not claim applicability at accelerating voltages other than 120 kV. It is also stated that 'The expression of the form given by equation (6) (above) clearly yields better agreement to the experimental data.' The basis for these statements is shown in Fig. 1 (after Zaluzec et al., 1983). Zaluzec et al. (1983) also proposed that, as a consequence of this change in definition of \( E_0 \), the agreement with experimental cross section data is better than other models (Fig. 1). They further suggest that this expression should be used for carrying out microanalysis of high Z elements (\( Z > 45 \)) using the high energy K shell X-rays.

As stated in the introduction, it is the purpose of this paper to discuss the differences between the experimental \( k_{AB} \) factor curve-fitting approach to a choice of \( Q \) and the theoretical curve-fitting approach. In discussing the Zaluzec parameterization of the Bethe formula we wish to take issue with the above criticisms and we will show that (a) the agreement with experimental data, considering the uncertainty in those data, is no better than can be obtained with

* There is inconsistency in the terminology of equation (11) between Zaluzec (1979a) and (1979b). In the former the X-ray line energy is used instead of \( E_0 \) while in the latter, \( E_c \) the ionization energy is used. This latter formulation seems more reasonable although it makes negligible difference in the calculation of \( c_s \) (equation 8) and therefore of \( Q \) (equation 6).

† For purposes of calculation note that \( m_0 c^2 = 511 \text{ keV} \) and

\[
\beta = \left[ 1 - \left( \frac{1}{1 + E_0 / 511} \right)^2 \right]^{1/2}
\]
Fig. 1. Comparison of experimental and calculated ionization cross sections for Al, Ni, Ag and Au as a function of accelerating voltage. The full lines are the calculated cross sections using the 'Zaluzec formulation' and the dotted lines are the calculated cross sections using the Bethe–Brown model with Dupouy's relativistic correction. The data are as follows: Al K (Hink & Ziegler, 1969), Ni K (Pockman et al., 1947), Ag K, open circles (Kirkpatrick & Baez, 1947), Ag K, closed circles (Rester & Dance, 1966), Au K, open triangles (Rester & Dance, 1966), Au K, closed triangles (Motz & Placious, 1964), Au K, closed diamond (Davis et al., 1972). (The 2-5 MeV data points for Ni and Ag are from Scholz et al., 1972.) (After Zaluzec et al. (1983).)

Discussion

(i) Experimental and theoretical comparison of Q

Zaluzec (1979a) reported that $b_5$ and $c_5$ in equation (6) can be determined analytically by fitting the equation to experimental data (similar to Fig. 1). It is our contention that the fit to experimental data obtained by Zaluzec et al. (1983) in Fig. 1 and similar figures (see Figs. 4.12 and 4.13 in Zaluzec, 1979a) is not intrinsically better than that using the Bethe (1930) cross section as reviewed by Powell (1976b) (i.e. exactly that used by Wood et al., 1984, and criticized other cross section models, (b) the choice of experimental data with which Zaluzec (1979a) and Zaluzec et al. (1983) compare their formulations is arbitrary, (c) the modification of equation (6) to include $\frac{1}{2} m_0 c^2 \beta^2$ without simultaneous modification of the fitting parameters leads to a physically unrealistic model at values of $E_0$ near $E_0$, giving rise to negative values of $Q$ and hence $k_{AB}$ and (d) whatever form of relativistic correction is applied to $Q$ the effect on $k_{AB}$ at 120 kV is insignificant. Finally, we wish to emphasize that, as is the case in the first approach (Goldstein et al., 1977) described above, any choice of the cross section, either theoretical or experimental, to be used in AEM should only be considered at a fixed kV, since these are the conditions under which microanalysis is carried out.
by Zaluzec et al., 1983). The values of $b_0$ and $c_0$ were simply parameterized by Zaluzec (1979b) until they fitted the experimental data. If the fit were not good, it would merely reflect a failure in the arithmetic rather than an incorrect version of the cross section. Clearly a similar approach could be applied to any valid cross section formulation, but the merits of this whole approach must be questioned, as we will now discuss.

Although there is only a limited amount of experimental data for $Q$ in the literature, we consider that Zaluzec et al.'s (1983) choice of experimental data shown in Fig. 1 is arbitrary. No rationale for their choice of data is given and, significantly, no error bars are shown. A search of the literature reveals that Motz & Placious (1964) in a detailed study, report that their experimental cross sections have an uncertainty of $\pm 15\%$ and Davis et al. (1972) similarly consider all the experimental errors in their cross sections and conclude that errors of $\pm 22\%$ are reasonable. Insertion of appropriate uncertainty bars to Fig. 1 would reduce the apparent discrepancy between the two approaches. In addition to the error bars on individual datum points, there is also a considerable variation in the absolute experimental values of $Q$ reported in the literature, as shown in Fig. 2 for Ag around 120 kV. A similar range of data can be found for Cu and Ni. Given the range of values in this figure, it is considered unreasonable to propose that any existing cross section data or theoretical formulation is absolutely more correct than any other. Moreover, it is worth noting that the data in Fig. 1 attributed to Kirkpatrick & Baez (1947) are in fact a combination of the data of Webster et al. (1933) and Clark (1935) modified by Kirkpatrick & Baez (1947). Furthermore the data of Pockman et al. (1947) in Fig. 1 are not absolute data but relative measurements standardized to the data of Smick & Kirkpatrick (1945).

![Fig. 2. Variation in the experimental ionization cross section data for Ag as a function of energy in the range of interest to AEM. Error bars are as reported in the original publications.](image-url)
Finally, the Au data due to Davis et al. (1972) are reported in Fig. 1 but the Ag data published in the same paper are not. These Ag data due to Davis et al. are significantly higher than the Ag data attributed to Kirkpatrick & Baez (1947) and used by Zaluzec et al. (1983) in Fig. 1, to illustrate 'good agreement' with their theory. In conclusion, therefore, it is contended that the choice of experimental data by Zaluzec et al. (1983) is arbitrary, the data show no error bars, and that the apparent fit with theory is good, merely because the constants $b_0, c_0$ have been adjusted until the fit is good. Furthermore, given these facts we again argue that it is unreasonable to claim that one particular cross section formulation is more correct than another, as proposed by Zaluzec et al. (1983).

(ii) Cross section behaviour close to the ionization edge

While returning to the original Williams (1933) relativistic correction of the Bethe (1930) expression, Zaluzec et al. (1983) retained the constants $b_0, c_0$ derived in the earlier work of Zaluzec (1979a, b) which yield the fits shown in Fig. 1. What is not shown in Fig. 1 however, is the behaviour of this particular cross section parameterization at energies close to the critical ionization energy, $E_c$. From Fig. 1 it is clear that the Zaluzec curve peaks at a higher energy than the Bethe-Brown model, but as shown in Figs. 3(a–c), extending the Zaluzec curve down to $E=E_c$ results in negative values of $Q$. Specifically $Q_{\text{Ni}}$ becomes negative at $\sim 9.4$ keV, $\sim 1.05$ keV above $E_c(\text{Ni})$; $Q_{\text{Ag}}$ becomes negative at $\sim 30.8$ keV, $\sim 5.3$ keV above $E_c(\text{Ag})$; and $Q_{\text{Au}}$ becomes negative at $\sim 117.5$ keV, $\sim 36.8$ keV above $E_c(\text{Au})$.

The reason for the failure of the Zaluzec et al. parameterization and the generation of negative values of $Q$, is as follows: Replacing $E=ev$ by the expression $\frac{1}{2}mc^2\beta^2$ has an important numerical consequence. For example, an electron accelerated through a potential of 100 keV has an energy of 100 keV, but the value of $\frac{1}{2}mc^2\beta^2$ is only 76.7 keV. Without further adjustment of the parameters $b_0$ and $c_0$, such a formulation predicts negative cross sections for a significant electron energy range above the edge energy. This behaviour persists even at non-relativistic velocities (e.g. the example of nickel listed above). While the Zaluzec parameterization yields positive cross sections for low energy K-edges excited by electrons accelerated at typical AEM operating voltages (100–200 kV), it is distinctly in error for high energy K-edges, such as that of gold. This is quite surprising, considering the claim by Zaluzec et al. (1983) that their parameterization is useful for high energy K-edges. Of course, it should be possible to fit the experimental cross section data to the full Bethe cross section with the Williams relativistic correction to obtain parameters which ensure sensible behaviour of the cross section at all energies above

![Fig. 3. (a) Nickel K ionization cross section as a function of energy, calculated using equation (6) with the Zaluzec et al. relativistic energy modification.](image)
Fig. 3. (b) Silver Kα ionization cross section as a function of energy, calculated using equation (6) with the Zaluzec et al. relativistic energy modification.

Fig. 3. (c) Gold Kα ionization cross section as a function of energy, calculated using equation (6) with the Zaluzec et al. relativistic energy modification.

the edge. Such behaviour is clearly desirable for practical AEM analysis, since the accelerating voltages utilized are less than a factor of 5 greater than the edge energies for many elements of interest.

(iii) Implications for analytical electron microscopy

There are two points that arise from the preceding discussion which are pertinent to the practice of X-ray analysis in the analytical electron microscope.

The first point is to recall the actual practice of AEM-based microanalysis. The use of $k_{AB}$ factors, from the expression given in equation (1) is only carried out at (i) fixed kV and (ii) by a ratio technique. From this standpoint the attempt by Zaluzec (1979a) and Zaluzec et al. (1983) to generate a cross section parameterization that is applicable across a range of kV from ~2 to ~2000 as shown in Fig. 1 is unrealistic, considering the lack of reliable data. The approach is also not relevant to current AEM practice since microanalyses in the AEM are never performed
over a range of kV. Consequently, what is needed is a cross section formulation which accurately describes the variation with atomic number, at constant kV, and not vice versa. Zaluzec’s approach is therefore not ideal when choosing values of Q to use in the calculation of \( k_{AB} \). To support this argument, we draw attention to Tables 1 and 2 which contain (a) calculated values of Q and (b) calculated and experimental \( k_{AFe} \) factors respectively, using the various approaches discussed in this paper. Examination of these tables reveals that: (a) for low Z elements the Zaluzec parameterization results in significantly higher cross section values, (b) for light elements the Zaluzec \( k_{AB} \) calculations disagree significantly with other calculations and experiment, (c) the Zaluzec et al. relativistic parameterization makes insignificant changes to the ‘non-relativistic’ \( k_{AB} \) calculation, and (d) either the Dupouy or the Williams relativistic corrections similarly make insignificant changes to the non-relativistic Bethe–Brown formulation. Moreover, the complex parameterization approach (equations 7–11) for fitting Q to selected experimental data (Zaluzec, 1979a) offers no advantages over the simpler approaches (Brown, 1974).

<table>
<thead>
<tr>
<th>Element</th>
<th>Model*</th>
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<tbody>
<tr>
<td>Si</td>
<td>( 0.76 \pm 0.04 )</td>
</tr>
<tr>
<td>Ti</td>
<td>( 0.88 \pm 0.03 )</td>
</tr>
<tr>
<td>Fe</td>
<td>( 1.0 )</td>
</tr>
<tr>
<td>Cu</td>
<td>( 1.17 \pm 0.009 )</td>
</tr>
<tr>
<td>Mo</td>
<td>( 3.8 \pm 0.09 )</td>
</tr>
</tbody>
</table>

*Units \( \times 10^{-54} \) cm²

**Table 1.** Comparison of ionization cross sections at 120 keV.

<table>
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<tr>
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</tr>
</tbody>
</table>

*Wood et al. (1984), 95% confidence limits.

**Table 2.** Comparison of \( k_{AFe} \) factors at 120 keV.

High kV K lines can be considered for microanalysis because of the uncertainty in values of Q for L lines and the multiplicity of L lines. However, from the behaviour of the Zaluzec modification seen in Figs. 1 and 3 it is obvious that this parameterization is not physically realistic for a substantial energy range above \( E_e \) for these heavier elements \((Z > \sim 45)\). Therefore to use the Zaluzec parameterization to calculate \( k_{AB} \) factors for high energy Kα lines is likely to introduce large errors and perhaps even negative values for \( k_{AB} \).

**CONCLUSIONS**

We can summarize our points on the use of ionization cross sections in the AEM thus: There is a great paucity of reliable cross section data in the literature and, where data for a particular element have been reported by different workers, e.g. Ag, there is as much as a factor of 1.75 in the range of reported results. To make an arbitrary selection from these data without a detailed discussion of the justification for the particular choices is unreasonable when proposing ‘improved cross sections.’ Moreover, in the energy range of interest for the AEM \((80–300 \text{ keV})\) there is sufficient uncertainty in the experimental data to make it difficult to
choose among the numerous cross section models which exist. What is required for practical analysis is not to demonstrate good agreement for individual elements over a range of overvoltage as Zaluzec has done, but to show good agreement for one selected voltage over relevant regions of the periodic table. Currently, the vast majority of AEM work is carried out at accelerating voltages between 100 and 200 kV, and this is liable to remain the case for many years, given the expense of both intermediate and high voltage AEMs. If one wishes to use a cross section to make calculations for high energy K lines of heavy elements as Zaluzec et al. (1983) have suggested, it is necessary for that cross section to model realistically the behaviour in the region of $E_c$ since analysis will be carried out at low overvoltages for these elements. In the region close to $E_c$ the fitting parameters proposed for the Bethe (1930)–Williams (1933) cross section by Zaluzec et al. (1983) yield physically unrealistic values since negative values of $Q$ are predicted well above $E_c$. Other expressions for the cross section such as Bethe–Brown, which have the advantage of producing positive values of $Q$ down to $E_c$ can be used for AEM microanalysis to produce satisfactory results. Given these uncertainties in $Q$, we would still advocate that determination of $k_{AB}$ factors by interpolation from experimentally determined values, is a better approach for practical microanalysis, than calculation using a parameterized universal cross section.

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