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Behavior of X-ray Mass Absorption Coefficients near Absorption Edges: Reynolds' Method Revisited

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Abstract

Reynolds' (1967) method for relating the mass absorption coefficient on the long wavelength side of a major element absorption edge to the intensity of the emission line of the element causing the absorption discontinuity is shown to be a special case of a more general relation. The systematic positive errors noted by Reynolds in using his method are consistent in sign and of similar magnitude to errors generated by neglecting the general relation. If the ratio of the mass absorption coefficient on the short wavelength side to that on the long wavelength side of a major element's absorption edge is plotted against the peak intensity of this element, the plots allow use of the general relation and permit simultaneous comparisons to be made to more than one standard. The technique is used to best advantage (in common geologic applications) in the analysis of elements of atomic numbers from calcium to iron.

Introduction

Quantitative X-ray fluorescence analysis requires that matrix absorption effects be either uniform or known if nonuniform when comparing X-ray emission line intensities of standards and unknowns. The use of standards very similar to the unknowns or the use of high dilution and/or heavy absorbers are techniques which make use of uniform absorption qualities of standards and unknowns. The absorption characteristics need not be specifically known. The use of internal standards or the use of iterative calculations based on the content of all major elements present or the use of mass absorption coefficients estimated from either transmitted or scattered radiation are methods which correct for non-uniform matrix absorption effects.

Reynolds (1963) described a very useful technique for determining the X-ray mass absorption coefficient of a rock (for wavelength regions near the primary X-ray beam not disrupted by major element absorption edges) by measuring Compton-scattered radiation generated by the primary X-ray beam interacting with the sample. This method has been checked by Powell, Skinner, and Walker (1969) and found to give results of high accuracy and precision. Inasmuch as there are elements of interest with emission lines of longer wavelength than the absorption edge of the heaviest element present, Reynolds' (1967) suggestion for calculating mass absorption coefficients in a wavelength region on a long wavelength side of a major element absorption edge when the coefficient on the short wavelength side is known is most welcome. A more general treatment of this problem is now presented and includes a comparison with Reynolds' treatment, followed by a suggestion for a better solution to the problem.

Discussion of Theory and Comparison Methods

In general the magnitude of the disruption of the smooth variation with wavelength of mass absorption coefficient of a sample in wavelength regions near the absorption edge of a major element present in that sample will be a function of how much of that element is present in that sample. If $\mu(\lambda_A)$ is the mass absorption coefficient of the sample in the region of high absorption relative to the edge (short wavelength side) and $\mu(\lambda_E)$ is the mass absorption coefficient of the sample in the region of the emitted line associated with the absorption edge (long wavelength side), then since the intensity I_E of the emission line of the element causing the absorption discontinuity increases with increasing amounts of that element present, we should expect that $[\mu(\lambda_A)/\mu(\lambda_E)]$ should increase with I_E.

Liebhafsky, Pfeiffer, Winslow and Zemany (1960) and Norrish and Chappell (1967) among others have justified the following expression for the intensity of an element's emission line I_E as a function of the weight fraction of the element present X_E and the absorption coefficients of the sample at the wavelengths of the absorbed and emitted radiation.

$$I_E = \frac{X_E I_0 K}{\mu(\lambda_A)\cdot\sec\theta + \mu(\lambda_E)\cdot\sec\phi} \tag{1}$$

where θ is the angle between the primary beam and the normal to the sample, ϕ is the angle between the secondary beam and the normal to the sample, I_0 is the intensity of the primary radiation, and K is the yield factor which is a measure of excitation, detection, and collimation efficiency.

Equation (1) can be rearranged to give

$$X_E = \frac{I_E}{I_0 K}\,[\mu(\lambda_A)\cdot\sec\theta + \mu(\lambda_E)\cdot\sec\phi] \tag{2}$$

The mass absorption coefficient of a sample at any wavelength is a linear function of the weight fraction of the components of the sample times the mass absorption coefficient of the component of the sample.

$$\mu(\lambda_A) = X_E\cdot\mu(\lambda_A)_E + (1 - X_E)\cdot\mu(\lambda_A)_R \tag{3}$$

where $\mu(\lambda_A)_E$ and $\mu(\lambda_A)_R$ refer to the mass absorption coefficients of the element causing the edge in question and the remainder of the sample, respectively. Rewriting:

$$\mu(\lambda_A)_R\cdot(1 - X_E) = \mu(\lambda_A) - \mu(\lambda_A)_E\cdot X_E \tag{4}$$

Similarly for the wavelength of emission:

$$\mu(\lambda_E)_R\cdot(1 - X_E) = \mu(\lambda_E) - \mu(\lambda_E)_E\cdot X_E \tag{5}$$

Dividing (4) by (5) and rearranging:

$$\mu(\lambda_A) = \mu(\lambda_E)\cdot\frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R} + X_E\left\{\mu(\lambda_A)_E - \mu(\lambda_E)_E\cdot\frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R}\right\} \tag{6}$$

At this point we can substitute (2) for X_E and obtain after some rearrangement:

$$\frac{\mu(\lambda_A)}{\mu(\lambda_E)} = \frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R} + \frac{I_E}{I_0 K}\left(\sec\phi + \frac{\mu(\lambda_A)}{\mu(\lambda_E)}\cdot\sec\theta\right)\cdot\left\{\mu(\lambda_A)_E - \mu(\lambda_E)_E\cdot\frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R}\right\} \tag{7}$$

Reynolds' (1967) equation (6) is analogous to equation (6) above. Reynolds' approach to substituting for X_E involved an implicit assumption which is not strictly correct for a situation involving a major element absorption edge in the wavelength range of interest. The implicit but incorrect assumption of Reynolds' equation (7) could have been stated this way.

$$\frac{\mu(\lambda_A)}{\mu(\lambda_E)} = \frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R} \tag{8}$$

If for the sample only the element in question has an absorption edge in the wavelength region of interest, the expression $[\mu(\lambda_A)_R/\mu(\lambda_E)_R]$ can be considered a constant, and the absorption expression in equation (2) can be recast into the following form:

$$\mu(\lambda_A)\cdot\sec\theta + \mu(\lambda_E)\cdot\sec\phi = \mu(\lambda_E)\cdot\left\{\sec\phi + \frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R}\cdot\sec\theta\right\} \tag{9}$$

Equation (2) could be then simplified:

$$X_E = \frac{I_E}{I_0 K}\cdot\mu(\lambda_E)\left\{\sec\phi + \frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R}\cdot\sec\theta\right\} \tag{10}$$

This is only strictly valid when there is no major element absorption edge between λ_A and λ_E, hence use of this expression will introduce errors when dealing with major elements. Substitution of expression (10) for X_E of equation (6) gives:

$$\frac{\mu(\lambda_A)}{\mu(\lambda_E)} = \frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R} + \frac{I_E}{I_0 K}\left(\sec\phi + \frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R}\sec\theta\right)\cdot\left\{\mu(\lambda_A)_E - \mu(\lambda_E)_E\cdot\frac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R}\right\} \tag{11}$$

Equation (11) above is analogous to equation (8) of Reynolds (1967). It can be seen that (11) linearly relates I_E to $[\mu(\lambda_A)/\mu(\lambda_E)]$, since $[\mu(\lambda_A)_R/\mu(\lambda_E)_R]$ can be regarded as a constant. Equation (11) differs from equation (7) only in the expression for the slope of the line. Equation (7) is not linear since the slope depends on $[\mu(\lambda_A)/\mu(\lambda_E)]$. The expressions for the slope differ by a factor ξ:

$$\xi = \frac{\sec\phi + \dfrac{\mu(\lambda_A)}{\mu(\lambda_E)}\sec\theta}{\sec\phi + \dfrac{\mu(\lambda_A)_R}{\mu(\lambda_E)_R}\sec\theta} \tag{12}$$

It can be seen that, for small amounts of an element present, $[\mu(\lambda_A)/\mu(\lambda_E)]$ approaches $[\mu(\lambda_A)_R/$

$\mu(\lambda_E)_R$] and ξ approaches 1. Evidently for small amounts of the major element, equation (11) is a viable approximation. The errors introduced by this approximation tend to cause $[\mu(\lambda_A)/\mu(\lambda_E)]$ to be evaluated at less than its true value. Consequently $\mu(\lambda_E)$ is overestimated and so is X_E. Note that Equation (2) must be used to find X_E rather than Equation (10) when X_E refers to a major element. Reynolds (1967) noted that systematic positive errors relative to accepted values were encountered in his analytical work. We have just seen that neglect of the general relationship will introduce systematic positive error. This error can be calculated for various materials, wavelengths, and spectrometer designs. For the example of iron in Reynolds' XRD-5 spectrometer the error introduced in G-1 (1.33 percent Fe) is negligible, and indeed his data for G-1 show no particular bias, but show relative errors of up to 8 percent. On the other hand Reynolds' iron-aluminum oxide mixtures (6–12 percent Fe) show a positive bias with "overall errors in the vicinity of +4 percent" and a spread of relative errors of about 8 percent. The relative error introduced by neglect of the general expression is calculated to be about 2 percent. Considering the 8 percent spread, this effect may be a substantial part of the 4 percent positive bias.

Graphical Method

The preceding discussion has suggested that the relation between $[\mu(\lambda_A)/\mu(\lambda_E)]$ and I_E is nearly linear. For selected ranges of $[\mu(\lambda_A)/\mu(\lambda_E)]$ the curves are indistinguishable from linear, and for low I_E the slope of the curve follows from equation (11). A useful way to avoid systematic bias in determining $[\mu(\lambda_A)/\mu(\lambda_E)]$ and to allow comparison of the sample to several standards simultaneously is to plot $[\mu(\lambda_A)/\mu(\lambda_E)]$ versus I_E. The resulting curve, in practice indistinguishable from a straight line although the slope may not be given by Equation (11), may be used to find $[\mu(\lambda_A)/\mu(\lambda_E)]$ for a sample. Figure 1 contains some examples of curves of $[\mu(\lambda_A)/\mu(\lambda_E)]$ versus I_E. For convenience in using such curves, calculated values of $\mu(\lambda_A)$, $\mu(\lambda_E)$, and $[\mu(\lambda_A)/\mu(\lambda_E)]$ for a variety of absorption edges are tabulated for the USGS standards in Table 1. Henrich's (1966) mass absorption coefficients and Fleischer's (1969) and Flanagan's (1969) tabulations of recommended analyses for the USGS standards are used to compute the values in Table 1.

When $\mu(\lambda_A)$ has been determined by Compton scattering (Reynolds, 1963), the value of $\mu(\lambda_E)$ is easily obtained. To determine the amount of major element in the unknown sample, an equation of the form

$$X_E{}^u = \frac{I_E{}^u}{I_E{}^s} \cdot \frac{[\mu(\lambda_A)^u \cdot \sec\theta + \mu(\lambda_E)^u \cdot \sec\phi]}{[\mu(\lambda_A)^s \cdot \sec\theta + \mu(\lambda_E)^s \cdot \sec\phi]} \cdot X_E{}^s \quad (13)$$

is used where superscripts u and s refer to unknown and standard. If the wavelength region around λ_E contains trace elements which have no major element absorption discontinuity intervening between the emission and absorption wavelengths, then equation (13) reduces to the simpler form used by

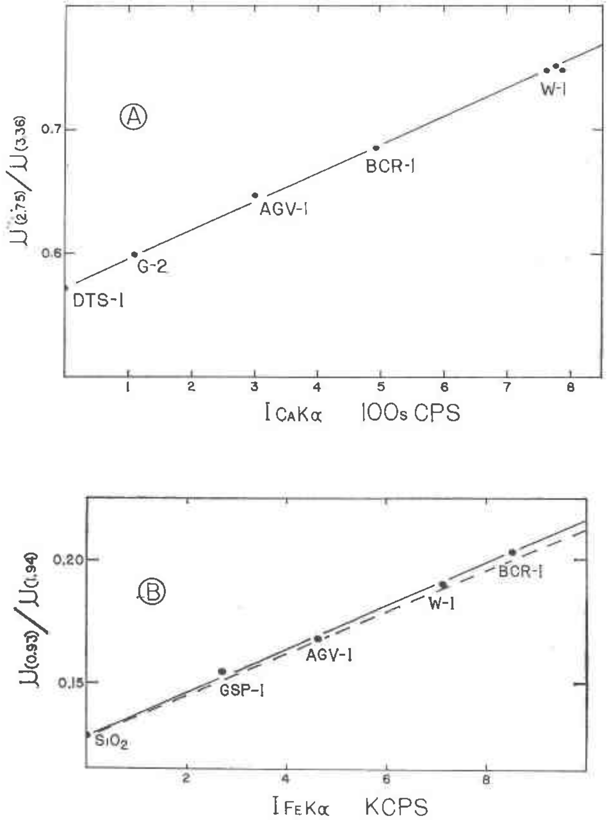

FIG. 1. Graphs demonstrating linear relation between I_E and $[\mu(\lambda_A)/\mu(\lambda_E)]$ for limited ranges of composition. Data are for pressed powder samples having 30 percent by weight cellulose as a binder. (A) Shows relations at the calcium absorption edge. The three points for W-1 correspond to different percentages of cellulose binder. (B) Shows relations at the iron absorption edge. The dashed line is drawn through SiO_2 and the value of $[\mu(0.93)/\mu(1.94)]$ which was calculated for W-1 by Reynolds' method. This line helps estimate the amount of systematic error introduced by not using the solid line.

TABLE 1. Mass Absorption Coefficient Data for U.S.G.S. Standards

	G-1	W-1	G-2	GSP-1	AGV-1	PCC-1	DTS-1	BCR-1
μ(.927)	10.82	16.25	11.23	12.25	13.45	12.04	12.39	17.09
μ(1.937)	76.20	83.32	76.54	78.19	78.12	60.70	61.92	80.81
μ(2.748)	199.7	213.7	196.8	200.8	198.8	157.5	159.5	200.2
μ(3.359)	336.7	278.6	326.6	333.1	304.1	270.8	277.7	289.9
μ(3.742)	388.6	368.2	386.9	384.0	375.7	365.5	374.7	371.0
μ(7.126)	990.9	1233.	1045.	1055.	1152.	1430.	1511.	1210.
μ(8.336)	1182.	1527.	1231.	1251.	1349.	2205.	2338.	1525.
μ(.927)/μ(1.937)	.1420	.1950	.1468	.1566	.1722	.1983	.2001	.2115
μ(1.937)/μ(2.748)	.3816	.3900	.3888	.3894	.3930	.3855	.3881	.4036
μ(2.748)/μ(3.359)	.5931	.7669	.6026	.6029	.6536	.5814	.5746	.6908
μ(3.359)/μ(3.742)	.8663	.7565	.8442	.8675	.8095	.7409	.7410	.7813
μ(3.742)/μ(7.126)	.3922	.2987	.3704	.3640	.3260	.2555	.2480	.3067
μ(7.126)/μ(8.336)	.8384	.8071	.8489	.8434	.8546	.6487	.6465	.7932

Reynolds:

$$X_E{}^u = \frac{I_E{}^u}{I_E{}^s} \cdot \frac{\mu(\lambda_E)^u}{\mu(\lambda_E)^s} \cdot X_E{}^s \tag{14}$$

Applications and Limitations of the Technique

Reynolds' (1963, 1967) Compton scattering technique for determining mass absorption coefficients coupled with the proposed method for extending the absorption coefficients across absorption edges is general in application but may be used to best advantage in situations that do not require (or where one is not able to) determine all the major elements present and where simple rock-powder samples may be used. This extension of Reynolds' technique is probably used to best advantage in the analysis of the elements calcium through iron in rock samples. The technique could be usefully applied in many other specific situations, for example the analysis of iron, copper, and zinc in sphalerite ores.

Instrumental factors conspire to limit the usefulness of the technique for atomic numbers below calcium. For the lighter elements a vacuum spectrograph is required which is normally capable of determining most of the rock forming major elements. For this situation some procedure of iterative calculation such as suggested by Norrish and Chappell (1967) is most useful. In addition, for the lighter elements, grain size and absorption property contrasts between mineral constituents often require fusion for homogenization, which introduces the possibility of using dilution and/or heavy absorbers with little extra effort.

The principal advantages of this technique are that it allows determination of specific elements without determining all the elements present and that it requires a bare minimum of sample preparation.

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