

Rapid Method for Background Corrections in Trace Element Analysis by X-Ray Fluorescence: An Extension of Reynolds' Method

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Abstract

A method is described whereby a sample's background intensity at the $K\alpha$ wavelength of an element can be obtained by reference to a calibration curve once its mass absorption coefficient has been determined by the Reynolds' method. Data presented indicate that, in standards with $\mu_{0.9\text{\AA}}$ ranging from 7 to 20 (most rocks and minerals), the reciprocal of the background intensity at the desired $K\alpha$ line is linearly related to μ so long as the standards are free of the analyzed element. The relationship remains linear even though the analyzed element occurs in the target or other parts of the spectrometer. For routine analysis involving many samples, an accurate estimation of background can be obtained from the analyses of as few as four standards, foregoing the time spent measuring the background of each sample.

Introduction

The Reynolds' method of quantitative trace element analysis by X-ray fluorescence (1963, 1967) is relatively fast and accurate. Recently, refinements to the method have been made in the analysis of elements from atomic number 20 to 26 (Walker, 1973) and the method adapted to spectrometers with a tungsten source for workers who lack a Mo tube as used by Reynolds (DeLong and McCullough, 1973). The major advantage of the method is that with a minimal amount of sample preparation the analyst can determine mass absorption coefficients of his unknowns and make matrix corrections so that a single standard, such as W-1, serves as a reference for the analysis of several elements. The method involves 3 major steps:

1. The intensity of $\text{Mo}K\alpha$ Compton scattered radiation (for a Mo target tube) is measured for each sample. The μ of each sample is derived from a calibration curve in which the $\text{Mo}K\alpha$ Compton intensity data of standards are plotted against μ .
2. Measurement of peak intensities at the $K\alpha$ line of each element sought.
3. Measurement of background intensities in the vicinity of $K\alpha$ lines.

The value obtained in Step 3 is subtracted from the value in Step 2 to give background corrected intensities (cps X) which are used in the expression

$$\text{ppm } X^u = \frac{\text{cps } X K\alpha^u}{\text{cps } X K\alpha^{\text{std}}} \cdot \frac{\mu_{0.9\text{\AA}}^u}{\mu_{0.9\text{\AA}}^{\text{std}}} \cdot \text{ppm } X^{\text{std}} \quad (1)$$

where X = element, u = unknown, and std = standard.

Step 3 may require counting times which are as long or longer than that to measure the peak intensity. Commonly, the background is measured in the vicinity of the analytical peak where the background is "flat" and a single background measurement can be made on either side of the peak. In cases where the background under a peak has a slope, the analyst generally measures background on both sides of the peak. Background measurements may be ignored if the difference between μ^u and μ^{std} is less than 5 percent. Since the method is designed to analyze a variety of geological material, background measurements are the rule rather than the exception.

Background measurements are extremely time consuming if a large number of samples are to be analyzed. A method is presented whereby the background is estimated from a calibration curve, and precludes the time spent in the measurement of background intensities for each sample.

Determination of Background

The theory on which Reynolds' method is based need not be repeated here. It is sufficient to mention that mass absorption coefficients of unknowns can be precisely determined ($\pm 2\%$), and that overall errors in trace element analysis of atomic number 28 to 47

are approximately ± 3 percent (Reynolds, 1963, p. 1133). The method was extended to include lighter elements and elements in heavy matrices (Reynolds, 1967). Refinements by Walker (1973) have reduced errors of light element determination to about 2 percent.

A sample placed in the X-ray beam of a fluorescence spectrometer emits the characteristic radiation of the sample elements and scatters the primary X-ray spectra. The fluorescence radiation of intensity I_f is superposed on a background of scattered radiation of intensity I_0 . Andermann and Kemp (1958) developed a technique whereby the primary continuum, scattered by the sample, is used as an internal standard to reduce absorption effects and instrumental variables. Since the whole thesis of this investigation is implicit in their presentation, a summary of their results necessarily follows.

The basis of their paper was to show that, although there is a strong dependency of line intensity, I_f , on matrix composition, the ratio I_f/I_0 remains essentially independent of changes in matrix composition. As such, the ratio is a linear function of concentration (Andermann and Kemp, 1958, p. 1308). In the development of the method, the authors list a set of approximations which relate matrix mass absorption coefficient, atomic number (Z), and the scattered and line intensities as follows: Since

$$\mu \sim Z^4$$

and

$$I_0 \sim Z^{-(3 \text{ to } 2)}$$

$$I_f \sim Z^4$$

then

$$I_f/I_0 \sim Z^{-(1 \text{ to } 2)}$$

Since the authors have shown that concentration of element X or

$$\text{ppm } X \propto I_f/I_0$$

and it is known that

$$I_f \propto 1/\mu$$

and that

$$\text{ppm } X \propto I_f \cdot \mu$$

it follows directly that

$$\mu \propto 1/I_0 \quad (2)$$

Stated otherwise, the background intensity at an analytical line is proportional to Z^{-2} and increases with decreasing matrix atomic number; *i.e.*, re-

ciprocal background intensity should be a linear function of μ (Eq. 2).

Ideally, background measurements are made at the goniometer position for a characteristic line of an element, when the particular element is absent from the sample which is the same in every other respect. In most cases such a blank is not obtainable, and background intensities must be obtained indirectly by making intensity measurements near the analytical line settings. As an extension of the Reynolds' method, I have used a series of standards of known μ as blanks and observed the variation of reciprocal background intensity at the $\text{CuK}\alpha$ and $\text{SrK}\alpha$ analytical lines as a function of μ . Copper was chosen as a means of testing the method for tube corrections because of copper contamination in the Mo target. Sr was selected because concentration values are classified as "recommended" in all standards (Flanagan, 1973) and the $\text{K}\alpha$ line is located near that of $\text{MoK}\alpha$. In this case the $\text{SrK}\alpha$ line is superposed on a sloping background.

Procedure

The $\mu_{0.9\text{\AA}}$ of U.S.G.S. Standards AGV-1 and BCR-1 were determined by the Reynolds' method (Table 1). Standards of known purity were then selected for preparation of the background *vs* $\mu_{0.9\text{\AA}}$ calibration curves ($\mu_{0.9\text{\AA}}$ values from Liebhafsky *et al.*, 1960). Specifically, ultra-pure compounds or metals, such as Al_2O_3 , SiO_2 , aluminum metal, magnesium metal, CaCO_3 , NaCl , and sulfur are easy to obtain, remain stable in pelletized form, are relatively inexpensive, and give an adequate range of μ values which embrace most geological materials. The analyst may use any suitable reagent grade compound for a standard as an alternative to the ultra-pure standards so long as he is certain that it is free of the element in question. In this investigation stock reagent-grade Cu-free CaF_2 and KNO_3 were used in the copper background determinations, and Sr-free sulfur in the Sr curves. All other standards were spectrochemically standardized materials from Johnson, Matthey and Company.

The intensity of the background at the goniometer setting of the analytical line is obtained from four or more standards and plotted as seconds per 10,000 counts (ordinate) *vs* $\mu_{0.9\text{\AA}}$ (abscissa). The slope (b_1) and intercept (b_0) of:

$$\text{SEC}/10\text{K} = b_0 + b_1 \mu_{0.9\text{\AA}} \quad (3)$$

are found by linear regression analysis. Plots (Fig. 1) and correlation coefficients (Table 1) strongly in-

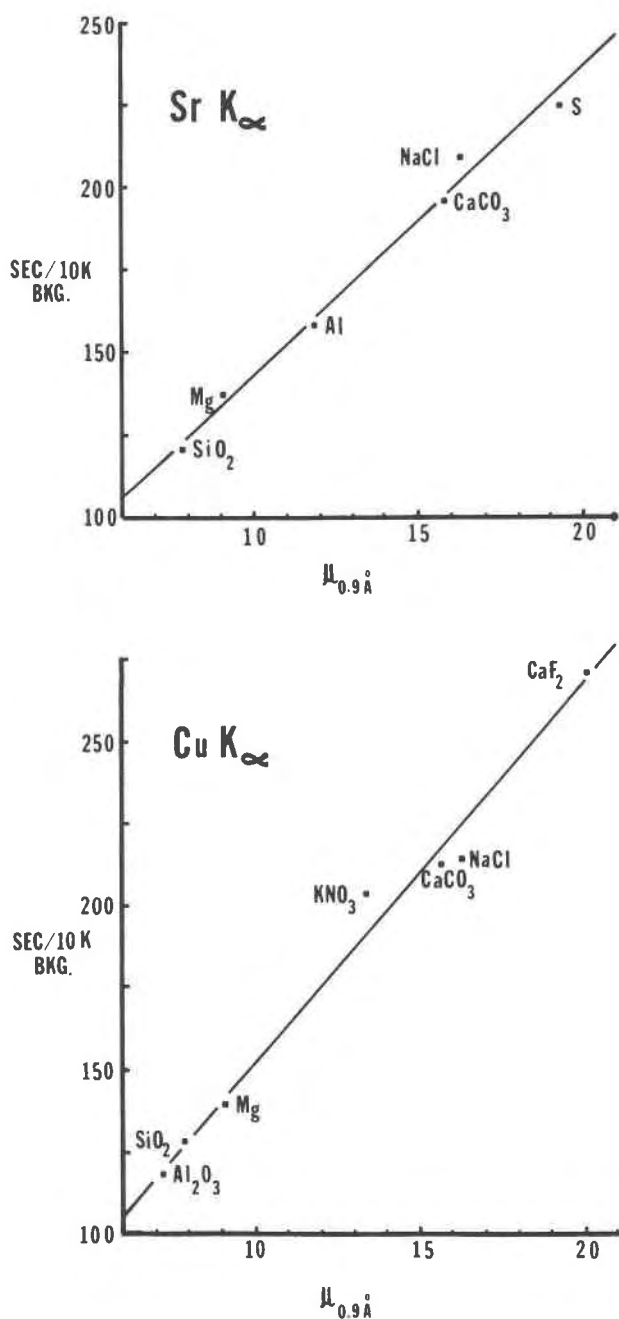


FIG. 1. Graphs demonstrating linear relationship between mass absorption coefficient of standards and reciprocal background intensities at the Sr and CuK α goniometer settings.

dicate that, within the range of μ 's, the relationship between reciprocal background intensity and μ is linear. The SEC/10K for each sample is then calculated from Equation (3), converted to CPS (A columns, Table 1) and subtracted from peak intensity. The concentration of the element is determined from Equation (1).

Standard background counting procedures were used to obtain background counts (10K) in the vicinity of the analytical line (B columns, Table 1). Background counts were taken on both sides of the SrK α line to adjust for the slope. Although data columns A and B were gathered after a shutdown interval of several days, the uncorrected peak intensities remained at the same approximate level in both analyses. The background intensities, as such, are not directly comparable since the data were not collected on the same day.

Experimental

All samples and standards were pelletized in aluminum caps at 21 tons pressure on a 1 $\frac{1}{4}$ " die. A Philips X-ray spectrometer with the following equipment was used: scintillation counter (with pulse height selection in use), LiF analyzing crystal, and Mo target fluorescence tube operated at 50 kV and 48 mA. The rotatable slits were set to the fine position in all intensity determinations related to estimation of $\mu_{0.9\text{\AA}}$ in the samples and standards, and in the measurement of Sr peak and background intensities. The coarse slits were used in the determination of CuK α peak and background intensities.

Discussion

Tube contamination and scattered radiation, which are treated by this method, are not the only contributions to the background at an analytical line. There are other contributions which depend on the analytical line and the composition of the matrix, e.g., peak overlap. Caution is also in order when using the method near the limit of detection, even if the effects of tube contamination are successfully overcome.

Table 1 shows a comparison of measured and reported values of Cu and Sr for the U.S.G.S. standards, BCR-1 and AGV-1, treated as unknowns with W-1 as reference standard in Equation 1. Much larger discrepancies are associated with the determination of Cu in the unknowns from background-corrected peak intensities, as measured empirically, than from the calibration method. The low background values obtained by the empirical procedures must be increased by an undetermined factor to account for the copper contamination from the tube, and apparently this uncertainty has caused the otherwise inexplicably high error in calculated concentration of Cu in BCR-1. The background predicted from the Cu calibration curve includes the tube contamination factor and appears to be less

TABLE 1. Equations for Background Correction Curves and Intensity Data for USGS W-1 (as standard), AGV-1 and BCR-1 (as unknowns)

Elements	Predictive Equation for Background at $K\alpha$ Line		Correlation Coefficients			
Cu	SEC/10K = 37.019 + 11.50 $\mu_{0.9\text{\AA}}$		0.988			
Sr	SEC/10K = 50.352 + 9.327 $\mu_{0.9\text{\AA}}$		0.995			
Unknowns						
	Standard W-1		BCR-1		AGV-1	
	A	B	A	B	A	B
Cu Pk.	77.80	76.63	51.76	51.92	76.85	78.29
Cu Bkg.	47.20	36.16	46.49	39.67	55.62	47.78
	30.60	40.47	5.27	12.25	21.23	30.51
ppm Cu reported*	-		19(+3.3%)	34(+85%)	64(+7.2%)	68(+13.9%)
	110		18.4		59.7	
Sr Pk.	173.36	174.89	257.25	260.23	594.21	602.32
Sr Bkg.	52.64	46.90	51.35	45.94	60.21	57.16
	120.72	127.99	205.90	214.29	534.00	545.16
ppm Sr reported*	-		330(0%)	324(-1.8%)	686(+4.4%)	661(+0.6%)
	190		330		657	
$\mu_{0.9\text{\AA}}$	15.2**		15.48		12.41	
* Flanagan (1973)						
** Reynolds (1963)						

error prone. Insofar as the reported values for Cu in AGV-1 and BCR-1 are classified as "averages" by Flanagan (1973), the calculated errors serve as a means of comparison between background correction methods, but the absolute magnitudes may be meaningless. The reported values of Sr, however, are recommended and the errors associated with the calibration method are of a magnitude which is generally acceptable in most geochemical investigations.

In this investigation all background and peak intensities were taken at preset 10,000 counts. An average of 3 minutes was required to accrue 10K background counts in the vicinity of the $\text{Cu}K\alpha$ peak in samples with $\mu_{0.9\text{\AA}} \approx 15$. In a hypothetical case involving the determination of copper in 100 samples whose $\mu_{0.9\text{\AA}} \geq 15$, at least 5 hours would be spent on background intensity determinations as compared to 30 minutes to establish a background calibration curve. This extension of Reynolds' method saves time without undue sacrifice in accuracy.

References

- ANDERMANN, G., AND J. W. KEMP (1958) Scattered X-rays as internal standards in X-ray emission spectroscopy. *Anal. Chem.* **30**, 1306-1308.
- DELONG, S. E., AND D. McCULLOUGH (1973) Compton-scattered tungsten X-rays as a measure of mass absorption coefficients in rocks. *Am. Mineral.* **58**, 1073-1075.
- FLANAGAN, F. J. (1973) 1972 values for international geochemical reference samples. *Geochim. Cosmochim. Acta*, **37**, 1189-1200.
- LIEBHAFSKY, H. A., H. G. PFEIFFER, E. H. WINSLOW, AND P. D. ZEMANY (1960) *X-ray Absorption and Emission in Analytical Chemistry*. John Wiley & Sons, Inc., N. Y.
- REYNOLDS, R. C. (1963) Matrix corrections in trace element analysis by X-ray fluorescence: Estimation of the mass absorption coefficient by Compton scattering. *Am. Mineral.* **52**, 1133-1143.
- (1967) Estimation of mass absorption coefficient by Compton scattering: Improvements and extensions of the method. *Am. Mineral.* **52**, 1493-1502.
- WALKER, D. (1973) Behavior of X-ray mass absorption coefficients near absorption edges: Reynolds' method revisited. *Am. Mineral.* **58**, 1069-1072.

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