FLUORESCENCE YIELDS: A NEW PARAMETERIZATION

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ABSTRACT

A new parameterization for the fluorescence yield of K, L and M lines is presented. The motivation was to find a universal parameterization in terms of energy, rather than in terms of atomic number (Z) the way it has normally been done. If the values of the fluorescence yield are plotted against energy, something close to a universal curve is found. However, the difference between the curves for K and L lines is significantly larger than the error and separate parameterizations for K, L and M are given. The uncertainties in the experimental data are very large and the parameterization is expected to be better than the experimental values in many cases. The parameterization values are probably good to 20%. The result presented may be of value in x-ray spectroscopy when values of the fluorescence yield are needed.

RESUMEN

Se describe un nuevo modo para representar la fracción de ionizaciones que resultan en la emisión de rayos X. En estudios anteriores, siempre se ha dado relaciones empíricas para representar los datos experimentales en términos del número atómico de los átomos. Aquí presentamos nuevas expresiones analíticas para esta fracción, pero en términos de la energía del rayo x emitido. Al hacerlo en esta forma, los valores para las líneas K, L y M caen muy cerca unos de los otros. La búsqueda de una curva universal de este tipo fue uno de los motivos del estudio. De hecho, resulto necesario utilizar ecuaciones diferentes para K, L y M. Las nuevas expresiones analíticas serán, en muchos casos, mejores que los datos experimentales (que traen errores muy grandes) y los valores dados tendrían un error de menos de 20%. Estos resultados serían útiles en la espectroscopia de rayos x para microanálisis.

Key Words: Fluorescence yield, microanalysis, energy-dispersive spectroscopy, curve fitting.

INTRODUCTION

When a core electron is knocked out of an atom, the return to the ground state may be achieved by two distinct mechanisms. A photon can carry away the excess energy – the fluorescent emission of a characteristic x-ray – or the energy may be given to an emitted electron through the Auger process. The fluorescence yield, ω, is the ratio of the number of ionization events that lead to x-ray generation to the total number of ionization events, x-ray plus Auger. This parameter is important in quantitative x-ray analysis performed in electron microscopy. Tabulations of experimental values and theoretical calculations of the fluorescence yield are required in the software used to obtain compositional data from x-ray spectra.

For didactic purposes, the data are often presented in the form of a graph of ω against the atomic number of the elements [1,2]. These graphs require three separate

curves for the K, L and M transitions, respectively (figure 1). The change in ω comes not from a change in the efficiency of the Auger process (which is approximately constant) but because of the change in efficiency of the x-ray emission process, which increases rapidly with the transition energy [3].

One of the authors (J.A.E.) has the recollection of once hearing in a class that that the relative probability of the two mechanisms is a function of energy - independent of atomic number. Unfortunately, he can not remember where this information came from. Pursuing this idea, if the data were plotted against emission energy, the curves might be brought into coincidence. Replotting the data of figure 1 in terms of the energy of the transition, see figure 2, indeed reveals that, in this form, the data fall on a near-universal curve. As indicated above, no originality is claimed for this observation although a search through texts on Auger spectroscopy and energy-dispersive spectroscopy (EDS) did not reveal any place where the data are presented in this way. In his book, Carlson [4] writes "Only when the transition energy exceeds roughly 10 keV is x-ray emission predominant". This indicates that he may have been aware of the idea that energy is a more natural scale for studying fluorescence yield. Figure 3 shows the same data as figure 2 but on log scales to show more clearly the data at low energies.

Fitting the Data

One book lists several ways in which attempts have been made to parameterize fluorescence yields [5]. Two of them are:

$$\omega = \frac{Z^4}{Z^4 + b}, \quad \left(\frac{\omega}{1-\omega}\right)^{1/4} = A + BZ + CZ^3 \quad (1)$$

Both of these and all the others listed are in function of Z, none of them as a function of energy. A more recent and complex list of parameterizations is given in Markowicz [6], but - still - none are given in terms of energy.

We here explore further the possibility of a successful parameterization in terms of energy. One of the authors

(D.C.J.) has compiled a very extensive tabulation of compilations of experimental data for the values of ω (Goldstein et al. [1], in the Database section of the CD-ROM accompanying the book, or on the web at http://pciserver/bio.utk.edu/metrology). The data set used in the figures is formed by taking the average of all the values given in this data base, for each element in turn. For the energy, we have used the energies of the dominant transitions: the emission energies for the $K_{\alpha 1}$, $L_{\alpha 1}$ and $M_{\alpha 1}$ lines.
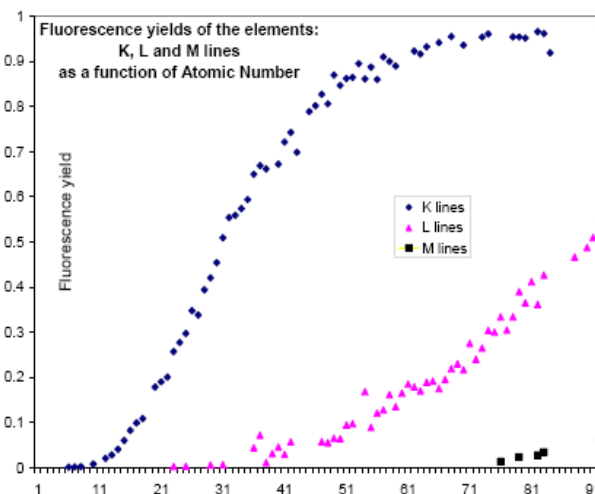

Fig. 1. A conventional plot of fluorescence yield as a function of atomic number (Z). The values for the K, L and M lines are widely separated.
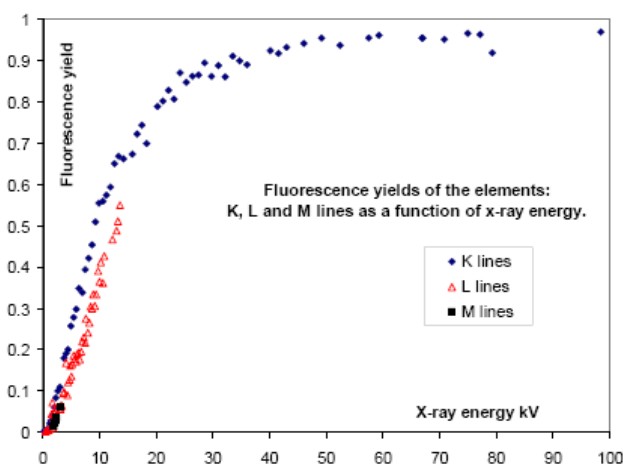

Fig. 2. The same fluorescence-yield data as in figure 1 but plotted against the x-ray energy rather than the atomic number. Plotted this way the data for K, L and M lines fall close together.
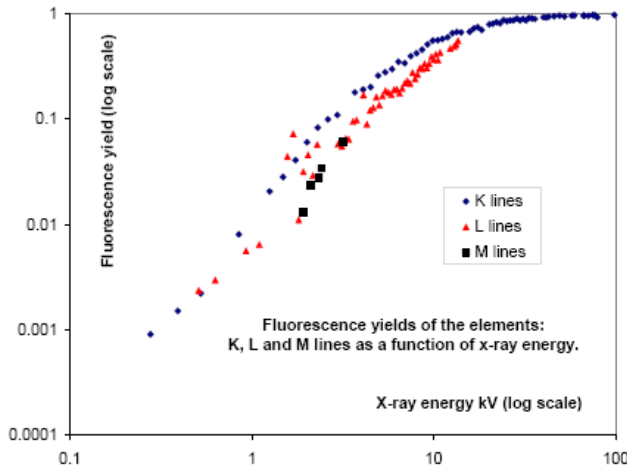
Fig. 3. The same data as figure 2, but the fluorescence yield and energy are plotted on log scales to show more clearly the asymptotic data at low energies.

We find that plotting the data in terms of ω is not the most useful form since, as can be seen in figures 1 and 2, the curve is asymptotic to 0 at low Z and asymptotic to 1 at high Z. Instead we choose to use $\omega/(1-\omega)$. Whereas ω is the ratio of the number of fluorescence events to the total number of events, $\omega/(1-\omega)$ is the ratio of the number of fluorescence events to the number of Auger events. ω is called the fluorescence yield. We will coin the term *fluorescence ratio* for $\omega/(1-\omega)$.

If we plot the fluorescence ratio against the square of the x-ray energy, we get something that is some approximation to a universal curve. A log-log plot, figure 4, makes things look better than they are, but, nonetheless, it does show that to some approximation

$$\frac{\omega}{1-\omega} = \frac{E^2}{C} \qquad (2)$$

Where E is the x-ray emission energy and C is a universal constant whose value is approximately $C = 100$ $(kV)^2$. In terms of ω, this translates to

$$\omega = \frac{1}{1+CE^{-2}} \qquad (3)$$

The form of this relation is not unexpected. Moseley's relation links the energy of the x-ray to Z^2, and, as

indicated above, the most important term of the parameterization of ω has usually been Z^4. It is not the form of the relation which has attracted our attention but the possibility that the parameters might be the same for K, L and M data when expressed this way.

Although the data plotted in figure 4 seem to lie close to a universal curve, a closer look shows that the data for the K lines differ significantly from the L and M lines. Furthermore, the data representing the K transitions do not fall on a straight line but on a line that is distinctly curved concave downwards.

K lines

As a result, we have sought to modify the simple expression:

$$\frac{\omega}{1-\omega} = \frac{E^2}{C} \qquad (4)$$

to represent better the data for the K lines.

Since,

$$\ln\left(\frac{\omega}{1-\omega}\right) = \ln\left(\frac{E^2}{C}\right) \qquad (5)$$

is the model that forms the basis of the plot in figure 4, the simplest way to model the slight curvature is

$$\ln\left(\frac{\omega}{1-\omega}\right) = \ln\left(\frac{E^2}{C}\right) + k\left[\ln\left(\frac{E^2}{B}\right)\right]^2 \qquad (6)$$

In terms of the original quantities, this translates to an expression:

$$\frac{\omega}{1-\omega} = \frac{E^2}{C} \cdot \left(\frac{E^2}{B}\right)^{k\ln\left(\frac{E^2}{B}\right)} \qquad (7)$$

Where B, C and k are empirical constants. A fit of the data to this expression, using Kaleidagraph (Synergy Software: http://www.synergy.com), gives

$$C(K) = 72 \pm 2 \quad (kV)^2$$

$$B = 6.0 \pm 1.5 \quad (kV)^2$$

$$k = -0.023 \pm 0.002$$

The data were fit to equation 6 rather than equation 7. Fitting to equation 7 would weight the values for high energies and give a very bad fit for the low energies. The data are plotted using these values of C, B and k, in figure 5 (see below for how the L and M data are plotted on this graph). The exponent of E can be treated as an adjustable parameter too, but the fit is not improved and the value is 2 better than 0.5% (and the other parameters change less than their errors).
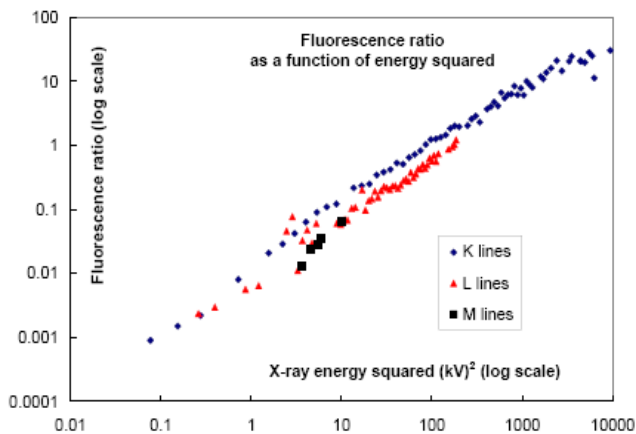

Fig. 4. The fluorescence data is here displayed with the fluorescence ratio, $\omega/(1-\omega)$ (instead of the fluorescence yield, ω) plotted against the square of the x-ray energy. Both scales are logarithmic. The data falls close to a universal curve with unit slope.
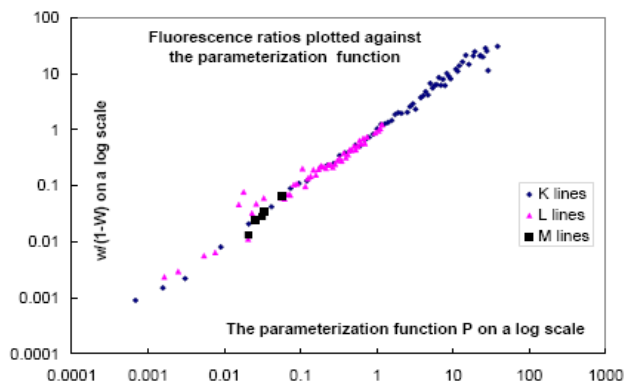

Fig. 5. A very substantial improvement in the fit is achieved by plotting the data of figure 4 with P, the parameterization function, as the horizontal axis instead of energy squared.
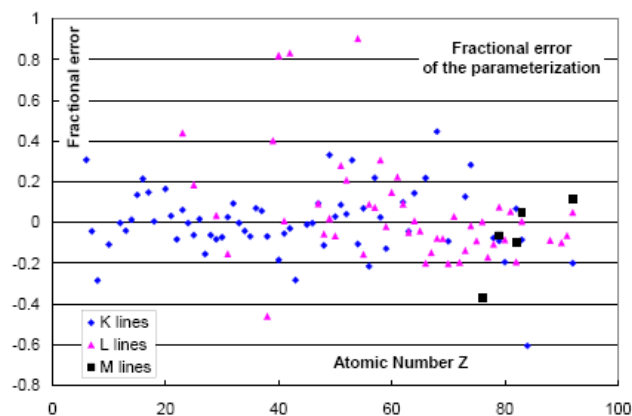

Fig. 6. The fractional difference in fluorescence ratio between the parameterized value and the mean of experimental values, plotted against atomic number. Two values deviate so far from the parameterization that they are outside the range of this graph, see text.

We set

$$\frac{E^2}{C} \cdot \left(\frac{E^2}{B}\right)^{k \ln\left(\frac{E^2}{B}\right)} = P \qquad (8)$$

where P is the parameterization function. Figure 5 shows a plot of P against $\omega/(1-\omega)$.

In addition, we have calculated

$$\frac{\frac{\omega}{1-\omega} - P}{P} \qquad (9)$$

which is the fractional error of the parameterization, for each data point. Values of this quantity are plotted, against Z, in figure 6. With the given values for C, B and k, all but twelve of the sixty four data points are within 20% of the predicted value and all but two are within 35%. One of the points is more than 60% off the line and this data point was not used in the parameterization. The effect of omitting this outlier was to change the values of B, C and k by less than their errors. Omitting other outliers also did not change the parameterization curve significantly.

In the above parameterization, we have chosen to model the slight curvature of the K-line data with a simple curve of the log plot. As can be seen in the second equation (1), other modelers have typically used a polynomial

approach. The same thing can be done here, though at the expense of losing the E^2 dominant term. The addition of a constant adjusts the curvature of the lower end of the plot in figure 3, while the addition of a higher power term adjusts the top end of the plot. The relation

$$\frac{\omega}{1-\omega} = AE^B - CE^3 - D \qquad (10)$$

where A = 1/60, B = 1.86, C = 1/16200 and D = 1/1200 with E in keV, gives residuals about as good as those shown in figure 6, which used equation 7.

Comparison with "Adopted values"

Two recent publications give lists of "adopted" or best values for K-line fluorescent yields (Goldstein et al. [1] in the Database section of the CD-ROM; [6]). These, in turn were largely obtained from earlier publications by Bambynek et al [7] and Krause [8], respectively. These numbers are a combination of computed values, experimental values and interpolated values from parameterizations. An attempt was made to judge the quality of the experimental values and weight them accordingly. Particularly as a result of the incorporation of empirical parameterization into these numbers, they show almost no scatter and give very smooth plots. In the present work we give all experimental values equal weight.

In figure 7, we show the data for K lines only from the data base [1] plotted against the square of the transition energy. On the same plot, we show lines representing the "adopted" values from Goldstein and Markowicz [1,6]. It can be seen that, while the general agreement is very good, there are discrepancies, especially for elements at the end of the range. While the "adopted data" are good from Z=14 to Z=74, outside this range the adopted data sets give values that are consistently higher than the experimental values for the fluorescence ratio (and therefore for the fluorescence yield).

L and M lines

 The data for the L lines have more scatter than the data for K lines and there is no evident curvature to the data in figure 3. The data were fit using

$$\ln\left(\frac{\omega}{1-\omega}\right) = \ln\left(\frac{E^2}{C}\right). \qquad (11)$$

The fit gives

$$C(L) = 159 \pm 4 \quad (kV)^2$$

Equation 11 (the same as equation 5) was used for the fit, rather than equation 4 for the same reason as equation 6 was used for the K lines, namely that equation 4 would over-weight the values of the fluorescence ratio at higher values of the energy. The scatter of the values for the L lines is greater than for the K lines. There are six of the fifty points with a fluorescence ratio that differs greatly (45% or more) from the fit. A fit with all the experimental values gives a fit that (by visual inspection) is poor where the data are consistent. A fit on the data without the six outliers is much better, and that is what is given here.

The data are plotted in this form in figure 5 and the error is plotted in figure 6. There are two points that are way off the top of the plot in figure 6. The scale has been set to make the data clear. With C = 159 $(kV)^2$, thirteen of the fifty four points fall outside 20%.

There are only five data points for M lines, and the scatter is large because major corrections must be applied to the experimental numbers to account for the multiple non-radiative recombinations which occur. There is no point in trying for perfect agreement and

$$C(M) = 175 \ (kV)^2$$

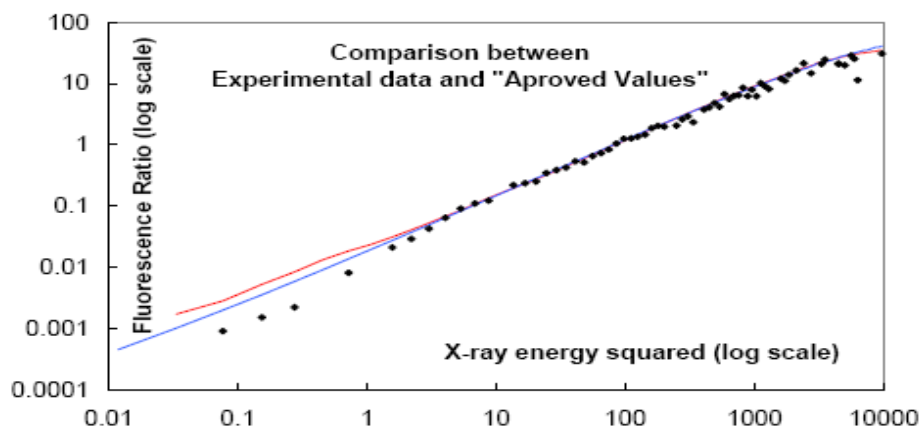gives a fit that puts four of the five points within 15%.

Fig. 7. This figure shows data for the K lines only. The experimental data from the database are shown as points. The two lines represent the "best data" from Goldstein and Markowicz [1,6], respectively. The "Goldstein" line (blue) is lower at the left and higher at the right than the line (red) using Markowicz data.

DISCUSSION

It can be seen that there is a very good fit to the data with the parameters derived. The fractional difference between the parameterization and the experimental values is given in figure 6. It is evident that there are a few values that lie very far from the parameterized curve. Reference back to the tabulated experimental data gives some clue as to why this might be. The point furthest off is for the rubidium L line. There are three experimental values for ω for rubidium, with a factor of more than ten between the largest and smallest. This corresponds to a factor of fifteen between the values of $\omega/(1-\omega)$. The next furthest data point is for the L line of krypton where there are two experimental values: one is more than five times the other. These points are the two that are cut off in figure 6, for them the errors are 350% and 200% respectively.

In interpreting figure 6, it should be noted that the fractional error is given for the fluorescence ratio, whereas the curve fitting was done for the log of the fluorescence ratio. This has the effect of making the distribution asymmetric for the points with a large fractional error.

Two problems bedevil this discussion of fluorescence yields: The experiments are difficult and the errors large; and we have no theoretical model to underpin the parameterization that we give. The fact that the errors in the experimental data are large means that we can not be clear as to whether the deviations from the fit are the result of real, element-to-element fluctuations in the yield, or whether the deviations are simply experimental error. As mentioned above, in those cases where experimental values are very far from the fit, there is every reason to suppose that experimental error is the explanation. It does not logically follow from this that the same explanation applies when the deviation is small. Nonetheless, it does seem likely that, in general, the parameterization may be more reliable than the experimental data. It would also seem that the parameterizations proposed here give better values than the "best fits" of Goldstein et al and Markowicz [1,6], especially for elements at the ends of the range. This can be seen by comparing figure 7 which shows their best fits deviating from experimental values at high and low energies, whereas, in figures 5 and 6, it can be seen that we obtain a good fit across the whole energy range.

We acknowledge that the lack of a theoretical model for our parameterization is a weakness. However, it is implausible that the way in which the data of figure 1 fall onto a near universal curve as a function of energy (figures 2 and 3) is simply coincidence. Therefore,

although we do not have an explanation for the result, we are comfortable –as a practical matter– going ahead and asserting that we find the parameterizations that we give to be useful. We see this as presenting a challenge to others to produce a model to account for the observations. We also concede that, in the case of the L and M lines, it would be desirable to give an account of how the radiationless, Coster-Kronig transitions affect the experimental determinations of the fluorescence yields and how they modify the use of the data in x-ray spectroscopy for microanalysis. We have not done this, but simply taken published experimental data at face value.

It is a disappointment that the "universal curve" that we sought does not exist. Although the data for K, L and M lines are much closer to each other when plotted against energy than when plotted against atomic number, there is still a factor of about 2 between the values for the K lines and the values for the L lines, near the middle of the range. We have been forced to use different parameterizations for K, L and M lines. This means that any theoretical model, which is developed, will have to account, not only for the similarity of the fluorescence yields when expressed as a function of energy, but also their differences.

CONCLUSION

Previous parameterizations of the data for fluorescence yield have been expressed as a function of atomic number. Here, we have developed new parameterizations as a function of the energy of the emitted x-ray. We had hoped that this would lead to a universal curve in which the fluorescence yield of K, L and M lines would be given by a single expression. Although, when plotted against energy, the experimental results lie close to a single curve, it turned out to be necessary to use different parameterizations for the K, L and M lines. We think it likely that the parameterizations we give are more reliable than the experimental values for individual

elements. We think it unlikely that the values of the parameterizations are in error by more than 20% in the yield. This new approach to handling fluorescence yields could be of some significance for x-ray microanalysis.

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