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X-Ray Fluorescence Analysis of Total Iron And Manganese in Soils[1]

By R. L. HANDY and E. A. ROSAUER

Abstract. Two methods are presented for the quantitative de-
termination of total iron and manganese in soils. The first necessi-
tates the preparation of a calibration curve and is applicable only
to soils having similar properties. In this method known incre-
ments of Fe_2O_3 and/or MnO_2 are added to the original soil, and
X-ray fluorescence intensities are obtained. Analysis of an un-
known then utilizes the resulting equation which expresses the
relation between intensity and concentration.

A second method, here called the two-point method, does not
require a calibration curve and is valid for a wider range of sam-
ples. A sample is analyzed for either iron or manganese, and
X-ray fluorescence intensities are obtained; then a known amount
of the element is added to the sample and intensities are again
measured. A suitable equation utilizing the two intensities for
the determination of the element in the original sample is pre-
sented. Data are included to indicate that this method is satis-
factory and accurate.

Materials subjected either to a high voltage electron beam or to
a high energy X-ray beam absorb part of the beam energy and
re-emit it as X rays. The X-ray spectrum thus generated is char-
acteristic of the elements in the sample, so the measurement of the
emitted wavelengths is a means for spectrochemical analysis. Since
emission intensities are proportional to concentrations of emitted
elements in the sample, quantitative relationships may also be set
up.

In the commercial X-ray spectroscope the sample is irradiated
with hard, short wavelength X rays from a tungsten tube. Second-
ary radiation emitted by the sample is collimated, then it is analyzed
by diffraction from a known crystal (Figure 1) which in effect sep-
arates the beam into component wavelengths. The θ angle at which
diffraction will occur appears in the Bragg equation

$$n\lambda = 2d \sin \theta,$$

where n = a whole number, including the order of diffraction,

λ = X-ray wavelength,

d = interplanar spacing in the crystal, and

θ = the angle between the X-ray beam and the reflecting
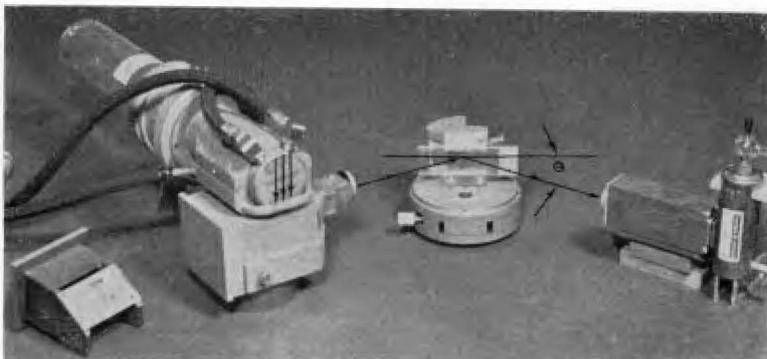planes in the crystal.

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Figure 1.   Schematic arrangement for X-ray fluorescence analysis. Hard X rays from a tungsten tube shoot down (triple arrow) and irradiate the sample contained in a sample drawer. Fluorescent X rays from the sample are then diffracted by a known crystal and detected with a counter tube, shown at right. The θ angle is specific for diffraction of a given wavelength.

In X-ray spectroscopy d is known and θ is measured, then the equation is solved for λ. This is in contrast with X-ray diffraction analysis, where λ is known and θ is measured, and the equation is solved for d.

For qualitative identification of elements in the sample, the θ angle may be scanned while diffracted intensities are continuously measured with a Geiger-Muller or scintillation counter and the counting rate recorded on a strip chart recorder. Each peak intensity then indicates a θ angle at which the Bragg equation is satisfied, and the emitted element may be identified from its wavelength by means of prepared tables. The identification may be checked at the various corresponding θ angles.

For quantitative measurement, the θ angle is set for the desired wavelength, and counts are made for measured time intervals. The X-ray intensity is then expressed in counts per second and is corrected for instrumental drift or crystal misalignment by re-run of a standard. A correction is also made for scattered radiation or background; this is made by subtracting counts at a nearby θ angle which does not coincide with the θ for other wavelengths emitted by other elements in the sample.

Unless objectionable overlapping of wavelengths from different elements occurs, the radiation usually selected for measurement is the strongest radiation, the Kα. Tungsten radiation applied to the sample causes ejection of electrons from inner shells to outer shells of the atoms; when the electrons fall back, the change in energy level results in fluorescent emission of X rays. Kα results from vacancies in the innermost K shell being filled by electrons from the next outer shell, the L shell. Radiation designated Kβ is emitted when vacancies in the K shell are filled from the third, or M shell.

Since this involves a greater change in energy level, $K\beta$ has a higher energy, i.e., a shorter wavelength. However, since filling of the K from the neighboring L is statistically more probable, $K\alpha$ radiation is the more intense.

ABSORPTION

Ideally a fluorescent intensity is proportional to the mass concentration of emitted atoms in the surface of the sample. At low or high concentrations of an element this is approximately true, and a linear relationship between intensity and concentration may be found.

With intermediate concentrations the linear relationships no longer hold, illustrating the effect of reabsorption of emitted rays before they leave the sample. The amount of absorption varies widely, depending on the X-ray wavelength and the identity of the elements in the sample. Mass absorption coefficients of different common soil elements for iron $K\alpha$ and manganese $K\alpha$ radiations are shown in Table 1.[2] As an example, the presence of calcium in a sample will reduce the fluorescent iron $K\alpha$ intensity far more than the presence of an equal amount of magnesium. Similarly, at high iron content the low absorption factor of iron for iron $K\alpha$ radiation ordinarily will mean disproportionately high iron $K\alpha$ intensities.

Table 1
Mass Absorption Coefficients of Different Elements for $FeK\alpha$ and $MnK\alpha$ Radiations

Element	Atomic Number	μ/ρ	
		$FeK\alpha$[1] (1.9373 Å)	$MnK\alpha$[2] (2.103 Å)
Mg	12	75.7	
Al	13	92.8	115
Si	14	116.3	
Ca	20	317	380
Cr	24	490	
Mn	25	63.6	
Fe	26	72.8	90

[1]Internationale Tabellen zur Bestimmung von Kristallstrukturen, Vol. 2, 1935.
[2]Interpolated from values in Handbook of Chemistry and Physics, Chemical Rubber Co., 35th Ed., Cleveland, Ohio, 1953.

Several solutions have been suggested for the absorption problem. The simplest is to prepare a calibration curve specific for soils having similar physical and chemical properties, and assume that absorption does not vary appreciably from sample to sample. Such a curve is presented for determination of manganese in a friable, calcareous loess. Measured increments of MnO_2 were added to samples of the

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[2]Fluorescent intensities are also affected by absorption of tungsten radiation; however, these absorption coefficients are so low they have relatively little effect.

loess and the fluorescent intensities were measured; an equation relating intensity to MnO_2 content was then found by the method of least squares.

Another approach is to add a measured amount of a reference standard to a sample and calibrate on the basis of emission intensity ratios between the unknown and the standard. The standard contains an element whose radiation is absorbed about the same as radiation from the element to be measured, which means that it will emit nearly the same wavelength and will have nearly the same atomic number. For example, for measurement of iron, a carefully measured amount of a cobalt compound might be added to the sample, since the atomic number of cobalt is one higher than that of iron. In general, the absorption of cobalt $K\alpha$ by different elements is much the same as and about proportional to the absorption of iron $K\alpha$. However, notable exceptions occur for elements near the absorption edge, which ordinarily occurs about two atomic numbers below the emitting element. That is, cobalt $K\alpha$ (at. no. 27) is greatly absorbed by manganese (at. no. 25). Similarly iron $K\alpha$ (at. no. 26) is most strongly absorbed by chromium (at. no. 24). Therefore, presence of variable amounts of manganese in a soil would strongly influence iron $K\alpha$ to cobalt $K\alpha$ intensity ratios and would affect the measurement of iron.

Another possibility for use of an internal standard is to go the other way in atomic number and select the next number lower. For measurement of iron, this would mean the use of manganese. Unfortunately, since soils already contain manganese, the intensities from the internal standard would be increased. Other standards may be selected, but the greater the difference in emitted wavelength between the standard and iron, the greater the difference in absorption factors.

Because these solutions are not entirely satisfactory, a different approach was tried. A measured quantity of the same material is added, in this example a compound of iron, and the original iron content is determined by algebraic extrapolation, here called the two-point method. So far the method has been used only in the linear response range (i.e., less than about 10 percent Fe_2O_3), but it should have good accuracy because of the identical absorption factors.

<center>PROCEDURE</center>

Standard samples were prepared with a friable, calcareous loess (Sample No. 20-2 VII) known to be low in manganese and iron. Carefully weighed increments of Fe_2O_3 or MnO_2 were added to the previously air-dried and pulverized soil in 1 oz. wide-mouth glass

bottles; glass beads were added as a mixing aid, and the bottles were put on a rotary mixer for a minimum of one hour.

Samples were packed dry into 1 in. x 1 in. x 0.1 in. bakelite holders and subjected to 50 kvp tungsten radiation. The tube was operated at 50 ma. A sodium chloride analyzing crystal was used, and the diffracted radiation was counted with a proportional counter tube. The count rates reported are from averages of ten second counts. A General Electric XRD-5 unit was used for the analysis.

<div align="center">RESULTS</div>

Manganese

Calibration data from the prepared MnO_2 reference samples are in Table 2. Conversion of percentage added to total percentage requires some algebraic gymnastics, since the base for calculation of percentage changes. That is, the added amounts are expressed as percentages of the total mix, but the constant amount originally in the soil is not a percent of total mix since the amount of the total mix changes as more material is added.

<div align="center">Table 2</div>
<div align="center">Manganese $K\alpha$ Calibration Data for Friable Less Soil</div>

Percent added MnO_2	Total Percentage MnO_2[1]	$MnK\alpha$, cps[2] $(2\theta = 43.79°)$
0	0.1536	57.8
0.05	0.204	77.1
0.10	0.253	102.0
0.15	0.303	110.7
0.20	0.353	135.0
0.25	0.403	150.6
0.30	0.453	169.3

[1]0% value from equation 4; all others from column 1 and equation 1.
[2]Corrected for background of 14.7 cps $(2\theta = 47.0°)$, and to reference count of 28,200 cps on pure powdered MnO_2.

If C is the added concentration of MnO_2 (for convenience expressed as a fraction), if X_0 is the concentration in the original sample, and if X is the total concentration, X at any point equals C plus X_0 corrected for the change in base, or

$$X = C + X_0 (1 - C). \qquad (1)$$

X_0 may be evaluated from the plot of intensity vs. added concentration, which will take the form

$$N = n + s'C, \qquad (2)$$

where N is intensity in counts per second, n is the counts per second for the original sample, s' is slope of the graph, and C is the added concentration.

From Figure 2 and equation (2) when $N = 0$, $C = b$, and

$$b = - \frac{n}{s'} \qquad (3)$$

Correction of b to the X scale to give a value for X_0 may be done by substituting in equation (1) and substituting $X = 0$, $C = b$.
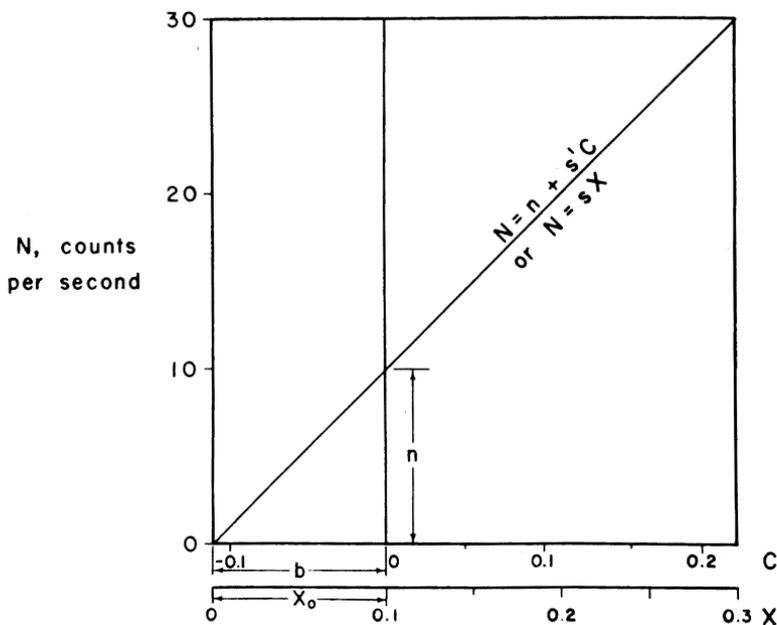
Figure 2.   Change of scale of abscissa from C, concentration added, to X, total concentration.

$$O = b + X_0 (1 - b)$$

$$X_0 = \frac{-b}{1 - b} = \frac{n}{n + s'} \tag{4}$$

Either b or s′ and n may be evaluated from a least squares fit of the data. Similarly the slope, s′, may be corrected to the X scale by equating the expressions for N and substituting for n from equation (3):

$$N = s'C + n = sX$$
$$s'C - bs' = sX$$
$$s = s' \ \frac{C - b}{X} \tag{5}$$

Combining equations (1) and (4),

$$X = C - \frac{b}{1 - b}(1 - C)$$
$$= C \frac{(1 - b) - b (1 - C)}{1 - b}$$
$$= \frac{C - b}{1 - b} \tag{6}$$

Substituting this value in equation (5),

$$s = s' (1 - b), \text{ or}$$
$$s = s' + n \tag{7}$$

In practice, s' and n may be obtained by the least squares method to allow calculation of s from equation (7). The concentration of MnO_2 in any sample is then

$$X = \frac{N}{s},$$

or expressed as a percentage,

$$P = 100\frac{N}{s}. \tag{8}$$

The resulting curve and equation for manganese are in Figure 3. Because of similarity of absorption factors the equation is expected to hold reasonably well for most calcareous loess soils. Intensities from leached samples should be somewhat higher due to the removal of calcium, which is a rather effective absorber for manganese $K\alpha$ (Table 1).
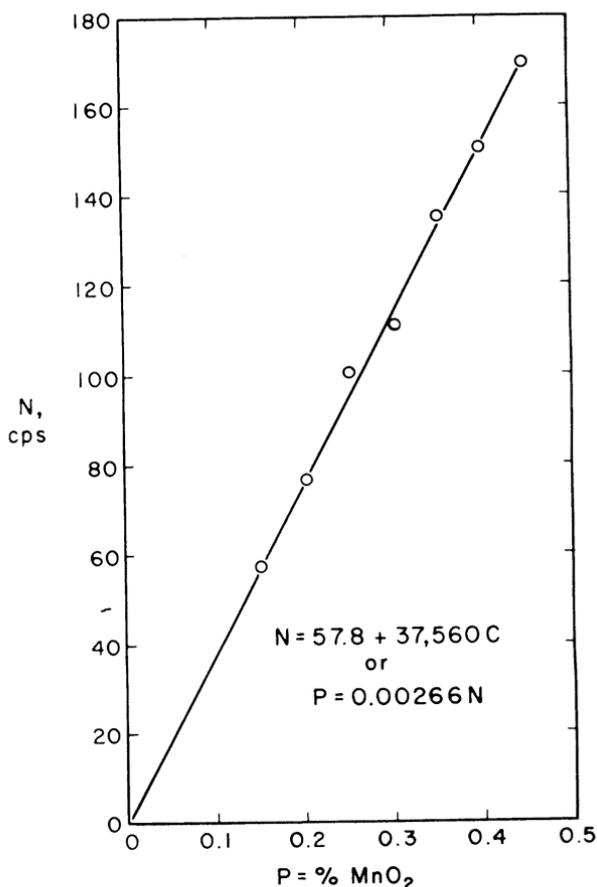

N = 57.8 + 37,560 C

or

P = 0.00266 N

Figure 3. Calibration curve for manganese $K\alpha$ radiation. Data from Table 2.

Iron

Calibration tests similar to those performed for manganese were run for iron with both Kα and Kβ radiations (Table 3 and Figure 4). Ordinarily determinations on unknowns would be by measurement of Kα, but Kβ may be used as a further check. Comparative chemical analysis and X-ray fluorescent data for two quite different loess samples are given in Table 4.

Table 3
Iron Calibration Data for a Friable Loess Soil

Percent added Fe$_2$O$_3$	Total percent Fe$_2$O$_3$[1]	FeKα, cps[2,3] ($2\theta = 40.18°$)	FeKβ, cps[2,4] ($2\theta = 36.30°$)
0	3.84	3,081	693
1.961	5.72	4,505	1,006
3.846	7.54	5,965	1,380
5.660	9.28	7,362	1,650
9.091	12.58	10,035	2,343
13.043	16.38	12,791	3,029

[1] 0% value from least squares fit of first four points and equation 4; all others from column 1 and equation 1.
[2] Corrected to FeKα count of 43,419 cps on pure powdered Fe$_2$O$_3$.
[3] Background counted at $2\theta = 43.0°$, varies from 19 to 27 cps.
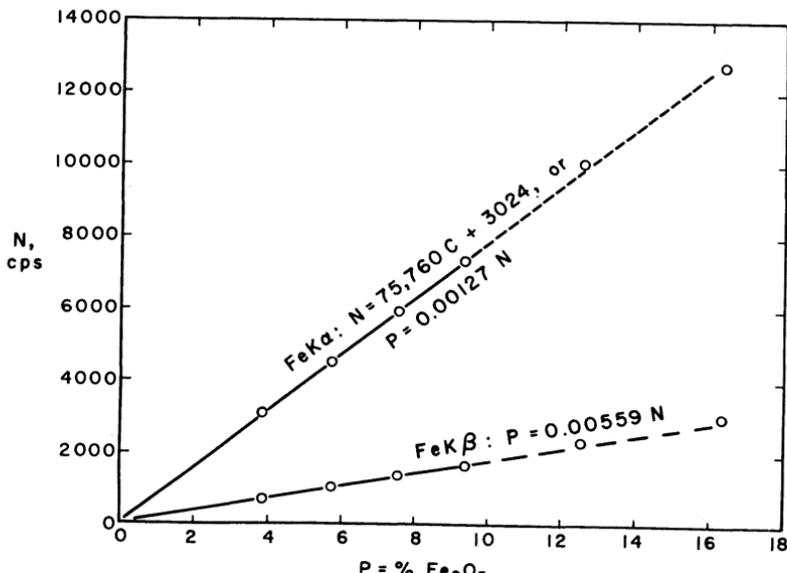[4] Background counted at $2\theta = 35.0°$, varies from 46 to 55 cps.

Figure 4.   Calibration curve for iron Kα and Kβ radiation. Data from Table 3. Curves are fit by least squares.

The equations of Figures 3 and 4 are expected to hold true for most loess samples, but it would be desirable to apply the fluorescent method to a wider range of samples without repeating the calibration curves. For this purpose a two-point method was devised. A sample is tested for an element, then a known amount of the element is

Table 4

Comparison of Iron Determinations on Two Loess Soils

Sample	FeKα cps[1]	Percent Fe_2O_3 (Fig. 3)	Percent Fe_2O_3 from chemical analysis
55-1 friable, calcareous loess	1924	2.44	2.70
43½-1; plastic, leached loess	3366	4.28	4.82

[1]Corrected for drift and background.

added to the sample, and the sample is retested. If a linear response is assumed, the two counting rates should be sufficient to establish the slope of the response curve and allow evaluation of the content of the element in the original sample. The upper limit of the linear response was not established for manganese, but for iron it is at about 10 percent to 14 percent Fe_2O_3 (Figure 4).

If X_0 is the concentration of the element in the original sample, C is the concentration added expressed on the basis of the whole sample, N_1 and N_2 are the corresponding count rates, and a linear response is assumed,

$$\frac{N_1}{N_2} = \frac{X_0}{X} \qquad (9)$$

Substituting for X from equation (1) and solving for X_0,

$$\frac{N_1}{N_2} = \frac{X_0}{C + X_0 (1 - C)}$$

$$X_0 = \frac{N_1 \, C}{N_2 - N_1 + N_1 \, C} \qquad (10)$$

Use of the Two-point Method

Several standard samples were selected to check the validity of the two-point method for determination of iron and manganese. Data are presented in Table 5.

Table 5
Iron and Manganese Contents By X-ray Fluorescent Two-point Method

Sample	Added Percent Fe_2O_3	$X_o =$ Percent Fe_2O_3	Reported Percent Fe_2O_3	Added Percent MnO_2	$X_o =$ Percent MnO_2	Reported Percent MnO_2
Nat. Bur. Std. No. 1a,[1] argillaceous limestone	1.511	1.659	1.63	0.385	0.071	0.038
Nat. Bur. Std. No. 56a,[1] phosphate rock				0.319	0.160	0.180
A.A.P.G. No. H-5,[2] kaolinite	0.62 3.95	0.327 0.320	1.00 1.00			
A.A.P.G. No. H-28,[2] montmorillonite	0.887 3.510	3.81 4.78	4.00 4.00			

[1]Published chemical analysis in National Bureau of Standards Circular C 398, Washington, 1946, pp. 18-19.
[2]Published chemical analysis in Analytical Data on Reference Clay Materials, American Petroleum Institute Project 49, New York, 1950, pp. 44-45.

The tests on an argillaceous limestone show close agreement between X-ray and chemical data for total iron, which is significant because absorption of iron $K\alpha$ by this sample is high. Manganese contents are not in close agreement, possibly due to the low content of manganese. At very low contents counting errors are magnified because of the low peak-to-background ratio, and closer results might be obtained by counting for longer times. The manganese data for the sample of phosphate rock show much closer agreement.

Two clays were analyzed for iron. One, a kaolinite, gave rather poor agreement between chemical and X-ray data, so the sample was re-run by the two-point method with a different content of added iron. The X-ray data from the two runs agree extremely well. The error may therefore be in sample differences or in chemical analysis, which may have been rounded off to one percent. Similarly, two runs were performed on a montmorillonite. They gave fairly good agreement, but difficulty was experienced in mixing, and this undoubtedly influenced X-ray results.

References

Because of the newness of application, the X-ray fluorescent method has been relatively little used for soils. Reading of a general nature plus a bibliography are in "Norelco Reporter", Vol. III, Nos. 2, 3, 4, 5, March-September, 1956.

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