A METHOD FOR QUANTITATIVE DETERMINATION OF SOIL MINERALS BY X-RAY DIFFRACTION

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ABRIDGMENT

•THIS paper describes the theory and initial test results for a method of quantitatively determining the amount of various mineral components in a soil sample by comparing X-ray diffraction peak intensities of the mineral in the sample with the intensities of the same peak in specimens that are a mixture of the original soil sample and known additional amounts of the mineral in question. That is, the component being determined is used as an internal standard.

Norrish and Taylor (2) expanded on the ideas of Klug and Alexander (1) and Von Engelhardt (4) to demonstrate that the measured intensity of an X-ray diffraction peak of a crystalline component in a sample is related to the weight fraction of that component in the sample as follows:

$$I_o = \frac{Kx}{\rho A_s} \tag{1}$$

where

I_o = measured intensity of the diffraction peak of a crystalline component in a soil sample,

ρ = true density of the component used to make the diffraction pattern,

x = weight fraction of the component being estimated,

K = constant for any particular peak of a particular component, and

A_s = mass absorption coefficient of the sample.

Norrish and Taylor pointed out that the use of this equation with internal standards is difficult because the mass absorption coefficients of the standard mixtures vary as the amount of known mineral content changes in the specimen. The derivation here takes this variable into account but assumes that the ratio of K/ρ will remain constant as long as the crystalline structure of the standard component added to the soil sample is essentially the same as that of the component occurring in the soil sample.

Equation 1 can be written as

$$I_o = \frac{Kx}{\rho(xA_s + x_2A_2 + x_3A_3 + \ldots)}$$

where

A_s = mass absorption coefficient of the component being measured,

A_2, A_3 = mass absorption coefficients of the other minerals in the soil, and
x_2, x_3 = weight fractions of those other minerals.

The true mass absorption coefficient of the sample consisting of components exclusive of the one being measured is A_1. These minerals exclusive of the one being estimated will be referred to as the matrix minerals. The true mass absorption coefficient of the matrix minerals is given by

$$A_1 = \frac{x_2}{1-x} A_2 + \frac{x_3}{1-x} A_3 + \ldots$$

Therefore,

$$A_1 = \frac{1}{1-x} (x_2 A_2 + x_3 A_3 + \ldots)$$

The term $x_2 A_2 + x_3 A_3 + \ldots$ can be called the apparent mass absorption coefficient of the matrix minerals, $\overline{A}_1$. Therefore,

$$I_o = \frac{Kx}{\rho(x A_a + \overline{A}_1)} \tag{2}$$

If a known quantity of the component being estimated is added to the sample, this mixture can be referred to as a specimen. Let c be the known added weight fraction of the component in the specimen and X be the composite or total weight fraction of the component in the specimen. The weight fraction of the sample in the specimen is $1 - c$, and the unknown weight fraction of the component in the specimen is $(1 - c)x$. Therefore, the total weight fraction of the component in the specimen is

$$X = (1 - c)x + c$$

The peak intensity produced by the total amount of the component in the specimen is

$$I_c = \frac{KX}{\rho A_c} = \frac{K[(1-c)x + c]}{\rho A_c} \tag{3}$$

where

I_c = peak intensity, and
A_c = complete mass absorption coefficient of the specimen.

The mass absorption coefficient in terms of the total and added weight fractions in the specimen is

$$A_c = X A_a + (1 - c)x_2 A_2 + (1 - c)x_3 A_3 + \ldots$$

which can also be written in terms of the unknown weight fraction of the component in the sample as

$$A_o = [(1 - c)x + c] A_a + (1 - c) (x_2 A_2 + x_3 A_3 + \ldots)$$

The value of the apparent mass absorption coefficient of the matrix minerals can be substituted into the above equation to give

$$A_o = [(1 - c)x + c] A_a + (1 - c) \overline{A}_1 \tag{4}$$

Substitution of equation 4 into equation 3 gives

$$I_o = \frac{K[(1 - c) x + c]}{\rho\{[(1 - c)x + c] A_a + (1 - c) \overline{A}_1\}}$$

The ratio of the peak intensities produced by the sample and the specimen is

$$\frac{I_a}{I_o} = \frac{[(1 - c)x + c](x A_a + \overline{A}_1)}{\{[(1 - c)x + c] A_a + (1 - c) \overline{A}_1\}x}$$

which can be written as

$$\frac{I_a}{I_o} = \frac{\dfrac{A_a}{\overline{A}_1} + \dfrac{1}{x}}{\dfrac{A_a}{\overline{A}_1} + \dfrac{1 - c}{(1 - c)x + c}} \tag{5}$$

If

$$\frac{A_a}{\overline{A}_1} = A$$

and this term is substituted into equation 5, then by adding and subtracting 1 the equation becomes

$$\frac{I_o}{I_o} = \frac{c/x}{Ax - Acx + Ac + 1 - c} + 1 \tag{6}$$

Now let $\dfrac{I_o}{I_o} - 1 = I$ and substitute it into equation 6 to give

$$\frac{c}{I} = x^2 A - Acx^2 + Acx + x - cx$$

Grouping terms gives

$$\frac{c}{I} = c[Ax - x\,(Ax + 1)] + x\,(Ax + 1) \qquad (7)$$

Let $m = [Ax - x(Ax + 1)]$ and $a = x(Ax + 1)$. Equation 7 becomes

$$\frac{c}{I} = mc + a \qquad (8)$$

such that, if the concentration of component added to the sample divided by the intensity ratio minus one is plotted versus the concentration of the component added to the sample for various concentrations, then a straight line with a slope of m and an intercept of a should result. From these experimentally determined values it should be possible to compute x, the unknown amount of the component in the soil sample. The values of a and m give two equations with two unknowns, x and A. Thus, it is also possible to compute experimentally the ratio of the mass absorption coefficient of the mineral A_s as well as the mass absorption coefficient of the matrix minerals.

EXPERIMENTAL PROCEDURE AND OBSERVATION

The reliability of this method was evaluated by preparing an artificial soil containing 5 percent hematite ground from a naturally occurring hematite and 95 percent kaolinite. This soil sample was then mixed with additional known amounts (5, 8, 12, 15, and 20 percent) of a chemically pure hematite. The intensities of the 100 peaks for the sample and each specimen were measured. The intensity ratio for each specimen was computed, and a plot of c/I versus c was prepared. The radiation used was molybdenum $K\alpha$, and the 100 reflection gives a peak at the 2θ angle of 15.15 deg. As shown in Figure 1, there is an overlap of the 15.15-deg peak and the next peak corresponding to both hematite and kaolinite at about 16.4 deg. Therefore, it is necessary to sketch the lower portion of both peaks to the base line so that the higher intensity caused by the overlap is equal to the sum of the areas of the two tails. The base line is determined by extending a straight line from one background level at a lower 2θ angle where there are no peaks to another low background at a higher 2θ angle. The area of the peak so defined was then measured with a planimeter.

Four intensity measurements were made on each specimen and the soil sample; then the intensity ratios were calculated by using the average intensities. The values of c/I were then calculated and plotted versus c. The graph is shown in Figure 2 with the regression line and 95 percent confidence limits. The hematite content determined from a and m is 5.15 percent, which compares favorably with the 5.00 percent of the artificial soil sample. The calculus method (3) of error analysis revealed that at the 5 percent significance level the range in calculated hematite contents is from 4.6 to 5.7 percent. Theoretical mass absorption characteristics for hematite and kaolinite were determined as 27.26 and 3.4 respectively. The theoretical value of the mixture of 5 percent hematite and 95 percent kaolinite is therefore 8.4. The mass absorption coefficient that was determined from Figure 2 and the parameters a and m is 6.11.

CONCLUSIONS

Based on the good agreement between the amount of hematite in the artificial soil sample and the amount of hematite estimated by the method described here, it is concluded that this method is a reliable method for determining various mineral com-

Figure 1. Example of definition of X-ray peak for intensity measurements.

Mineral = Hematite
Radiation = Mo - K$_\alpha$
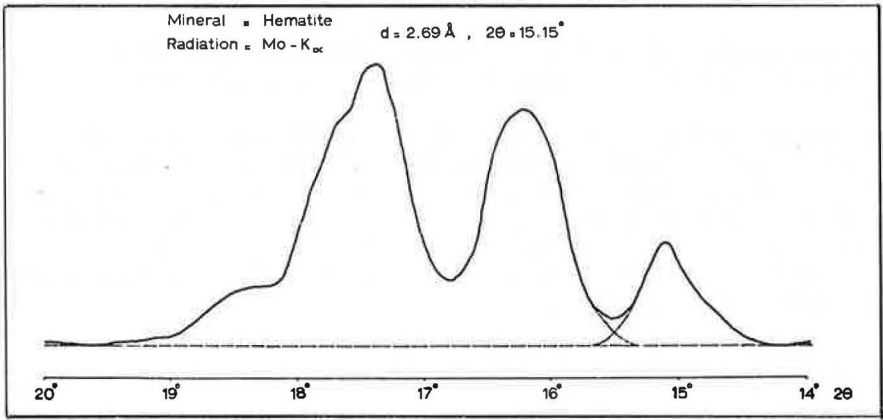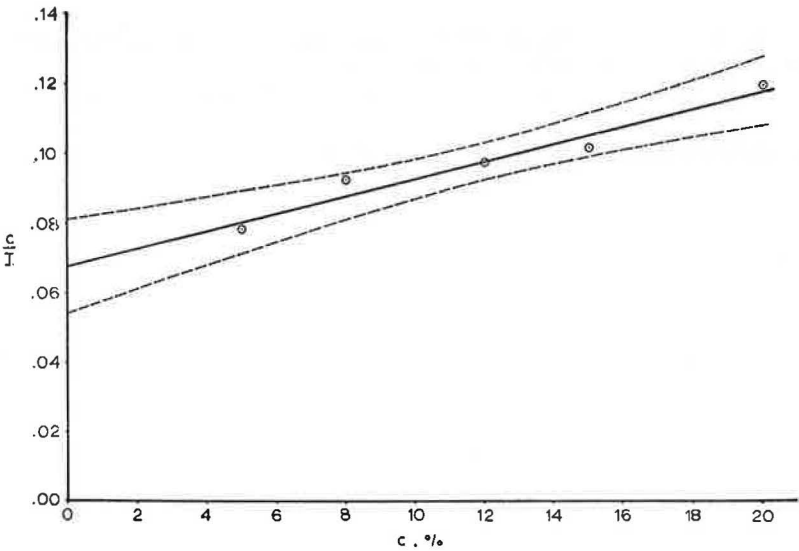d = 2.69 Å , 2θ = 15.15°

Figure 2. Concentration-intensity ratio versus concentration of hematite based on average values of peak intensity.

ponents in natural soils. The fair agreement between theoretical and experimentally determined mass absorption coefficients is taken as further evidence of the reliability of this method.

One source of the variability in the four individual values is interpreted as arising from the judgment that goes into the definition of each peak due to the overlap of sequential peaks.

Another source of scatter in the values may be the variability in the time rate of X-ray photon densities due to voltage alternation. Thus, on any given determination a different population of grains in the powder will be irradiated; this will result in varying intensities for each individual determination. Rotating the sample should minimize this effect. It is recommended that in subsequent evaluations of this technique the samples be rotated in the plane of the sample holder so as to give a better statistical sample of the crystallites being irradiated.

ACKNOWLEDGMENTS

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