Determination of Cliff–Lorimer $k$ factors for Philips EM400T

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The Cliff-Lorimer standardless ratio technique for thin foil X-ray microanalysis requires the knowledge of $k$ factors that relate the measured characteristic X-ray intensities to the composition of the specimen. This paper reports the determination of a comprehensive set of $k$ factors at 120 kV for a Philips EM400T analytical electron microscope, using well characterized mineral standards and homogeneous single-phase alloys. The experimental data are compared with previous experimental results and also with calculations from first principles of the theoretical $k$ factor values.

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The Cliff-Lorimer ratio approach$^1$ to in-situ quantification of thin film X-ray microanalysis data has gained popularity due to its simplicity. It is a standardless technique that for a binary system $A$-$B$ relates the characteristic peak intensities above background $I_A$ and $I_B$ to the actual concentration of the species in wt-%, $C_A$ and $C_B$, according to the relationship:

$$\frac{C_A}{C_B} = \frac{k_{AB} I_A}{I_B}$$  \hspace{1cm} (1)

where $k_{AB}$ is termed the Cliff-Lorimer factor. This factor is independent of variations in specimen thickness if the ‘thin film criterion’ is fulfilled. This criterion assumes that X-rays are neither absorbed nor fluoresced in the specimen.

By convention, $k_{AB}$ factors are ratioed to Si, i.e. tabulation usually occurs as $k_{ASI}$, $k_{BSI}$, etc., and the values are called $k$ factors. When Si is not present in the specimen the relative $k_{AB}$ factor can be obtained by dividing the appropriate $k$ factors, for example

$$k_{AB} = \frac{k_{ASI}}{k_{BSI}}$$

Since $I_A$ and $I_B$ are measured simultaneously their ratio is independent of fluctuations in beam current although, as shown by Goldstein et al.$^2$, the $k$ factors decrease with increasing operating voltage. To date, the only comprehensive range of $k$ factors for $K_{\alpha}$ lines determined experimentally are those reported by Cliff and Lorimer$^1$ and Lorimer et al.$^2$ which cover a selection of elements with characteristic peaks in the range 1–10 keV. These results were obtained using an EMMA-4 analytical instrument which utilizes a mini-lens to form a probe down to \~10$^2$ nm. Limited work has been carried out on modern analytical instruments$^4$ but most reported results refer to a single $k_{AB}$ determination for a system of interest to the investigator. The aim of the present work is to calibrate our Philips EM400T system by determining, experimentally, a comprehensive range of $k$ values, thereby allowing future quantitative analyses to be carried out without reference to standards at the time of the analysis. The experimental values are compared with the experimental results of Lorimer and coworkers$^1,3$ and calculated values using the method of Goldstein et al.$^2$

EXPERIMENTAL PROCEDURE

The $k$ values were determined from a set of well characterized mineral standards and single-phase homogenized alloys summarized in Table 1. The minerals marked CL in Table 1 are the original standards used by Cliff and Lorimer and were prepared and chemically analysed in their laboratory. The mineral samples prepared in our laboratory were crushed under methanol and the slurry dispersed ultrasonically to separate out the finest particles. These samples were floated onto formvar and placed on carbon-coated Be microscope grids.

A series of single-phase alloys (also listed in Table 1) were induction-cast and homogenized. Composition and homogeneity were determined by electron microprobe analysis. Thin foils were prepared by diamond wafering thin slices from bulk samples, then electrodischarge machining 3 mm discs. These discs were ground to \~250 $\mu$m on SiC 600 mesh paper. Final thinning to electron transparency was accomplished by jet polishing followed by ion beam thinning to remove any residues deposited on the foil from jet polishing.

Measurements of $k$ factors were carried out using a Philips EM400T analytical electron microscope fitted with an EDAX energy-dispersive Si(Li) detector. The detector resolution was nominally 153 eV FWHM at Mn $K_{\alpha}$. Specimens were held in a Be low-background holder to minimize background X-ray emission from specimen-generated bremsstrahlung. All analyses were carried out at 120 kV with an emission current of 25–40 $\mu$A and a minimum of 10000 counts were collected for each peak in the spectrum.
Principles, limits, statistical evaluation

DISCUSSION of paper by Tixier, Thomas, and Bourgeot

P. J. STATHAM:
When concentration values are determined by normalization to a total of say 100%, the statistical error is not as straightforward to define as for the ratio of two concentrations. What method would you suggest for estimating errors for normalized results?

R. TIXIER:
In normalizing the results one introduces one more relationship between the variables. From a statistical point of view this could be taken into account, in the calculation of the precision, as a reduction of the number of degrees of freedom. I would suggest that the problem in normalization is that it is prone to introduce systematic (non-random) errors, thus reducing the accuracy.

G. W. LORIMER:
As Dr Tixier points out, it is important not to use too simple an approach to the quantitative analysis of thin foils. However, it is also important not to complicate the problem in such a way that so many calculations and corrections have to be made that there is no time left in which to carry out the analysis!

R. TIXIER:
Of course, as you suggest, one can select arbitrarily very fast ways of getting the wrong result. On the other hand, physical calculations and corrections are usefully made at least one time by hand, to understand how it works. Subsequently these can be done by your spectrometer mini-computer in a matter of a few seconds.

J. I. GOLDSTEIN:
I am surprised that you did not observe fluorescence in your Fe-Cr alloy. Can you explain why Lorimer and his colleagues observe such a fluorescence effect while you do not?

R. TIXIER:
I do not know how Lorimer et al. came to observe such a high fluorescence in their experiments. In our measurements, and considering the attainable precision, fluorescence was found to be a negligible effect in the range of specimen mass thicknesses observable. This is consistent with theory and also with observations by others.
To ascertain the limits of applicability of the thin film criterion for a given system, the effect of absorption on the $k_{AB}$ factor for each system was determined using the equation:

$$CF = \left[ \frac{(\mu/p)_{A}^{\text{spec}}}{(\mu/p)_{B}^{\text{spec}}} \right] \times \frac{1 - \exp - \left[(\mu/p)_{B}^{\text{spec}} \csc \alpha(\rho t)\right]}{1 - \exp - \left[(\mu/p)_{A}^{\text{spec}} \csc \alpha(\rho t)\right]}$$

(2)

where $CF$ is the correction factor applied to the value of $k_{AB}$; the terms $(\mu/p)_{A}^{\text{spec}}$ and $(\mu/p)_{B}^{\text{spec}}$ are the mass absorption coefficients of $A$ and $B$ in the specimen, $\rho$ is specimen density, $\alpha$ is the take-off angle (~20° in a Philips EM400T), and $t$ is the measured film thickness in cm.

Wherever possible, systems that required an absorption correction of <10% were used. In the results discussed below, only the values of $k_{eq}$ and $k_{eq}$ were corrected. If the system satisfied the thin film criterion for foil thicknesses up to 500 nm, or the material appeared to be beam-sensitive, data were collected by rastering the beam over a thin area of 250 nm². For systems showing significant absorption below a foil thickness of 500 nm, data were collected from a spot 5-10 nm in diameter. The thickness of the foil in the analysis area was determined by the contamination spot separation method. Although this technique is known to overestimate the actual thickness, the absorption correction was of the order of the counting statistics error.

Thin edges of crushed minerals and foil regions transparent at 120 kV were chosen for analysis. Counting time was varied to give at least 10,000 accumulated counts from each element at each data point. Integration of peak counts and background subtraction were effected by the EDAX SWTHIN program using full shell integrated counts and adjusted to determine $K_a$ intensities. Typical spectra...
collected are shown in Figs. 1 and 2, while Fig. 3 shows a typical peak and background fit to Fig. 2 given by the SWTHIN program.

THEORETICAL CALCULATION OF k FACTORS

Goldstein et al.² have developed a method for calculating k factors for Ka lines of any element X as a function of operating voltage. The equation for \( K_{xS1} \) and for \( K_a \) lines:

\[
k_{xS1} = \frac{(Q_K \omega_K A/K)_{Si}}{(Q_K \omega_K A/K)_X} \frac{\varepsilon_{Si}}{\varepsilon_X} \tag{3}
\]

where \( Q_K \) is the ionization cross-section for K lines, \( \omega_K \) is the fluorescence yield for K lines, \( a \) is the ratio of \( K_a/(K_a + K_b) \), \( A \) is the atomic weight, and \( \varepsilon \) is the EDS detector efficiency. The value of \( \varepsilon \) can be obtained by taking into account the absorption of X-rays as they enter the EDS detector in the Be window, gold surface layer and silicon dead layer:

\[
\varepsilon_X = \exp \left[ -\left( \frac{\rho}{\rho_B} \right)_X Y_B \frac{X}{K_{Si}} \right] \exp \left[ -\left( \frac{\rho}{\rho_B} \right)_{Au} Y_{Au} \frac{X}{K_{Si}} \right]
\]

where \( \rho/\rho_B \), \( \rho \) and \( Y \) are the appropriate mass absorption coefficients, densities and thicknesses of the Be window and the gold and silicon layers. In equation (3) only \( Q_K \) varies with operating voltage.

To calculate \( k_{xS1} \) the Green-Cossett² cross-sections were chosen. Values of \( \omega_K \) were taken from the fitted \( \omega_K \) values of Bambynek et al.⁸ using the Burhop equation.⁹ The values of \( a \) and \( \mu/\rho \) were obtained from Heinrich et al.¹⁰ and Heinrich¹¹ respectively. The detector parameters, as suggested by Zaluzec,¹² used in this calculation are \( Y_{Be} = 7.6 \mu m \) (0.3 mm), \( Y_{Au} = 0.02 \mu m \) and \( Y_{Si} = 0.1 \mu m \).

RESULTS AND DISCUSSION

Figure 4 shows a selection of the k factor measurements plotted as a function of \( K_n \) characteristic X-ray energy. In Fig. 5 the experimental results are compared with the calculated k factors for 120 kV using the method outlined above. In Fig. 6 the results of Cliff and Lorimer¹ and Lorimer et al.³ for 100 kV are compared with the results of this study. Table 2 gives a summary of all the data used in Figs. 4, 5 and 6. In addition experimentally measured k factors for P, Cr, Ni, Mo and Ag are listed. The error bars associated with the data in Figs. 4, 5 and 6 are discussed in the next section.

Comparison with calculated values

From Fig. 5 it is clear that above Si the calculated and experimental values follow the same trend: increasing with increasing \( K_n \) energy. It is not possible at this stage to explain any differences between the calculated and experimental values with certainty but the following factors should be considered:

(a) There are alternative expressions for ionization cross-sections \( Q_K \) which may result in closer agreement between theory and experiment. However, use of the cross-section expression recommended by Powell¹³ yields an even greater discrepancy between calculated and measured k factors.

(b) The customary practice of ratioing each k factor to Si means that any error in the values for Si used in equation (2) will introduce a systematic error into the calculated data plotted in Fig. 5.

The experimental k value for Al coincides with the theoretical value but both Mg and Na show values significantly greater than the calculated figures. There is strong evidence, as reported by Mehta et al.,¹⁴ that mass volatilization of Na occurs when Albite is exposed to the electron beam. The specimen was invariably observed to degrade in the EM400 during the time necessary to accumulate 10,000 counts, so this factor may contribute to the discrepancy in Na values. Yet this does not explain the high value for Mg. It is assumed that carbon contamination either on the specimen or on the Be window was not a limiting factor. This is considered reasonable in view of the minimal observed contamination in the ion-pumped stage of an EM400T. Another possible limitation on the quantification procedure is the current inadequacy of the EDAX SWTHIN program in terms of an accurate description of the continuum background at the low energy end of the spectrum where the bremsstrahlung intensity changes rapidly with
Error bars represent 95% confidence limits.

4 Variation of experimentally determined $k$ factors with characteristic X-ray energy for a selection of elements studied.

5 Comparison of experimental results in Fig. 4 with calculated $k$ factors at 120 kV.

Open circles: reported by Lorimer et al.\textsuperscript{3}

Dotted error bars (where shown) reported originally by Cliff and Lorimer\textsuperscript{1}

6 Comparison of experimental results in Fig. 4 with previous experimental work of Lorimer and coworkers.
energy. Any underestimation of the actual intensity of Na and Mg Kα X-rays would result in an increase in the values for $k_{NaSi}$ and $k_{MgSi}$.

Comparison with previous experimental data
In Fig. 6 the current data are compared with the experimental results of Lorimer and coworkers. The data points shown are those given in the latest paper by Lorimer et al. but the error bars (where shown) are those reported in the original work of Cliff and Lorimer, since the later work showed no error bars. In the majority of cases there is overlap between the experimental results, although invariably the errors in this current investigation are significantly lower. Discrepancies at the lower end of the energy range may be related to the problems of specimen degradation, relative differences in carbon contamination rates between the EMMA4 and the EM400T, and differences in the methods of data handling. But in conclusion it is clear that significant differences in the value of $k_{AB}$ exist and the necessity for the empirical determination of $k$ factors for a specific instrument are obvious.

QUALITY OF DATA
The error bars on the experimental data in Figs. 4, 5 and 6 represent the relative error at the 95% confidence limit for the $k$ factors, determined using the Student $t$ analysis for 30 individual readings taken from ~10 different areas on each sample. The calculated error in $k_{AB}$ can be given by:

$$\% \text{ error} = \frac{t_{\text{95}}}{\text{n}} \frac{S_c}{\sqrt{n}} \times 100$$

where $t_{\text{95}}$ is the Student $t$ value for $n$ readings and a 95% confidence level, $S_c$ is the standard deviation for $n$ readings, and $k_{AB}$ is the mean $k_{AB}$ value.

If the $k_{AB}$ values are interpolated, individual errors must be added after each interpolation. As shown in Table 2, the final cumulative error in the $k_{AB}$ value may be considerably larger than the original $k_{AB}$ value. Clearly errors in interpolated $k$ factors will always be larger than experimentally determined factors. To obtain the most accurate experimental data it is always advisable to create the required standards so that interpolation errors need not be taken into account. However, it is occasionally impossible to create the required standards (for example if suitable single-phase alloys or stoichiometric intermetallic compounds cannot be found) and in this case interpolation of existing $k$ factor data or calculated $k$ factors is the only possible route for quantification.

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REFERENCES
DISCUSSION of paper by Wood, Williams, and Goldstein

P. DOIG:
Do you consider it necessary to use long-exposure STEM probe excitation of standard foils to establish accurate $k$ values? We found that for our metal foils better X-ray counting statistics were obtained, with virtually no contribution from contamination deposition, by using a low beam current in a condensed TEM probe $\sim 1 \mu m$ diameter. Our foils were of uniform thickness.

D. B. WILLIAMS:
No, we do not consider it necessary to use long exposures in STEM mode to obtain the necessary counts, except (a) in the cases where specimens are of a very non-uniform thickness (as was often the case for the crushed mineral samples) and (b) in cases where significant absorption is expected and therefore the accurate local thickness has to be determined.

P. J. STATHAM:
In your abstract you imply an instrumental dependence of $k$ factors but omit to mention the efficiency of the Si(Li) X-ray spectrometer which probably provides the largest source of uncertainty in $k$ values for elemental lines below 2 keV. Are these instrumental factors associated with the microscope that you consider to be important?

D. B. WILLIAMS:
The instrumental factors referred to in the abstract certainly include the variability associated with different EDS detectors below X-ray energies of 2 keV, but also we are concerned about the accuracy of the $\pm 20^\circ$ take-off angle that Philips report for their EM400T. If this figure is wrong by a few degrees then significant errors can be introduced into absorption correction factors, as discussed in the text of the review paper by Professor Goldstein (these proceedings).

G. CLIFF:
We have found that $k$ values determined on EMMA-4 in 1974 for $K_\alpha$ radiation from Ti to Mo are still valid today on both EMMA-4 and an EM400T. The $k$ values from Na to Ti are significantly different on the two instruments. This reinforces the suggestion that $k$ values should be experimentally determined for elements $Z < Si$.

D. B. WILLIAMS:
We too have found it necessary to redetermine $k$ factors if the detector is changed, but otherwise we are confident that the values reported in this investigation will remain viable for the life of our EM400T.
A thin film k-value calibration for low atomic number elements has been developed for use in the analysis of powdered silicate mineral samples using a modified AEI EM6G transmission electron microscope. Peak interference and background difficulties can be overcome by computer peak deconvolution and background correction procedures. Element loss and carbon contamination effects are reduced because of the large beam diameter (~3 μm) of the instrument. The loss characteristics of Na and K vary with the containing lattice. For this reason, element loss profile determination should precede the quantitative analysis of any unfamiliar mineral containing these elements.

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Microprobe analytical systems have been successfully applied to the major element analysis of silicate and aluminosilicate minerals for many years. While high resolution thin film microanalysis using the transmission electron microscope has been applied to specific mineral systems (Champness et al., Lorimer and Cliff) little has been published on the problems associated with the use of this technique for routine major element mineral analysis.

The special problems associated with the analysis of the low atomic number elements have been investigated. An element k-value calibration has been developed for the element range Na to Fe for routine analysis of finely powdered silicate minerals.

**EQUIPMENT**

The microanalytical equipment used comprised a modified AEI EM6G transmission electron microscope coupled to a Link Systems Model 290 analyser and Kevex energy-dispersive detector (resolution 146 eV, beryllium window thickness ~8 μm). The level of backscattered electrons entering the detector was significantly reduced by placing an Eclipse button magnet 50 mm in front of the beryllium window (Hall) while extraneous and bremsstrahlung X-radiation from the stage and surroundings were effectively removed using a specially modified Swann double-tilting cold stage (Swann and Swann) and careful carbon shielding of areas of the tilting tube, specimen holder and stage exposed to backscattered electrons. Full details of the modifications are given by Fitzgerald and Storey.

When fully focused the EM6G has a beam diameter of approximately 3 μm which is significantly larger than in the majority of transmission microscopes specifically designed for microanalysis (e.g. EMMA: 0.1 μm). Although the large beam diameter has considerable disadvantages in terms of spatial resolution it has many advantages in low atomic number element microanalysis where element volatility and instrumental carbon contamination become increasingly important.

**CALIBRATION STANDARDS**

Independently analysed silicate minerals were used as standards for the determination of the low atomic number element k-value calibration for the instrument. A convenient compositional spread of the range of elements under investigation in a variety of lattice environments was thus obtained. The k-value independence of composition could therefore be tested and any crystal lattice effects assessed. The minerals used are listed in Table 1.

**EXPERIMENTAL PROCEDURES**

The mineral samples were finely fragmented and suspended in acetone. Single droplets of the dilute suspensate were deposited on carbon film superstrates on carbon-coated nylon microscope grids.

An accelerating voltage of 100 kV and a beam current of 200 μA were used. Mineral spectra were recorded for typical analytical live times of 200 s. Total spectral count rates were of the order of 1000 c/s for mineral grains in the size range 1–3 μm.

**k-VALUE CALCULATION**

Calculation of elemental k values followed the equation proposed by Cliff and Lorimer:

\[
k_{\text{Si}} = \frac{C_{\text{X}}}{C_{\text{Si}}} \cdot \frac{I_{\text{Si}}}{I_{\text{X}}} \tag{1}
\]

where \(I_{\text{Si}}\) and \(I_{\text{X}}\) are the simultaneously recorded \(K_{\alpha}\) characteristic X-ray intensities and \(C_{\text{Si}}\) and \(C_{\text{X}}\) the weight fractions of the elements Si and X in the thin film. Calibration of \(k\) values for low atomic number elements is complicated by several interrelated elemental and instrumental factors. With decreasing atomic number fluorescent yields decrease, resulting in poorer peak-to-background ratios. Low-energy Na and Mg characteristic X-rays are more readily absorbed within the thin film and in passing through the Be detector window, resulting in breakdown of the relationship of equation (1).

Energy-dispersive detectors record characteristic X-radiation as a Gaussian energy pulse where the area under the Gaussian peak, the peak integral intensity, reflects the...