The estimation of mass absorption coefficients by Compton scattering: extensions to the use of Rh$K\alpha$ Compton radiation and intensity ratios

PETER K. HARVEY AND BRIAN P. ATKIN

Department of Geology
University of Nottingham
Nottingham, England

Abstract

The intensity of Compton scattered Rhodium $K\alpha$ X-rays may be used to estimate mass absorption coefficients for that wavelength (0.645Å). Such coefficients are usually within 2% and frequently within 1% of their calculated values. The relationship between the mass absorption coefficient and Compton intensity is, to a good approximation, logarithmic. As a ratio, however, to a suitable monitor sample the ratio relationship is virtually linear over the range encountered in most rocks and may be treated as such for the purpose of matrix correction.

Introduction

The systematic inverse relationship between the intensity of Compton scattered radiation and the mass absorption coefficient (μ) at the same wavelength has been known in X-ray spectroscopy for many years. Reynolds (1963, 1967) first described the relationship for a molybdenum X-ray tube (Mo $K\alpha$ Compton radiation) and this work has been extended to tungsten (DeLong & McCullough, 1973; W$L\alpha$ Compton radiation) and silver (Franzini *et al.* 1976; Ag $K\alpha$ Compton radiation) X-ray tubes.

The Compton scatter method for estimating μ is now widely used, particularly for the analysis of trace elements, and relies on the observation (Hower, 1959) that relative absorptions between a sample and some mass absorption monitor (or standard) are virtually constant between adsorption edges. Provided that the relative jump across an absorption edge is small, the effect of the edge is usually ignored. This condition prevails when the absolute concentration difference between the sample and monitor is small or the mass absorption coefficient for the given element is small, or both are small. For trace elements the concentration term is usually sufficiently small that the effect of the absorption edge for that element may be ignored. In this manner the relative mass absorption may be considered a constant from the wavelength of the measured Compton Scatter line until the absorption edge of the first major element is crossed. As Hower (1959) pointed out, this is iron (Fe $K\alpha$ edge: $\lambda = 1.744$Å) for most common rocks.

The main purpose of this note is to describe the relationship between the rhodium K Compton intensity and the mass absorption coefficient. The rhodium anode X-ray tube is potentially the most useful general purpose anode available for geological samples.

All analytical data reported here were obtained on a Philips PW1400 spectrometer equipped with a 100 kV, 3 kW generator and rhodium anode X-ray tube. For measurements at the Rh$K\alpha$ Compton wavelength the following operating conditions were used: 60 kV/40 mA, LiF$_{200}$, fine (150μ) collimator and scintillation counter.

Relationship between μ and RhK Compton intensity

Both the $K\alpha$ and $K\beta$ Compton peaks may be measured but the former was chosen for this study because of its better counting statistics (p½ - b½ : $K\alpha = 87.6$; $K\beta = 28.9$; for pure SiO$_2$). The use of a fine collimator together with a LiF$_{200}$ crystal gives a good separation of the $K\alpha$ Compton and $K\alpha_{1,2}$ rhodium peaks while providing a higher intensity than can be obtained with the alternative LiF$_{220}$ crystal.

Possible sources of interference are a series of ThL and Nb$K\beta$ lines. Zr and Mo K lines also occur in the immediate vicinity. We have measured sets of spiked samples containing these elements at the Compton angle and find no detectable interference up to at least 1% for each element. Indeed after relatively small additions (approximately 2000 ppm for Mo, and 250 ppm for Zr) the Compton count rate

begins to decrease and continues to do so at a rate that can be precisely predicted from the actual change in mass absorption coefficient, at the Compton wavelength.

Figure 1 shows the relationship between the Compton $K\alpha$ peak intensity and computed mass absorption coefficient for a set of 46 geochemical reference standards. The relationship is non-linear and very similar to that reported by Franzini *et al.* (1976) for a silver tube. The mass-absorption coefficients were computed for a wavelength of 0.65Å and contributions were included for about twenty of the "most common" trace elements in addition to the normal major elements. We have found it necessary to include the effects of these trace constituents because although the concentrations involved are small many of the elements have high absorption coefficients and for some samples, at least, the cumulative effects on the sample mass absorption coefficient may be significant. This effect is illustrated in Figure 1 where a histogram shows the percentage of the sample mass absorption coefficient that is due to these 'trace' constituents; about 20% of the standards have more than 5% of their mass absorption coefficients due to the "trace" elements. The most extreme standard represented is the South African lujarite NIM-L with a 'trace' contribution of over 20%. The latter is due mainly to an unusually high zirconium concentration (>1%Zr) but high Nb and Sr are also important.
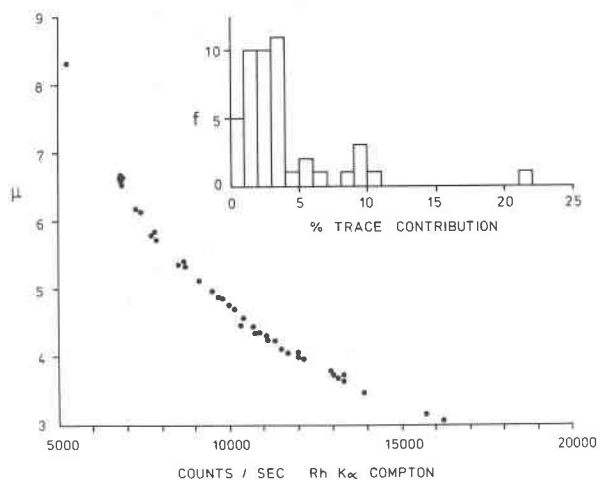

Fig. 1. Relationship between the Rhodium $K\alpha$ Compton intensity and computed mass absorption coefficient, at 0.65Å wavelength, μ. Inset histogram shows the percentage of the values of μ that is due to elements normally regarded as occurring in "trace" quantity. See text for explanation.

Using only the major elements (Si, Al, Ti, Fe, Mg, Ca, Na, K, Mn, P, O) to calculate μ leads to a reasonable amount of scatter below the line shown in Figure 1. Essentially the Compton intensity can yield a good estimate of μ, and generally a better estimate than could be obtained by calculation based on major elements alone. At any other wavelength the Compton relationship may deteriorate as (trace) element absorption edges are crossed. In short, the commonly accepted "constant" absorption ratios between major element absorption edges (Hower, 1959; Walker, 1973) are simply acceptable approximations except where the "trace" element contribution is high; errors of the order of those shown in the histogram in Figure 1 could then be involved in the trace element determinations. Corrections for these effects could be made using the methods of Reynolds (1967) or Walker (1973), though many analysts would not consider it necessary where "trace" elements are involved. Further, these methods are efficient for two or three absorption edge corrections, but are less viable as errors accumulate successively over several absorption edges. We provide an alternative solution to this problem elsewhere (Harvey and Atkin, 1982).

Estimation of the mass absorption coefficient

Following investigation of several models we agree with Franzini *et al.* (1976) that a simple logarithmic function is most suitable for the estimation of μ; in particular

$$\mu = \exp(\gamma_0 + \gamma_1 \ln C) \qquad (1)$$

where C is the Rh Compton $K\alpha$ count rate and γ_0, γ_1 are regression coefficients.

For the standards shown in Figure 1 and computed values of μ at a wavelength of 0.65Å the estimates of γ_0 and γ_1 are 3.58462 and -0.88258 respectively. This regression yields a skewed error distribution with 70% of the expected values within 1% of their corresponding calculated values and 85% within 2%.

For routine analytical purpose absolute count rates are subject to long term drift and for matrix corrections it is more satisfactory to determine a Compton intensity ratio to a monitor sample and use that ratio as an indirect estimate of μ, or rather, the matrix correction term. Figure 2 shows this relationship for the same reference standards as are plotted in Figure 1: r_1 is the mass absorption ratio μ_s/μ_m, where μ_s is calculated mass absorption coef-
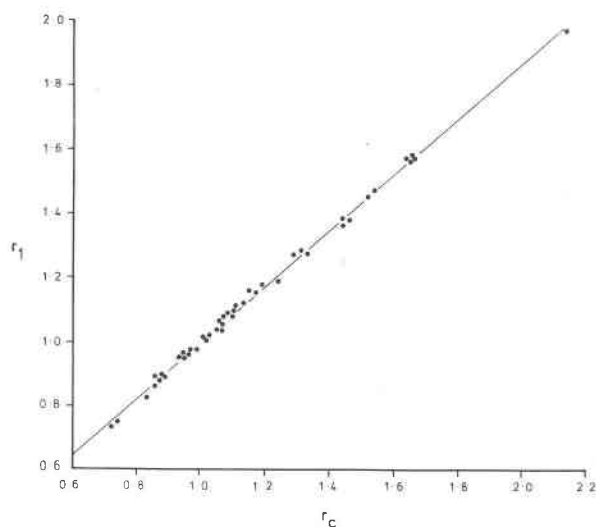
Fig. 2. Relationship between the mass absorption sample/monitor ratio ($r_1 = \mu_s/\mu_m$) and (inverse) Compton monitor/sample ratio ($r_c = C_m/C_s$). An andesite was employed as the monitor sample. See text for explanation and discussion.

ficient for a reference standard (or any samples) and μ_m is the same for the monitor. Similarly, r_c is the (inverse) ratio of Compton intensities (C_m/C_s). From equation 1 r_1 and r_c are related as:

$$r_1 = r_c^{-\gamma_1} \qquad (2)$$

With a value of -0.88258 for γ_1 the relationship between r_1 and r_c is weakly non-linear, but for simplicity it may be treated as linear over a limited range such as that shown in Figure 2. The geochemical reference standards used to construct Figures 1 and 2 (listed later) themselves cover a fairly wide compositional range and hence the linear relationship drawn in Figure 2 has a wide application. The positive intercept in this line on the r_1 axis is a direct consequence of the non-linearity and extrapolation outside the range $0.6 \leq r_c \leq 2.4$. Within this range the relative error induced by using the linear relationship as opposed to equation 2 is never greater than 1%. For more extreme values of r_c it may be necessary to use an alternative monitor sample or employ equation 2 directly for matrix corrections.

Discussion and conclusions

The Rhodium Compton $K\alpha$ intensity is inversely proportional to the calculated mass absorption coefficient at the same wavelength. The relationship is logarithmic and essentially the same as that described by Franzini *et al.* (1976). The mass absorp-

tion coefficient, μ, can be estimated either from this logarithmic relationship or from a linear ratio equation against a monitor sample. The latter approach is not subject to drift and is the best method for routine mass absorption corrections. The limited set of samples used here shows that the estimate of μ obtained in this way is usually with 2% of the calculated value, and frequently within 1%.

Note on geochemical reference standards

The following geochemical reference standards were used for this study: (USGS) DTS-1, PCC-1, GSP-1, G-2, AGV-1, W-1, SCo-1, BHVO-1, RGM-1, SDC-1, QLO-1, STM-1, MAG-1, BCR-1, SGR-1; (CCRMP) SY-2, SY-2; (CRPG) Mica-Fe, GA, GH, BR; (ANRT) GS-N, BX-N, DR-N, DR-N, FK-N, UB-N, VS-N, BE-N, MA-N, AN-G; (NIM) NIM-D, NIM-G, NIM-L, NIM-N, NIM-P, NIM-S; (Nottingham) N-1000, N-1001, N-1003, N.1005, N-1006, N-1007, N1011; (MRT) T-1; (LEN) NS-1.

The sources for these standards (except Nottingham) are given, according to the codes given in brackets, by Abbey (1977).

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