ELECTRON PROBE MICROANALYSIS OF SPHALERITE

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ABSTRACT

Sources of error inherent in the use of pure element standards for the electron probe microanalysis of sphalerites are reviewed, and comparisons made between methods available for their correction. Combination of these methods yields simple matrix correction parameters which can be applied to observed intensity ratios, after the latter have been corrected for instrumental errors (dead time, drift and background), to yield refined values compensated for absorption, fluorescence and atomic number effects.

Electron probe microanalysis has been suggested (Williams, 1965) to be a useful technique for the major-element analysis of sphalerite samples, an essential part of geochemical studies of many sulfide deposits. Use of the electron probe offers definite advantages over other commonly employed techniques if the samples are chemically inhomogeneous or contain inseparable inclusions of other minerals; in fact it is particularly suitable for the study of small scale inhomogeneities, from which valuable data concerning delicate equilibrium adjustments can be derived (Barton, Bethke and Toulmin, 1963).

The principal sources of error in electron probe analysis are by now clearly defined, but satisfactory universal correction techniques have not yet been developed. This contribution reviews the particular problems encountered in sphalerite analysis, compares some of the methods which might be employed to overcome them, and outlines the basis for a simple correction procedure. Similar procedures can be readily developed for many other sulfide systems, although the factors discussed below will have to be carefully reviewed in each case in view of certain obvious limitations.

Quantitative electron probe analysis can be performed in either of two ways: (1) by comparing the intensities of characteristic X-radiations derived from the sample with those derived, under similar conditions, from calibration standards of similar, known compositions; or (2) by comparing the sample intensities with those derived from standards of accurately known but significantly different compositions (usually pure elements or simple, stoichiometric compounds of the elements concerned).

The first method is simpler in some respects and is generally favoured where it is applicable. However, it requires a "library" of standards which must be accurately analysed and homogeneous to the submicron level, and which must cover the full range of compositions expected in the samples to be analysed. If calibration standards are too widely spaced in composition, it may be necessary to develop formulae for inter-

polation along the lines of those required for single standards, and much of the simplicity of this approach will be lost.

Natural sphalerites are rarely suitable for use as calibration standards because of their common chemical inhomogeneity; furthermore, they vary relatively widely in their contents of iron, manganese and, to a lesser extent, cadmium, so that a large number of standards is required. Synthetic sphalerites are not difficult to prepare, but they also present problems of homogeneity, they are difficult to obtain in a form suitable for mounting as permanent standards, and the same range of compositions is required.

The alternative use of single standards presents other difficulties, principally in the application of corrections for the matrix effects consequent upon the chemical differences between samples and standards. The complex phenomena involved have been discussed extensively in the literature, and a variety of correction techniques has been proposed; these have been reviewed by Duncumb and Shields (1963), Archard and Mulvey (1963) and Smith (1965). In fact, the newcomer to the field of electron probe analysis is faced with an extensive, sometimes contradictory literature on correction procedures whose relative merits are difficult to evaluate. The intention of this contribution is to examine the extent of the discrepancies between selected procedures, and to choose a combination yielding optimum results in the specific case of sphalerite microanalysis. The physical basis of matrix errors is treated in sufficient detail to provide a basis for description of the procedures discussed; for more complete treatments the reader is referred to the reviews quoted earlier.

Experimental Details

The instrument employed during this investigation was an Applied Research Laboratories Electron Microprobe X-Ray Analyser (EMX), in the Department of Geophysics and Geochemistry of the Australian National University. X-ray excitation was achieved by a beam of 20 keV electrons, normal to the sample surface, and focussed to a minimum spot size less than 1 μ in diameter. The X-ray take-off angle in this instrument is constant at 52.5°. Detector pulses were amplified and read on scalers to enable simple evaluation of statistical parameters; fixed time counting was used throughout since it is suited to multichannel analysis. Sphalerite is not particularly susceptible to damage by a beam of electrons of this energy, so that counting times of 100 seconds were employed, broken into two intervals of 50 seconds each, with intermediate specimen translation to avoid contamination effects. A beam current[1] of 100 μA yielded effec-

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[1] In this discussion, *beam current* refers to the current at the anode, *probe current* to the current incident upon the specimen surface (normally measured with a Faraday cage in-

tive specimen currents of approximately 0.05 μA; the latter were integrated over each counting interval and used as the basis for instrumental drift corrections.

Standards employed were fragments of "spectrographically pure" iron, manganese and zinc, mounted in epoxy resin and polished by conventional methods. Most of the analyses were made, in connection with another project, on sphalerites from the Zeehan lead-zinc field in Tasmania; these usually contain less than 0.3 percent cadmium, which has therefore been neglected in the following discussion. Extension of the principles involved to relatively high-Cd sphalerites presents little difficulty. The three channels of the A.R.L. instrument were employed for the simultaneous determination of Fe, Mn and Zn, using the characteristic Kα radiations in each case; in the absence of a fourth channel, sulfur was not separately determined, but reliance was placed on the stoichiometry of FeS, Mns and ZnS in the sphalerite structure.

Both samples and standards were sputtered with a carbon coat. The carbon thicknesses employed were somewhat less than those recommended by Smith (1965), but were kept as uniform as possible.

Analytical runs were begun by counting on each of the three standards, including counts on either side of the Kα peaks to establish background rates. Under normal conditions of stability, up to ten sphalerites could then be analyzed before returning the standards to check the extent of drift and provide a basis for its correction.

CORRECTION PROCEDURES

All observed X-ray intensities were first corrected for dead time, specimen current drift and background. Dead time and background corrections were made by standard procedures; the drift correction, to which little reference is made in the literature, compensates for electronic instability, and is performed by plotting the total integrated specimen current (i_s) for each analysis as a function of time. It is necessary only if no provision is available for monitoring the probe current (and adjusting it if necessary to maintain a constant value) during an analytical run. Since specimen current is a function of mean atomic number of the target, it varies from standards to samples and from one sample to another; however, a "drift curve" can readily be plotted from measurements made on the periodically returned standards, with intervening sample measurements being used to define the general form of the curve. Application

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serted in place of the specimen) and *specimen current* to the actual current collected by the specimen (*i.e.* the "effective electron current" of Poole and Thomas (1962), or the probe current minus the back-scattered electrons).

of the drift correction is based on the assumed proportionality, for a given element in a given target, of X-ray intensity and specimen current.

Use of the drift correction has two principal advantages—a reduction in the frequency with which standards need to be interpolated between samples, and a considerable improvement in precision. Table 1 shows the effect of extreme correction of intensities measured on the iron standard; the significance of the correction is apparent.

MATRIX CORRECTIONS

The intensity of characteristic line spectra of target elements can only be safely considered as proportional to the weight concentrations of those

TABLE 1. SIGNIFICANCE OF DRIFT CORRECTION

Time (mins.)	1	2
0	27220	24000
42	26000	23900
80	23900	23900

1. FeK$_\alpha$ count rate from pure iron standard, corrected for dead time and background, in counts per second.

2. Ditto, after further correction for drift.

elements (the first approximation of Castaing, 1951) if they are related to equivalent intensities from standards of similar composition. If this criterion cannot be satisfied (as, for example, when pure element standards are employed), then it is necessary to consider the relative effects of the sample and standard matrices on the generation and attenuation of the X-ray quanta. These effects are conventionally grouped under three headings, *viz.*, absorption, fluorescence and "atomic number" effects. Although the physical phenomena involved are to some extent interrelated, the simplification is convenient, and forms the basis of most suggested correction procedures.

Absorption. Proper evaluation of the absorption correction requires a knowledge, for both samples and standards, of the depth distribution of electron energy, the mass absorption coefficient of the target (a function of composition) and the X-ray take-off angle. Of these, the depth distribution function is only known semiquantitatively, and uncertainty is also attached to some mass-absorption coefficients (Smith, 1965). To date most absorption correction techniques have been based empirically on extrapolations of the experimental data of Castaing and Descamps (1955) and Castaing (1960). The basic theory of this approach has been

exhaustively reiterated in the literature and need not be further discussed here; the result of the experimental work was the production of a set of curves expressing $F(\chi)$ as a function of χ, electron energy, and target atomic number, where $\chi = \mu/\rho \csc \psi$ (μ/ρ = mass absorption coefficient of target for the radiation concerned, ψ = take-off angle) and $F(\chi)$ is in effect the ratio of the measured intensity to that which would have been measured had there been no absorption.

If I' = measured intensity, then the true intensity I, corrected for absorption, is given by

$$I = I'/F(\chi)$$

Relating this to intensities derived from standards,

$$\frac{I}{I_o} = \frac{I'}{I_o'} \cdot \frac{F[\chi]}{F(\chi)}$$

where I and $F(\chi)$ refer to the sample and I_o and $F[\chi]$ to the standard.

Extrapolations of the data of Castaing and Descamps to a wider range of targets and electron energies are typified by the tables and curves of Birks (1963). These achieve a useful simplicity by treating the variation of the absorption intensity function with atomic number as a relatively small second-order correction, and using the copper data of Castaing and Descamps for all elements.

Column 1 of Table 2 lists the correction factors $F[\chi]/F(\chi)$ calculated from the data of Birks for a range of hypothetical sphalerite compositions; separate factors are of course required for Fe, Mn and Zn. Pure element standards are assumed throughout. Multiplication of the apparent intensity ratios by the appropriate factors yields refined values, corrected for absorption errors.[1]

An alternative approach to extrapolation of the same experimental data is that of Philibert (1963), who derived the analytical expression

$$F(\chi) = \frac{1}{[1 + (\chi/\sigma)]\{1 + h[1 + (\chi/\sigma)]\}}$$

where σ (a function of incident electron energy) and h (a function of atomic number) were assigned empirical values adjusted to fit the data of Castaing and Descamps. Smith (1965) has offered a set of "i" values to substitute for the original h values of Philibert; these are the products

[1] In the calculation of these factors, the mass absorption coefficients employed have been obtained from the tables of Heinrich (1964); in the case of some sphalerites the calculated values have been confirmed by experimental measurements on an X-ray fluorescence spectrograph.

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TABLE 2. VARIATION OF MATRIX CORRECTION PARAMETERS WITH COMPOSITION

I: Iron

	FeS (wt per cent)	Absorption		Fluorescence		Generation Factor		
		1 Birks $F[X]/F(\chi)$	2 Philibert Smith $F[\chi]/F(\chi)$	3 Wittry G	4 Reed $(1+\gamma)$	5 Experimental α	6 Poole & Thomas α	7 Long & Reed/Smith "α"
MnS =0.0%	1.0	1.023	1.031	0.091	1.100	0.994	1.005	0.992
	5.0	1.023	1.030	0.082	1.093	0.993	1.003	0.991
	9.0	1.022	1.030	0.074	1.088	0.992	1.002	0.987
	13.0	1.022	1.021	0.066	1.080	0.990	1.001	0.986
	17.0	1.021	1.021	0.058	1.072	0.989	0.999	0.985
	19.0	1.021	1.021	0.058	1.069	0.985	0.999	0.984
MnS =5.0%	1.0	1.022	1.021	0.079	1.091	0.992	1.003	0.990
	5.0	1.022	1.021	0.071	1.086	0.991	1.001	0.987
	9.0	1.022	1.021	0.063	1.080	0.989	1.000	0.985
	13.0	1.021	1.020	0.056	1.071	0.988	0.999	0.984
	17.0	1.021	1.012	0.048	1.064	0.987	0.997	0.983
	19.0	1.021	1.012	0.043	1.062	0.986	0.996	0.981
MnS =10.0%	1.0	1.022	1.021	0.066	1.086	0.990	1.000	0.988
	5.0	1.021	1.021	0.059	1.079	0.989	0.999	0.987
	9.0	1.021	1.012	0.051	1.069	0.987	0.997	0.986
	13.0	1.021	1.012	0.044	1.064	0.986	0.996	0.981
	17.0	1.020	1.012	0.037	1.058	0.985	0.994	0.980
	19.0	1.020	1.010	0.033	1.055	0.984	0.994	0.980

II: Manganese

	FeS (wt per cent)	1 Birks $F[X]/F(\chi)$	2 Philibert Smith $F[\chi]/F(\chi)$	3 Wittry G	4 Reed $(1+\gamma)$	5 Experimental α	6 Poole & Thomas α	7 Long & Reed/Smith "α"
MnS =1.0%	1.0	1.038	1.030	0.051	1.060	1.003	1.019	0.967
	5.0	1.037	1.029	0.046	1.056	1.001	1.018	0.966
	9.0	1.037	1.029	0.040	1.051	1.000	1.016	0.963
	13.0	1.037	1.028	0.035	1.049	0.999	1.015	0.962
	17.0	1.036	1.028	0.030	1.045	0.997	1.014	0.960
	19.0	1.036	1.028	0.028	1.043	0.996	1.013	0.960
MnS =5.0%	1.0	1.037	1.029	0.047	1.056	1.001	1.017	0.966
	5.0	1.037	1.029	0.041	1.051	0.999	1.016	0.965
	9.0	1.037	1.028	0.036	1.049	0.998	1.014	0.961
	13.0	1.036	1.028	0.031	1.045	0.996	1.013	0.960
	17.0	1.036	1.028	0.026	1.041	0.995	1.011	0.959
	19.0	1.036	1.027	0.025	1.039	0.994	1.011	0.958
MnS =10.0%	1.0	1.037	1.029	0.040	1.051	0.999	1.014	0.964
	5.0	1.037	1.028	0.035	1.048	0.997	1.013	0.963
	9.0	1.036	1.028	0.030	1.044	0.996	1.011	0.960
	13.0	1.036	1.027	0.027	1.041	0.994	1.010	0.958
	17.0	1.035	1.027	0.024	1.037	0.993	1.009	0.957
	19.0	1.035	1.027	0.023	1.035	0.992	1.008	0.957

III: Zinc

	FeS (wt per cent)	1 Birks $F[X]/F(\chi)$	2 Philibert Smith $F[\chi]/F(\chi)$	3 Wittry G	4 Reed $(1+\gamma)$	5 Experimental α	6 Poole & Thomas α	7 Long & Reed/Smith "α"
MnS =0%	1.0	1.003	1.003	—	—	0.945	0.955	0.942
	5.0	1.004	1.005	—	—	0.943	0.953	0.941
	9.0	1.005	1.007	—	—	0.942	0.952	0.936
	13.0	1.007	1.009	—	—	0.941	0.951	0.935
	17.0	1.009	1.011	—	—	0.939	0.949	0.934
	19.0	1.010	1.012	—	—	0.939	0.499	0.934

TABLE 2—(*continued*)

	FeS (wt per cent)	Absorption		Fluorescence		Generation Factor		
		1 Birks $F[X]/F(\chi)$	2 Philibert Smith $F[\chi]/F(\chi)$	3 Wittry G	4 Reed $(1+\gamma)$	5 Experimental α	6 Poole & Thomas α	7 Long & Reed/Smith "α"
MnS =5.0%	1.0	1.004	1.006	—	—	0.943	0.953	0.940
	5.0	1.005	1.007	—	—	0.941	0.951	0.939
	9.0	1.007	1.009	—	—	0.940	0.950	0.934
	13.0	1.009	1.011	—	—	0.939	0.949	0.934
	17.0	1.011	1.013	—	—	0.937	0.947	0.932
	19.0	1.012	1.014	—	—	0.937	0.947	0.931
MnS =10.0%	1.0	1.005	1.007	—	—	0.941	0.950	0.937
	5.0	1.007	1.009	—	—	0.939	0.949	0.936
	9.0	1.009	1.011	—	—	0.938	0.947	0.934
	13.0	1.011	1.013	—	—	0.937	0.946	0.931
	17.0	1.014	1.015	—	—	0.935	0.945	0.930
	19.0	1.016	1.016	—	—	0.935	0.944	0.930

of further empirical adjustments leading to better agreement with experimental observations.

As Philibert indicated, his equation actually includes a partial correction for atomic number effects (since it tends to $1/(1+h)$ as χ tends to zero) and it is therefore not strictly comparable with factors obtained from the extrapolation of Birks. The absorption portion of Philibert's expression may be written (Smith, 1965) as

$$\frac{(1 + h)}{[1 + (\chi/\sigma)]\{1 + h[1 + (\chi/\sigma)]\}}.$$

Column 2 of Table 2 lists absorption factors calculated from this expression, after substitution of Smith's i values for Philibert's h values. The similarity to factors derived from Birks' data is not surprising since both sets are derived ultimately from the same experimental results; it simply confirms that either method of correction can be employed, according to individual inclination.

Absorption corrections have also been studied by Green (1963) and Duncumb and Shields (1964), who have considered electron energy in terms of the overvoltage $(E_O - E_K)$ (where E_O = probe voltage and E_K = critical excitation potential of the relevant radiation), rather than in terms of E_O alone. Duncumb and Shields modified the Philibert absorption factor by addition of an overvoltage correction, yielding a good fit with experimental data; the tables of Adler and Goldstein (1965) incorporating this correction were not available to the author at

the time of writing and accordingly are omitted from this compilation. In cases where absorption corrections are of greater magnitude, the effects of the overvoltage correction should be investigated.

Green's data has likewise been neglected in the present work, largely because of doubts concerning its applicability to targets whose mean atomic number differs appreciably from that of the element being determined (Smith, 1965). Finally, the approach of Archard and Mulvey (1963) has also been omitted from consideration because the relatively complex calculations involved are not warranted by the small corrections required.

Smith (1965) reports unsatisfactory results when any of these methods is applied to light elements in silicate matrices, but recommends the use of either Birks' or Philibert's factors for elements higher than Si in the Periodic Table. The present work supports this recommendation in the case of sphalerites.

Fluorescence. Departures from linear weight-intensity relationships may also arise in part from fluorescent enhancement of characteristic radiation induced by the continuum or by characteristic X rays of adequate energy produced by excitation of other elements in the matrix.

Green and Cosslett (1961) have given an expression for the calculation of the extent of continuum fluorescence; Smith (1965) has shown that this expression reduces conveniently to

$$P \sim 10^7 (\langle Z \rangle Z_A{}^3)^{-1}$$

where P is the ratio of direct to indirect production, $\langle Z \rangle$ is the mean atomic number of the target, and Z_A is the atomic number of the element being determined. Table 3 lists P-values calculated from this expression for Zn, Fe and Mn targets, and for a sphalerite of typical composition; in all cases continuum fluorescence contributes less than 8 percent of the total yield and, more importantly, there is little difference between samples and standards. This effect has accordingly been ignored in subsequent calculations, although it may be of considerable significance in other cases where atomic number separation between samples and standards is more extreme (in such cases it may be compensated by atomic number corrections if these are made experimentally).

Characteristic fluorescence arises when portion of the characteristic spectrum of another matrix element has wavelengths shorter than the absorption edge of the measured radiation. In the case of sphalerites, there are three possibilities which require investigation: (1) excitation of FeK_α, by ZnK_ι, (2) excitation of MnK_α by ZnK_α, and (3) excitation of MnK_α by FeK_β.

TABLE 3. CALCULATED CONTINUUM FLUORESCENCE YIELDS

Element sought	Matrix	P
Zn	Zn	12.4
Zn	$(Zn_{0.94}Fe_{0.05}Mn_{0.01})S$	14.7
Fe	Fe	21.7
Fe	$(Zn_{0.94}Fe_{0.05}Mn_{0.01})S$	22.7
Mn	Mn	25.6
Mn	$(Zn_{0.94}Fe_{0.05}Mn_{0.01})S$	25.6

Methods of correction for characteristic fluorescence have been proposed by Castaing (1951), Wittry (1957, 1962), Birks (1961, 1963) and Reed (1965). Castaing's formula is relatively difficult to use (Wittry, 1962), and Birks' correction is based empirically on data collected on a probe having a different take-off angle from that used by the author, but does not incorporate an emergence angle factor. Accordingly the methods of Wittry and Reed were selected for comparison.

Wittry expresses the fluorescent contribution in the form of a function G, such that

$$\frac{I}{I_o} = \frac{I'}{I_o'} \cdot \frac{F[\chi]}{F(\chi) + G}$$

G itself is the product of subfactors G_1, G_2, G_3 and, if relevant, an overall dilution multiplier (for systems of more than two elements). G_1 is a function of the difference in atomic numbers $(Z_A - Z_B)$ between the exciting (A) and excited (B) elements, G_2 of the ratio Z_A/Z_B and the concentration of B, and G_3 of Z_A. Wittry provides curves for the determination of these factors.

Wittry's treatment is derived for the binary case, but a method for extension to ternary systems is indicated. Sphalerites, however, are essentially four-element systems, so that a further extrapolation of Wittry's treatment is required. This involves some additional approximation, *viz.*, the assumption of similar mass absorption coefficients of Fe, Mn and S for ZnK_α, of Zn, Fe and S for MnK_α, and of Zn, Mn and S for FeK_α. This assumption is not altogether unreasonable in the present case, but it may invalidate this procedure in other mineral systems. In such cases, calculations to allow for significant differences in mass absorption coefficients become unduly complex, and Castaing's method may be more suitable.

Following Wittry's Table 1 (1962, p. 16), the following parameters
were used for the calculation of the sub-factors:

System	Element sought	G_1	G_2	G_3	Multiplier
Zn→Fe Mn S	Fe	$Z_{Zn}-Z_{Fe}$	Z_{Zn}/Z_{Fe}; $(C_{Fe}+C_{Mn})$	Z_{Zn}	$\dfrac{C_{Zn}}{(1-C_{Fe})}$
	Mn	$Z_{Zn}-Z_{Mn}$	Z_{Zn}/Z_{Mn}; $(C_{Fe}+C_{Mn})$	Z_{Zn}	$\dfrac{C_{Zn}}{(1-C_{Mn})}$

In the derivation of the dilution multiplier, *e.g.*, for the calculation of
Zn→Fe fluorescence, Mn and S are regarded as joint diluents of the sys-
tem Zn-Fe (hence the necessary assumption of similar mass absorption
coefficients). Thus (C_C+C_D) has been substituted for C_C in Wittry's
corresponding expression. Column 3 of Table 2 lists values of G calcu-
lated for the range of sphalerite compositions; it is apparent that these
values are small in the case of iron and smaller still for manganese. In
both cases, however, they are significant, and their incorporation has
been found to lead to improved precision.

The excitation of MnK_α by FeK_β has also been considered in terms of
excitation by an imaginary element of $Z\sim27$ (the wavelength of CoK_α is
similar to that of FeK_β) and allowing for an average $K_\beta:K_\alpha$ intensity
ratio of 1:6. This approach represents a further approximation in view of
the sparse information on K_β excitation efficiencies; the results, however,
indicated that the effect involved is small and of possible significance only
for very accurate work on high-iron sphalerites, in which cases it may
approach 10 percent of the ZnK_α excitation. Corrections for this effect are
not included in Table 2.

Reed (1965) has presented an alternative fluorescence correction pro-
cedure based on assumptions differing slightly from those of Wittry.
Reed's procedure for multielement targets containing element B excited
by element A is to let

$$C_B = \frac{K_B}{1 + \gamma}$$

where C_B = true weight concentration of B, K_B = apparent concentra-
tion of B corrected for all factors other than fluorescence, and γ, the
fluorescence factor, is given by

$$\gamma = C_A \cdot J(B) \cdot \frac{\mu_A^B}{\mu_A} \cdot D \cdot [g(x) + g(y)]$$

C_A is the weight concentration of element A. $J(B)$, determined from Reed's tables, is a function of the element determined, the type of radiation (K or L) measured and the type (K or L) of the exciting radiation. μ_A^B and μ_A are mass absorption coefficients for element B and the sample respectively for the exciting radiation of element A. D is a function of incident electron energy and of $Z_A - Z_B$ (corresponding to Wittry's G_1). $g(x)$ and $g(y)$ are functions of the absorption parameters x and y, where

$$x = \frac{\mu_B}{\mu_A} \cdot \operatorname{cosec} \psi; \quad \text{and} \quad y = \frac{\sigma}{\mu_A}$$

(the mass absorption coefficients being those of the target for the radiations indicated, and σ being the electron mass absorption, or "Lenard," coefficient. Values of σ (after Philibert) and curves for the determination of $g(x)$ and $g(y)$ are given by Reed.)

Values of $(1+\gamma)$ for the range of sphalerite compositions are given in Column 4 of Table 2. These are not directly comparable with Wittry's G-values, but the relative effects of the two methods on the final correction parameters are apparent from Table 5 below.

Calculation by Reed's method of the fluorescence of MnK_α by FeK_β gives very similar results to those obtained by Wittry's method, and confirms that this is generally an insignificant source of potential error. The more efficient excitation of MnK by FeK quantum energies is outweighed by the low concentration of Fe relative to Zn and by the lower K_β intensity.

"Atomic Number" Effects. Where samples and standards differ significantly in composition, differences in the depth distribution of electron energy will also become significant, and it is necessary to correct further the observed intensity ratios. The term "atomic number effects" is frequently used to describe these differences, although Smith (1965) has pointed out that atomic number is not the only variable involved, so that he prefers the term "generation factor." Whatever the name employed, the effects remain at present imperfectly understood, and this has led to a variety of approaches to the derivation of the necessary correction factors.

Castaing (1951, 1963) introduced the concept of α-parameters associated with each element, such that the true concentration C_A of element A in a multielement target is derived from the intensity ratio k by

$$C_A = k \times \frac{\Sigma C_i \alpha_i}{\alpha_A}$$

He suggested that appropriate values of α_i *for a given system* could be determined experimentally by analysis of alloys of known composition within that system. The assumption that α for a multielement target is a linear combination of the α-parameters of the constituent elements is not universally valid, but would appear to be reasonable for a given accelerating voltage, for systems having a limited range of mean atomic numbers. Philibert's $(1+h)$ factor is based on a similar approximation.

Poole and Thomas (1962) extended this treatment by further resolution of the factors inherent in α-parameters. Following Castaing (1960) they showed that the distribution of excitation in depth is a function of both target deceleration or stopping power S_i and an electron backscatter coefficient λ_i, and that for fixed time counting,

$$\alpha_A = S_A \lambda_A$$

λ_i is defined as the ratio between the intensity which would be emitted if there were no backscattering and that which is actually emitted, and S_i is defined as $-(\partial E/\partial z)/\rho$. Values of S for various elements have been calculated by Nelms (1956, 1958); using these and various experimentally determined values of α for alloys of known composition, Poole and Thomas calculated a series of empirical values of λ_i. Extrapolation of these data allows calculation of α-parameters for other elements and systems (within the limits indicated above). Ziebold and Ogilvie (1963) presented a convenient curve relating α to Z, based on the data of Poole and Thomas; strictly speaking this refers only to 30 keV electrons, but Poole and Thomas suggest that the variation with electron energy of the S-factor at least is not pronounced when standard:sample intensity ratios are considered, so that it would appear possible to use Ziebold and Ogilvie's curve down to 20 keV.

Variations of atomic number are not extreme when Fe, Mn and Zn are determined in sphalerites using pure element standards, and this suggested that the approaches of either Castaing or Poole and Thomas might be used with reasonable success. Accordingly, α-parameters were determined experimentally as follows: α_{Zn} was assigned an arbitrary value of 1.33 (the value indicated by Ziebold and Ogilvie) and, from intensity measurements (corrected for absorption) on Zn and ZnS, a corresponding value of 1.56 was determined for α_S. This was used in turn to determine values of (1) 1.40 for α_{Fe}, measured on pure Fe and FeS (troilite), and (2) 1.41 for α_{Mn}, measured on pure Mn and MnS (low-iron alabandite). These values are in reasonable agreement with those of 1.52, 1.40 and 1.42 respectively derived from Ziebold and Ogilvie's curve, thus confirming that the latter may be used with reasonable success at least as low as 20 keV.

Using these α-parameters, a series of correction factors was then cal-

culated for the range of sphalerite compositions, and these are given in Column 5 of Table 2; correction factors calculated by the method of Poole and Thomas from the data of Ziebold and Ogilvie are given in Column 6.

The significance of this correction is demonstrated in Table 4, which compares the apparent composition of a typical sphalerite after correction for absorption and fluorescence with that after further correction for atomic number effects (using the experimental parameters). The small atomic number corrections for Fe and Mn are not surprising, since the mean atomic number of sphalerite lies, according to composition, between 24.5 and 25.5, and the atomic numbers of iron and manganese are 26 and 25 respectively. The effect on Zn ($Z = 30$), however, is more marked and indicates that evaluation of this factor is necessary even when atomic number differences are not extreme.

TABLE 4. SIGNIFICANCE OF "ATOMIC NUMBER" CORRECTIONS

	1	2
ZnS	85.9	91.2
FeS	7.8	7.9
MnS	0.8	0.8
	94.5	99.9

1. After correction for instrumental factors, absorption and fluorescence.
2. After further correction for "atomic number" effects.

The derivation of Poole and Thomas assumes that the ionization cross-section is independent of the overvoltage ($E_O - E_K$), but this is not altogether supported by experimental or theoretical data. Duncumb and Shields (1963) and Green (1963) have considered the problem in terms of penetration, ionization and backscatter factors; this approach culminated in the development by Long and Reed of an as yet unpublished (except by Smith's reference) formula whereby the counting rate for a given target is multiplied by the factor

$$\{5.16 + \ln\left[(E_O + E_K)/2\right] - \ln\langle Z\rangle\} \times \left\langle\frac{Z}{A}\right\rangle \times R^{-1}$$

where the angle brackets $\langle\rangle$ indicate weighted means, and $R =$ Green's backscatter coefficient.

Smith (1965) empirically modified this expression to

$$\{4.7 + 0.9\ln(E_O - E_K) - \ln\langle Z\rangle\} \times \left\langle\frac{Z}{A}\right\rangle \times R^{-1}$$

suggesting that the new value for this first factor gave better results for light elements in silicate matrices. The author understands (J. V. P. Long, pers. comm.) that Long and Reed have since recommended a further modification of the first factor to 4.54, to be used in conjunction with their original form of the second overvoltage factor, rather than the modification suggested by Smith.

In Column 7 of Table 2 are listed values of the correction parameters (*relative to those of pure element standards*) calculated from Smith's expression; the form in which these and the other atomic number correction parameters are expressed requires them to be *divided into* the intensity ratios after the latter have been corrected for absorption and fluorescence, using the method of successive approximation where necessary. Agreement with the corrections calculated from the experimental data or by the methods of Poole and Thomas is reasonably good. The largest discrepancy is found in the case of Mn; a correction parameter close to unity would be expected if atomic number considerations alone were involved, and this is confirmed by the experimental measurements. Factors calculated from the data of Poole and Thomas are of the order of 1 to 2 percent higher, possibly because this data is appropriate for 30 keV electrons. On the other hand, the Long and Reed/Smith parameters are 3 to 4 percent lower; examination of the calculations shows that this difference stems from the significance of the $\langle Z/A \rangle$ factor in Smith's expression. Z/A does not vary smoothly throughout the Periodic Table, and in this particular case a fortuitously significant difference appears between Z/A for Mn and $\langle Z/A \rangle$ for sphalerite, even though there is little difference in $\langle Z \rangle$. It is apparent, however, that these discrepancies are of very small magnitude in terms of uncertainties inherent in other aspects of the correction procedures. Indeed, the agreement observed is sufficiently encouraging to support the use of mathematical corrections in cases where more complex compositions preclude the experimental approach.

COMPOSITE CORRECTION FACTORS

Smith (1965) has foreshadowed the development, over the next few years, of linear correction formulae which may be applied to the electron probe analysis of various groups of rock-forming minerals, avoiding (in the groups for which formulae are available) the necessity for tedious calculations for each analysis. With the development of such a formula for sphalerite in mind, the extent of variation between different combinations of the procedures described above has been examined.

It is obvious from Table 2 that the choice between the absorption correction procedures of Birks and Philibert is of no great significance in this case; for convenience correction factors calculated from the data of Birks

have been used in the calculations discussed below, but other analysts have preferred Philibert's approach.

The extent of discrepancies arising from the choice between the two fluorescence and three atomic number correction procedures outlined above can be examined conveniently by calculating final correction parameters based on various combinations of these procedures. For each

TABLE 5. EQUATIONS FOR CALCULATION OF COMBINED CORRECTION FACTORS

Correction Method			Correction Factor[1]
Absorption	Fluorescence	"Atomic Number"	
A. Iron:			
Birks	Wittry	Experimental	$0.939 + 0.0020X + 0.0025Y$
Birks	Reed	Experimental	$.933 + .0018X + .0017Y$
Birks	Wittry	Poole and Thomas	$.929 + .0020X + .0025Y$
Birks	Reed	Poole and Thomas	$.923 + .0018X + .0017Y$
Birks	Wittry	Long and Reed/Smith	$.940 + .0022X + .0024Y$
Birks	Reed	Long and Reed/Smith	$.934 + .0091X + .0016Y$
B. Manganese:			
Birks	Wittry	Experimental	$0.979 + 0.0015X + 0.0014Y$
Birks	Reed	Experimental	$.975 + .0011X + .0012Y$
Birks	Wittry	Poole and Thomas	$.964 + .0015X + .0014Y$
Birks	Reed	Poole and Thomas	$.958 + .0011X + .0014Y$
Birks	Wittry	Long and Reed/Smith	$1.015 + .0016X + .0016Y$
Birks	Reed	Long and Reed/Smith	$1.010 + .0013X + .0013Y$
C. Zinc:			
Birks	—	Experimental	$1.061 + .0009X + .0006Y$
Birks	—	Poole and Thomas	$1.050 + .0009X + .0006Y$
Birks	—	Long and Reed/Smith	$1.064 + .0011X + .0006Y$

[1] $X =$ weight percent FeS; $Y =$ weight percent MnS

possible combination, combined correction parameters can be calculated for a range of sphalerite compositions. Equations expressing the variation of the final correction parameter with composition have been derived in this fashion, and the results are given in Table 5; it was assumed that the correction parameter is a linear function of both Fe and Mn content over the relatively limited compositional range involved, and the equations were computed from the calculated data by standard mathematical procedures.

It is evident from Table 5 that discrepancies between the various combinations are remarkably slight, particularly when their effects on the

relatively small contents of iron and manganese are considered. In practice satisfactory results are achieved by using the following simplified expressions to derive factors by which observed intensity ratios can be multiplied (after correction for dead-time, background and drift) to correct for matrix errors:

Iron: Correction factor $= 0.94 + 0.002(X + Y)$
Manganese: Correction factor $= 0.97 + 0.002(X + Y)$
Zinc: Correction factor $= 1.06 + 0.001(X + Y)$

where $X =$ weight percent FeS and $Y =$ weight percent MnS.

It is difficult to evaluate the accuracy of these expressions and/or the experimental technique in the absence of a sufficiently wide range of homogeneous analyzed sphalerites. However, 50 analyses of sphalerites apparently ranging from 0 to 15.0 percent FeS and from 0 to 1.3 percent MnS yielded analysis totals ranging from 95.6 to 104.2 percent, with a mean of 99.7 percent and a standard deviation of 2.1 percent of the mean. These results are regarded as satisfactory, since the analyses were performed on a routine basis with no particular emphasis placed on the avoidance, for example, of fluorescence effects from adjacent grains of

TABLE 6. REPLICATE ANALYSES—SPHALERITE Z33(a) (T.L.E. MINE, ZEEHAN, TAS.)

	4/2/65	3/3/65	16/6/65	1/10/65
Point I:				
FeS	5.2	5.4	5.3	5.4
MnS	0.9	0.9	0.9	0.8
ZnS	94.0	n.d.	93.6	n.d.
	100.1	—	99.8	—
Point II:				
FeS	6.6	6.9	6.7	6.9
MnS	1.5	0.9	0.8	0.8
ZnS	92.9	n.d.	91.8	n.d.
	101.0	—	99.3	—
Point III:				
FeS	3.7	3.9	3.9	3.9
MnS	0.5	0.5	0.4	0.5
ZnS	95.4	n.d.	95.2	n.d.
	99.6	—	99.5	—

other minerals, and since the dispersion optics available necessitated the measurement of ZnK_α in the second order, with reduced characteristic intensities, high background and hence relatively poor counting statistics.

Precision was tested by replicate analyses, over a period of eight months, of three carefully marked areas on a single polished section. The results are presented in Table 6; with the exception of the unexplained anomalous values for this first analysis of Point II, the precisions are within the limits currently considered to be satisfactory for electron probe analysis.

It is therefore concluded that the expressions quoted may be conveniently used to calculate simple matrix correction parameters, applicable to measurements made at 20 kV on instruments having the same geometry as the A.R.L. unit; the same procedures may be followed to calculate similar parameters for other instruments. It is intended to investigate further the applicability of these methods to other sulfide and related systems where absorption, fluorescence and atomic number effects are of greater magnitude.

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