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QUANTITATIVE ANALYSIS OF ELEMENTS IN SEDIMENTS AND SOILS BY X-RAY FLUORESCENCE*

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Abstract—Previous applications of the method of known additions for quantitative X-ray fluorescent analysis have assumed a linear relationship between peak intensity and concentration of the element being analyzed. This assumption is true for soils or sediments containing small amounts of the element in question. In this paper, an equation is derived which takes into account both absorption and enhancement and thus is applicable to samples containing high concentrations of the element. The equation was tested by analyzing an artificial soil sample containing 60% kaolinite and 40% hematite, i.e. the sample contained 28% by weight iron. The fluorescent analysis utilizing the equation derived here resulted in an iron content of 27%. In addition, nine soils from Hawaii were analyzed by this method and the results of these analyses compared with analyses by atomic absorption. The agreement between the two methods is good. It is concluded that the method and equations proposed here provides a reliable measurement of elements in a soil sample which contains high concentrations of the elements in question.

INTRODUCTION

This paper describes a quantitative X-ray fluorescent method to determine the amount of various elements in soils and sediments. The basis of the analysis is a comparison of X-ray fluorescent peak intensities of the element in the sample with intensities of the same element in specimens of the original sample plus known additional amounts of the element in question. In other words, the element to be determined is used as an internal standard. Although use of the element to be determined as an internal standard was suggested by many authors, a linear relationship between the intensity and the concentration of the element was assumed (Adler, 1966; Birks, 1959; Handy and Rosauer, 1959; Jenkins and deVries, 1967). This assumption is true only when the concentration of the element in the soil and the additional known amounts are rather low. Otherwise, due to the effects of absorption and enhancement the relationship between the intensity and the concentration is not linear (Adler, 1966; Birks, 1959; Blokhin, 1965; Cullity, 1967; Jenkins and deVries, 1967; Müller, 1972). The method described here takes both absorption and enhancement into account and is applicable to soil samples containing high concentrations of the element in question.

THEORY

For a direct quantitative analysis of a sample, it is necessary to have a relation between the measured peak intensity of a particular element and its percentage in the sample. Such a relation, however, is usually governed by the matrix effects which include both absorption and enhancement as shown below, therefore a direct correlation is impossible.

Birks (1959) gives a complete derivation of the equation for expected fluorescent intensity. Both absorption and enhancement are taken into consideration in that derivation. If an assumption is made that the exciting radiation is monochromatic, the following expression is obtained for intensity;

$$I_{fx} = \frac{Q_x I_{po} \rho_x}{(\mu_p \csc\phi_p + \mu_f \csc\phi_f)\rho}[1 - e^{-(\mu_p \csc\phi_p + \mu_f \csc\phi_f)\rho L}], \quad (1)$$

where

I_{fx} = expected fluorescent intensity of some characteristic line of element x;
Q_x = excitation constant of element x;
I_{po} = intensity of the primary radiation;
ρ_x = density of element x in the layer dl which is shown in Figure 1;
ρ = density of the sample;
μ_p = mass absorption coefficient of the sample for the primary radiation;
μ_f = mass absorption coefficient of the sample for the fluorescent radiation;
ϕ_p = angle at which primary radiation strikes the surface of the sample, as shown in Figure 1;
ϕ_f = angle at which fluorescent radiation emerges, as shown in Figure 1;
L = the distance from the surface of the sample to the layer dl, as shown in Figure 1.

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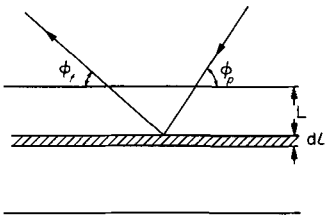


Fig. 1. Primary and fluorescent radiation paths through a thick specimen.

The expression, $(\mu_p csc\phi_p + \mu_f csc\phi_f)$, in equation (1) accounts for absorption and enhancement, which was verified experimentally by Beattie and Brissey (1954).

Now, if L is allowed to go to infinity and ρ_x/ρ is expressed by x, which is the weight fraction of the element to be measured, equation (1) becomes simply:

$$I_{fx} = \frac{Q_x I_{po} x}{(\mu_p csc\phi_p + \mu_f csc\phi_f)}. \tag{2}$$

By definition, mass absorption coefficients, μ_p and μ_f can be expressed as:

$$\mu_p = x\mu_{xp} + (1 - x)\mu_{mp} = x(\mu_{xp} - \mu_{mp}) + \mu_{mp}; \tag{3}$$

$$\mu_f = x\mu_{xf} + (1 - x)\mu_{mf} = x(\mu_{xf} - \mu_{mf}) + \mu_{mf}, \tag{4}$$

where μ_{xp} and μ_{mp} are mass absorption coefficients of the element being determined and the matrix material for primary radiation, respectively. Parameters μ_{xf} and μ_{mf} are mass absorption coefficients of the element being determined and the matrix material for fluorescent radiation, respectively.

Substitution of equations (3) and (4) into equation (2) gives:

$$I_{fx} = \frac{Q_x I_{po} x}{x\{(\mu_{xp} - \mu_{mp})csc\phi_p + (\mu_{xf} - \mu_{mf})csc\phi_f\} + \{\mu_{mp} csc\phi_p + \mu_{mf} csc\phi_f\}}. \tag{5}$$

The terms $\{(\mu_{xp} - \mu_{mp})csc\phi_p + (\mu_{xf} - \mu_{mf})csc\phi_f\}$ and $\{\mu_{mp} csc\phi_p + \mu_{mf} csc\phi_f\}$ are constants, and can be designated as A and B, respectively. Therefore, equation (5) becomes:

$$I_{fx} = \frac{Q_x I_{po} x}{Ax + B}. \tag{6}$$

The matrix effects (i.e. absorption and enhancement) are accounted for in this equation by the parameters Q_x, A and B. As is shown by the following analysis, these effects can be eliminated by addition of known quantities of the element being determined to the sample.

When a known quantity of the element being determined is added to the sample, this mixture is referred to in this paper as the specimen. However, it is usually more expedient to add a compound of the element rather than the pure element. Therefore, in addition to the element in question, other elements are added to the sample. Let C be the known added weight fraction of the element in the specimen and k be the weight fraction of the element in the compound added. Then, the weight fraction, C_0, of the elements other than the element being determined can be obtained from:

$$C_0 = \frac{1 - k}{k} \cdot C. \tag{7}$$

Now, the weight fraction of the *sample* in the *specimen* is $(1 - C - C_0)$ and the unknown weight fraction of the *element* in the *specimen* is $(1 - C - C_0)x$. Therefore, the total weight fraction of the element in the specimen is:

$$X = (1 - C - C_0)x + C. \tag{8}$$

Substitution of equation (7) into equation (8) gives

$$X = \left(1 - \frac{C}{k}\right)x + C. \tag{9}$$

Obviously, the mass absorption coefficients of the specimen for primary and fluorescent radiations will be different than those of the sample. These coefficients can be expressed in the following manner;

$$\mu'_p = X\mu_{xp} + \left(1 - X - \frac{1 - k}{k}C\right) \times \mu_{mp} + \frac{1 - k}{k} C\,\mu_{op}$$

or

$$\mu'_p = X(\mu_{xp} - \mu_{mp}) + C\left(\frac{1 - k}{k} \times \mu_{op} - \frac{1 - k}{k}\mu_{mp}\right) + \mu_{mp} \tag{10}$$

and

$$\mu'_f = X(\mu_{xf} - \mu_{mf}) + C\left(\frac{1 - k}{k} \times \mu_{of} - \frac{1 - k}{k}\mu_{mf}\right) + \mu_{mf}, \tag{11}$$

where μ'_p and μ'_f are mass absorption coefficients of the specimen for primary and fluorescent radiations, respectively, and μ_{op} and μ_{of} are mass absorption coefficients of the added elements other than the element being measured for primary and fluorescent radiations, respectively.

Now, fluorescent intensity, I_{fc}, produced by the total amount of the element in the specimen can be expressed as:

$$I_{fc} = \frac{Q_x I_{po} X}{(\mu'_p csc\phi_p + \mu'_f csc\phi_f)}. \tag{12}$$

Substituting equations (10) and (11) into equation (12), and recalling that the terms $\{(\mu_{xp} - \mu_{mp})csc\phi_p + (\mu_{xf} - \mu_{mf})csc\phi_f\}$ and $\{\mu_{mp} csc\phi_p + \mu_{mf} csc\phi_f\}$ are

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the constants A and B, gives:

$$I_{fc} = \frac{Q_x I_{po} X}{AX + B + C\left\{\left(\frac{1-k}{k}\right)(\mu_{op} - \mu_{mp}) \times csc\phi_p + \left(\frac{1-k}{k}\right)(\mu_{of} - \mu_{mf})csc\phi_f\right\}}. \quad (13)$$

The term $\{(1 - k/k)(\mu_{op} - \mu_{mp})csc\phi_p + (1 - k/k)(\mu_{of} - \mu_{mf})csc\phi_f\}$ also is a constant which can be designated as D. Thus equation (13) takes the following form:

$$I_{fc} = \frac{Q_x I_{po} X}{AX + B + DC}. \quad (14)$$

Then, by dividing equation (14) by equation (6), the ratio of the peak intensities produced by the specimen and the sample can be expressed as follows:

$$\frac{I_{fc}}{I_{fx}} = \frac{X(Ax + B)}{x(AX + B + DC)}.$$

The value of X as defined by equation (9) can be substituted into the above equation to give:

$$\frac{I_{fc}}{I_{fx}} = \frac{\left\{\left(1 - \frac{C}{k}\right)x + C\right\}\{Ax + B\}}{x\left[A\left\{\left(1 - \frac{C}{k}\right)x + C\right\} + B + DC\right]},$$

or

$$\frac{I_{fc}}{I_{fx}} = \frac{Ax^2 - \frac{AC}{k}x^2 + ACx + Bx - \frac{BC}{k}x + BC}{Ax^2 - \frac{AC}{k}x^2 + ACx + Bx + DCx}.$$

By subtracting 1 from both sides of the above equation, one can obtain the following equation:

$$\frac{I_{fc}}{I_{fx}} - 1 = \frac{BkC - BCx - DkCx}{Akx^2 - ACx^2 + AkCx + Bkx + DkCx}. \quad (15)$$

By letting $I_{fc}/I_{fx} - 1$ be equal to I and grouping the terms, equation (15) becomes:

$$I = \frac{C(Bk - Bx - Dkx)}{C(Akx + Dkx - Ax^2) + Akx^2 + Bkx}$$

and

$$\frac{C}{I} = C\left(\frac{Akx + Dkx - Ax^2}{Bk - Bx - Dkx}\right) + \left(\frac{Akx^2 + Bkx}{Bk - Bx - Dkx}\right). \quad (16)$$

Now letting

$$m = \left(\frac{Akx + Dkx - Ax^2}{Bk - Bx - Dkx}\right)$$

and

$$n = \left(\frac{Akx^2 + Bkx}{Bk - Bx - Dkx}\right),$$

equation (16) becomes a linear equation:

$$\frac{C}{I} = mC + n. \quad (17)$$

If C, the concentration of the element added to the sample, is plotted vs C/I, a straight line will be obtained with a slope of m and an intercept of n. From these experimentally determined values it is possible to compute x, the unknown weight fraction of the element in the sample.

By adding 1 to the expression for m and then dividing it by n, all the unknown quantities are eliminated except x, and the following equation results:

$$\frac{m + 1}{n} = \frac{k - x}{kx}. \quad (18)$$

Solving equation (18) for x, the following expression is obtained:

$$x = \frac{kn}{k(m + 1) + n}, \quad (19)$$

where, once more, m and n are experimentally determined slope and intercept and k is the weight fraction of the element in the compound added.

EXPERIMENTAL PROCEDURE AND RESULTS

The method was tested by measuring the iron content in an artificial soil composed of 60% kaolinite and 40% hematite, i.e. the artificial soil contained 28% by weight elemental iron. In addition to applying the fluorescent method to the artificial soil, eight soils from the islands of Oahu and Kauai were analyzed for their iron contents and the results of the fluorescent analyses compared with the results of wet chemical analyses.

A GE-XRD-5 spectrogoniometer was used in the experimental fluorescent analyses of soil samples. Specimens were prepared by adding known quantities of hematite to them. Tungsten radiation operated at 50 kvp and 25 mA was used for excitation. The fluorescent radiation was analyzed using a flat NaCl single crystal and a gas flow tube detector (10% methane + 90% argon). The diffraction peak corresponding to the K_x characteristic radiation of iron $\lambda = 1.9373$ Å) and (200) spacing of NaCl crystal (2.82 Å) was recorded on a strip chart recorder (at 40.14° 2θ angle). Relative integrated intensities were determined by measuring the peak areas above the base line using a planimeter.

The representative samples of each soil were mixed with five additional known amounts (between 5 and 20%) of a chemically pure Fe_2O_3, to prepare the specimens. Steel rings 4.5 mm thick were used as sample holders to satisfy the assumption of infinite thickness of the sample, which is necessary for equation (2). Sample holders were made large enough not to intercept the excitation radiation and were checked by blank tests. For consistency of volume and weight

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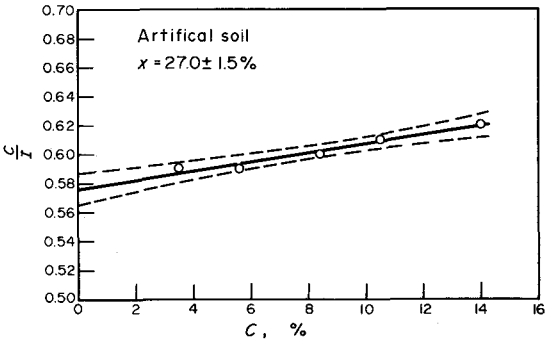


Fig. 2. Experimental results of artificial soil containing 28% iron.

percentages, specimens were compressed into rings at a constant porosity.

Three separate intensity measurements were made on each soil sample and specimen, and the intensity ratios calculated using the average intensities. The values of C/I were calculated and plotted vs C. The slope, m, and intercept, n, of the resulting line were determined by regression analysis for each soil series. Equation (19) was then used to calculate the amount of iron in each soil. Note that, in this particular study k is equal to 0.7 which is the weight fraction of Fe in Fe_2O_3. Figure 2 is the graph of C/I vs C for the artificial soil. Figure 3 shows a typical C/I vs C plot with the regression line drawn for Lihue soil series. The good linear fit of the experimental data is partial verification of the reliability of the theory.

The fluorescent analysis of the artificial soil resulted in an iron content of 27.0% which is in good agreement with the 28.0% iron in the sample. The calculus method of error analysis revealed that at the 5% significance level the calculated iron contents is from 25.5% to 28.5%.

The natural soils used to test the method are from the islands of Oahu and Kauai, Hawaii. All are basalt derived Oxisols and Ultisols and are quite rich in iron. Samples for iron analysis were prepared by mixing the trimmings from thin-walled tube samples from 3 different borings and various depths within the B horizon. The mixture was then quartered with a sample splitter. In this way, it was attempted to analyze the material that is representative of the B horizon. Data on sample site location and the geologic and climatic setting are given by Tuncer (1976). The

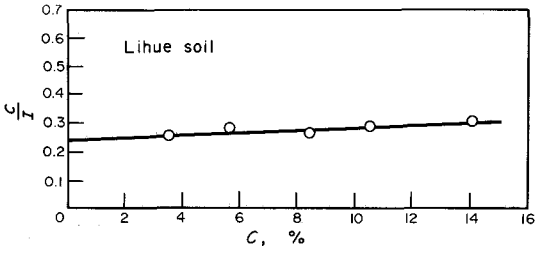


Fig. 3. Graphical solution of equation (17) for five experimental points; as exemplified by Lihue soil series.

method described above was utilized to determine the percentage of elemental iron in those soils.

The natural soils were analyzed for iron content by atomic absorption spectrophotometry. Colorimetric analysis was used on the natural soil samples as well as on the artificial soil.

For the atomic absorption analysis, about 0.5 g of each sample was covered with 20 ml of a mixture of perchloric, phosphoric and nitric acids in the ratios 2:2:1 by volume. The mixture was heated to remove all easily oxidizable organic material and to fume away the nitric and phosphoric acids. After cooling, the mixture was diluted with 100 ml of distilled water and filtered to remove the insoluble residues. The resulting clear solutions were diluted to known volumes, usually 500 ml, and analyzed for iron in a Perkin–Elmer 305B atomic absorption spectrophotometer with an oxidizing air–acetylene flame and a single element hollow cathode lamp. The absorption line to determine the iron was 327 nm and the working curve was from 0–80 ppm. Three replicate dissolutions of each sample were analyzed and the results agreed within 1%.

The same digestion process which was used for the atomic absorption analysis was used for the colorimetric analysis. The color reagent was 1,10 phenanthroline and the method of analysis is that described by Diehl (1970, p. 315) and the instrument used was a Technicon AutoAnalyzer. The data for the fluorescent analysis and the two chemical analyses are shown in Table 1.

DISCUSSION AND CONCLUSION

It is recognized that in both of the chemical analyses used to check the results of the fluorescent analysis there is the possibility of errors arising from the fact that natural soils are chemically complex materials and the presence of ions other than iron may give misleading results. Lee and Güven (1975) observed that iron determinations by atomic absorption are subject to severe interference by silicon and aluminum. In order to minimize such errors in the atomic absorption analysis, the 372 nm absorption line was used in the range of 0–80 ppm because of the exceptional lack of adjacent non-absorbing lines. Similarly, the 1,10 phenenanthroline was used for the colorimetric analysis because few ions interfere with the formation of the color. However, there is greater deviation between the fluorescent results and the chemical results for the analyses of the natural soils. This is interpreted as being due to the complex chemistry of the natural soils.

One possible source of uncertainty in the X-ray fluorescent analysis may come from the determination of the baseline. A small variation in the location of baseline may change the measured peak area and such a change would be reflected in the percentage of the element in question.

On the basis of these results, it is concluded that

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Table 1

Soil Series	Elemental Fe content by fluorescent analysis (wt. %)	Elemental Fe content by atomic absorption (wt. %)	Elemental Fe content by colorimetric analysis (wt. %)
Molokai	11.4	13.5	14.1
Lahaina	11.9	12.7	12.6
Wahiawa	12.4	14.3	15.3
Lihue	14.3	14.3	15.7
Manana	16.3	17.1	16.8
Paaloa	17.3	18.9	18.7
Kapaa	24.8	26.5	25.0
Halii	28.1	30.4	31.4
Artificial soil (28% Fe)	27.0	No data	26.6

X-ray fluorescent analysis with the method of known additions and the equations which take into account the absorption effects of the added internal standard provides a fairly reliable measurement of elements in a soil sample which can be used at higher concentrations and at nonlinear ranges of the concentration–intensity relationships.

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REFERENCES

1. Adler, I. (1966) *X-ray Emission Spectrography in Geology. Methods in Geochemistry and Geophysics*, 4: Elsevier, Amsterdam.
2. Beattie, H. J. and Brissey, R. M. (1954) Calibration method for X-ray fluorescence spectrometry: *Anal. Chem.* **26.** 980.
3. Birks, L. S. (1959) *X-ray Spectrochemical Analysis*: Interscience, New York.
4. Blokhin, M. A. (1965) *Methods of X-ray Spectroscopic Research*: Pergamon Press, Oxford.
5. Cullity, B. D. (1967) *Elements of X-ray Diffraction*: Addison–Wesley, Reading, MA.
6. Diehl, H. (1970) *Quantitative Analysis*: Oakland Street Press, Ames, Iowa.
7. Handy, R. L. and Rosauer, E. A. (1959) X-ray fluorescence analysis of total iron and manganese in soils: *Proc. Iowa Acad. Sci.* **66.** 237–247.
8. Jenkins, R. and deVries, J. L. (1967) *Practical X-ray Spectrometry*: Phillips Technical Library.
9. Lee, R. W. and Güven, N. (1975) Chemical interferences in atomic absorption spectrometric analysis of silicates in the fluoboric–boric acids matrix: *Chem. Geol.* **16.** 53–58.
10. Müller, R. O. (1972) *Spectrochemical Analysis by X-ray Fluorescence*: Plenum Press, New York.
11. Tuncer, E. R. (1976) Engineering behavior and classification of lateritic soils in relation to soil genesis: Unpublished Ph.D. thesis, Iowa State University, Ames.

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