

ESTIMATION OF IRON OXIDES IN SOIL CLAYS BY PROFILE REFINEMENT COMBINED WITH DIFFERENTIAL X-RAY DIFFRACTION

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ABSTRACT: A procedure is described for the quantitative estimation of hematite, goethite and lepidocrocite in soil clays by differential X-ray diffraction combined with profile refinement. The method has been applied to clays from 12 palaeosol horizons from south-east England. Samples containing as little as 1% dithionite-extractable iron can be analysed in this way. The hematite:goethite ratio is determined to within $\pm 3\%$ for soil clays having $\sim 2.5\%$ of each oxide and to within 10% in less favourable cases. The concentration of oxides in the soil determined solely from X-ray diffraction and from a combined chemical analysis/X-ray method are in good agreement. In addition to improving the accuracy and extending the range of iron-oxide concentrations over which analysis can be carried out, the method may, in principle, be used to provide information about the cell parameters and line profiles of each component present.

Iron oxides often form an important component of the inorganic fraction of soils (see e.g. Schwertmann & Taylor, 1977) and considerable effort has recently been devoted to the development of improved methods for their analysis. So far, the techniques used have mainly involved Mössbauer spectroscopy and X-ray diffraction, combined with chemical methods, although it has been suggested that Fourier-transform IR spectroscopy may also be of value (Fysh & Fredericks, 1983). Mössbauer spectroscopy would appear to have considerable advantages since the spectra are specific to the local environment of the Fe nuclei and thus both crystalline and amorphous components can be studied, without interference from the matrix. However, there are considerable difficulties in the correct interpretation of these Mössbauer spectra, arising from the effects of Al substitution in the structure and small particle size which produce reduced Zeeman splittings (Golden *et al.*, 1979). For example, it has been suggested (Bigham *et al.*, 1978) that spectra previously interpreted as showing the presence of akaganéite (β -FeOOH) could in fact be due to hematites or goethites that were either finely divided, chemically substituted, or both. Similar conclusions were reported by Goodman & Lewis (1981) and both sets of authors concluded that low-temperature measurements (preferably at 4 K) are essential if meaningful results are to be obtained.

Conventional X-ray diffraction is greatly hindered by the low concentrations and small particle sizes of the iron oxides in soils, which often produce broad peaks that are weak when compared to those from the clay mineral matrix. One possible solution to this problem is to concentrate the iron oxides by boiling the sample in 5 M NaOH (Norrish & Taylor, 1961; Kämpf & Schwertmann, 1982a) before estimating their proportions by X-rays (Kämpf & Schwertmann, 1982b). The severe chemical treatment required by this

concentration procedure can, however, lead to conversion of the iron oxides from one form to another and, in particular, to the destruction of lepidocrocite (Schwertmann & Taylor, 1972a,b; Kämpf & Schwertmann, 1982a). An alternative way to examine the oxides is the differential X-ray diffraction method developed by Schulze (1981). Diffraction patterns are collected before and after treatment of the clay-size fraction to remove the iron oxides, whose pattern can then be inferred from the difference pattern. Removal of the iron oxides can be achieved either by relatively mild chemical treatment such as the dithionite-citrate-bicarbonate method (Mehra & Jackson, 1960) or possibly by physical methods such as separation in high, non-uniform magnetic fields (Schulze & Dixon, 1979). The method as described by Schulze suffers from two disadvantages. First, the patterns to be subtracted may not be exactly matched in 2θ and thus spurious peaks can result in regions where the intensity is changing rapidly. Secondly, the pattern after treatment must be multiplied by an arbitrary scale factor before subtraction, chosen to give a subjectively estimated acceptable background in the difference pattern. This factor results from both the increase in the mass fraction of the clay minerals after removal of the iron oxides and the consequent change in the absorption coefficient of the sample. It will also reflect possible differences in preferred orientation of the clay mineral matrix between the treated and untreated samples. Bryant *et al.* (1983) proposed a modified version of the differential X-ray method in which $\alpha\text{-Al}_2\text{O}_3$ is used as an internal standard to facilitate the matching of the patterns in 2θ and scaling of intensities. Although in principle an improvement, this modification does have the disadvantages that the internal standard will not correct for differences in preferred orientation and cannot be removed from the sample. Also, inspection of the published difference patterns show a number of very sharp features which must be spurious. These probably arise from inadequate matching in 2θ and could prove troublesome when coincident with iron oxide peaks.

Neither Schulze (1981) nor Bryant *et al.* (1983) describe quantitative analyses using differential diffraction and the method of Kämpf & Schwertmann (1982b), which relies on dissolution of the clay minerals by NaOH, is limited to kaolinitic soils. If it can be assumed that crystalline iron oxides are quantitatively dissolved by dithionite treatment, the differential diffraction method could provide a basis for precise quantitative analysis, applicable to most soil clays regardless of their mineralogy. It is apparent, however, that a more rigorous analysis of the data is required. The approach used in the present work is similar to that of Rietveld (1969) for refining crystal structures from powder diffraction data, in which the calculated point-by-point profile of the diffraction pattern is fitted to the observations. Essentially our procedure is to fit, by least-squares, a calculated intensity profile to the observed profile of the untreated clay specimen. The calculated profile is obtained by adding together at every observed 2θ , the intensity, weighted in proportion to the amount present, from the treated clay (obtained experimentally) and from the iron oxide components (derived from the patterns of pure standards), together with a constant background term (arising from the increased Fe-K fluorescence in the untreated sample). When the patterns have broad and partially overlapping peaks a method of this type should produce better quantitative results than one based on integrated intensity measurements and also provides an estimate of their accuracy. Results obtained from 12 different soils indicate that the mass fractions of the different iron oxides present in the clay fraction can be determined even when the total amount of iron extractable by dithionite is less than 1%.

The immediate impetus for the present study came from our research on non-calcareous

brown soils in Britain and in particular on soils from south-east England formed during previous interglacials. The colours of these ancient buried horizons are thought to indicate weathering in warmer conditions and may depend on the amounts and types of iron oxides present. Study of the iron oxides is therefore helpful in the classification and ultimately in theories of the pedogenesis of these soils, which in turn can provide information about the climates of former times and the morphology of ancient land surfaces.

THEORY

Assuming an 'infinitely thick' flat specimen of a 'fine powder' (i.e. negligible absorption by individual particles), an approximation normally valid for dispersed clay minerals (Brindley, 1980), the total intensity diffracted at each point, i , in 2θ (I_i^{mix}) by a mixture of components (j) is given by

$$I_i^{mix} = \sum_j I_o Q_j^i S A_j \frac{g_j}{\rho_j} \left(\frac{\bar{\rho}}{\bar{\mu}} \right) \quad (1)$$

(International Tables, 1968 p. 195), where

- g_j = mass fraction of j th component
- ρ_j = density of j th component
- $(\bar{\mu}/\bar{\rho})$ = average mass attenuation coefficient of the mixture
- I_o = incident beam intensity
- S = incident beam area.

Q_j^i is a function dependent on the square of the structure factor of the j th component and $A_j = 1/2$ for Bragg-Brentano geometry. Full definitions of these quantities are given in International Tables, 1968, p. 195. Equation (1) may be rewritten more concisely as

$$I_i^{mix} = \sum_j B_j(2\theta) \frac{g_j}{\rho_j} \left(\frac{\bar{\rho}}{\bar{\mu}} \right) \quad (2)$$

The functions $B_j(2\theta)$ may be obtained in the following way. The term from the clay after extraction of the iron oxides cannot easily be calculated and is therefore obtained from the observed pattern. The terms from the iron oxides could, in principle, be calculated from the known structures. In practice, we have found it more convenient in the present work (see discussion) to obtain them from patterns collected from standards, whose peak widths are then adjusted to correspond to those in the soil clay (see below). Equation (2) may then be written in the form

$$\begin{aligned} I_i^{mix} &= \sum_j I_{ij}^{o'} g_j \left(\frac{\mu_j}{\rho_j} \right) \left(\frac{\bar{\rho}}{\bar{\mu}} \right) \\ &= \sum_i I_{ij}^{o'} a_j \end{aligned} \quad (3)$$

where (μ_j/ρ_j) is the mass attenuation coefficient of the j th component. $I_{ij}^{o'}$ is obtained from the observed pattern of each component, $I_j^o(2\theta)$, by addition of an origin shift in 2θ , Δ_j , followed by linear interpolation and, for the iron oxides, by broadening of the peaks.

The peak broadening function used is a Gaussian of unit area, $y(2\theta)$, defined by

$$y(2\theta) = \frac{2\sqrt{\ln 2}}{H_j \sqrt{\pi}} \exp\left(-\frac{4 \ln 2}{H_j^2} (2\theta)^2\right)$$

which is numerically convoluted with the iron oxide patterns after their backgrounds have been subtracted by linear interpolation. The halfwidth parameter of the Gaussian, H_j , was usually assumed to be the same for all the oxides although some refinements were also carried out in which it was allowed to take different values for each one. In the present work, in which a diffracted beam monochromator was not used, an additional term, constant with respect to 2θ , must also be introduced to allow for the diminished background (mainly Fe-K fluorescent radiation) produced by the sample after removal of the iron oxides.

The parameters a_p , Δ_j and H_j are obtained by minimization of the function

$$\sum_i w_i (I_i^{mix} - \sum_j I_{ij}^o a_j)^2$$

with the weights, w_p , set equal to unity. Minimization was carried out using the non-linear least-squares routines available in the NAG FORTRAN LIBRARY (Numerical Algorithms Group, 1983), the necessary derivatives being calculated numerically.

Derivation of the mass fractions, g_p , from the parameters refined, a_p , requires a knowledge of mass attenuation coefficients. Determination of the *ratios* of the mass fractions of the iron oxides requires only a knowledge of the attenuation coefficients of the oxides themselves, which can be calculated from their known compositions. If the *absolute amounts* of oxides in the sample are required, then it is necessary

(i) to know the attenuation coefficients of either the treated or untreated clay samples and to assume $\sum g_j = 1$;

or preferably

(ii) to obtain the attenuation coefficients of both the treated and untreated clay samples, in which case no assumption about $\sum g_j$ need be made. The attenuation coefficients of the clays may be either calculated from their determined chemical composition or measured directly. If only crude totals are required an adequate estimate could probably be made from the known values for pure clay minerals.

EXPERIMENTAL DETAILS

Chemical treatment and analysis

The soil samples were shaken with 'Calgon' overnight in an end-to-end shaker and sieved to remove material $>63 \mu\text{m}$ in size. The $<2 \mu\text{m}$ fraction of the soil was then obtained by sedimentation, flocculated with MgCl_2 and centrifuged. It was washed to remove excess Mg and freeze dried. Removal of the iron oxides was carried out by the sodium dithionite-citrate-carbonate method (Mehra & Jackson, 1960). The 'untreated' sample was treated in the same way with the sodium citrate-bicarbonate buffer, omitting the sodium dithionite. Treated and untreated specimens were saturated with magnesium. Elemental analysis of the samples before and after extraction (for Na, Mg, Al, Si, P, K,

Ca, Ti, Mn and Fe) was carried out by Inductively Coupled Plasma Atomic Emission Spectroscopy. A second set of samples (not used in the X-ray work) were extracted with ammonium oxalate as described by McKeague & Day (1965) and the amount of iron extracted determined colorimetrically using the method given by Avery & Bascomb (1974, p. 37).

X-ray diffraction

Any difference in preferred orientation between the treated and untreated samples will lead to spurious features in the difference pattern and considerable care was therefore taken in preparing the specimens. The samples, which had been given as nearly identical chemical treatment as possible, were crushed by hand using an agate mortar and pestle and were drifted down a roughened surface inclined at about 60° to the horizontal into an X-ray specimen holder sandwiched between two glass plates. One plate was permanently attached to the holder. The other, removable, plate had a roughened surface made by painting Durofix adhesive on to the glass through a square nylon mesh having about 30 threads/cm. This roughening extended to just above the final fill level of the powder. The samples were consolidated by shaking gently (not tapping) the specimen holder for about six seconds and the upper glass plate was then removed carefully, avoiding smearing, to leave a fairly smooth surface. The density of the powders was about 0.66 g cm^{-3} corresponding to a packing density of approximately 25%. The specimens were approximately $20 \times 15 \times 1.6 \text{ mm}$ in size, their thickness being such that they could be assumed infinitely thick.

Intensities were measured with a Philips vertical powder diffractometer and Fe-filtered Co- $K\alpha$ radiation (fine-focus tube operated at 34 kV, 32 mA for the clay samples and 34 kV, 12 mA for the iron oxide standards). A 2° divergence slit was used with anti-scatter and receiving slits 1.15 mm and 0.6 mm wide respectively. Soller slits were used in the incident beam but not in the diffracted beam. For materials which have intrinsically broad reflections, these conditions will produce a large gain in diffracted intensity at a small cost in resolution (Brown, 1980). Measurements were made over the range $36\text{--}52^\circ$ in 2θ (2.897 \AA to 2.042 \AA in d -spacing) in step-scanned mode, counting for 20 s at each point. Steps of 0.05° in 2θ were used except at the ends of the scan range ($36\text{--}37^\circ$ and $50\text{--}52^\circ$), where 0.1° steps were used. The observed counts were corrected for dead-time (Klug & Alexander, 1974, p. 335) for a measured effective resolving time of $4.2 \mu\text{s}$, the maximum correction being approximately 6%.

RESULTS AND DISCUSSION

To provide a simple test of the method some initial analyses were made of mixtures of the synthetic iron oxide standards. Table 1 lists the results obtained together with the measured cell parameters of the oxides and the values assumed for their mass attenuation coefficients. The cell parameters were obtained from diffraction patterns (Co- $K\alpha$, $\lambda = 1.79026 \text{ \AA}$) of iron oxide-NaCl mixtures, the NaCl pattern having been previously calibrated against an internal standard of finely ground silicon (International Union of Crystallography standard material). The lattice constants of hematite and lepidocrocite are in good agreement with those previously reported (Schwertmann *et al.*, 1979; Brown, 1980), whilst those of goethite suggest a composition of about $\text{Fe}_{0.9}\text{Al}_{0.1}\text{O}\cdot\text{OH}$ (Fey &

TABLE 1. Analysis of synthetic iron oxide standards.

(a) Parameters of iron oxide standards				
Space group	Hematite ⁽ⁱ⁾ <i>R</i> $\bar{3}$ <i>c</i>	Goethite ⁽ⁱⁱ⁾ <i>Pbnm</i>	Lepidocrocite ⁽ⁱⁱⁱ⁾ <i>Cmcm</i>	
<i>a</i> (Å)	5.0396 (6)	4.606 (2)	3.070 (2)	
<i>b</i> (Å)	—	9.893 (1)	12.537 (9)	
<i>c</i> (Å)	13.753 (4)	3.005 (1)	3.873 (1)	
Mass attenuation coefficient (μ/ρ) for Co-K α (cm ² g ⁻¹)	44.6	41.6 (pure) 41.9 (10% Al-substituted)	41.6	
(b) Analysis of mixtures				
	Hematite	Goethite	Lepidocrocite	Profile <i>R</i> -factor ^(iv) (%)
A	0.25	0.75	—	0.4
B	0.262 (1)	0.738 (1)	—	
A	0.50	0.50	—	0.5
B	0.524 (1)	0.476 (1)	—	
A	0.75	0.25	—	0.7
B	0.750 (1)	0.250 (1)	—	
A	0.258	0.478	0.264	0.5
B	0.260 (1)	0.473 (1)	0.267 (1)	

A—Nominal mass fraction of mixture.

B—Mass fraction determined by X-rays.

(i) Synthetic hematite (from Al-free synthetic goethite by heating at 400°C for one hour). Cell parameters by least squares from 104, 110, 113 reflections.

(ii) Synthetic aluminous goethite (prepared by Dr M. Pyrah by hydrolysis of mixed Fe/Al nitrate solutions with excess NaOH and aged at 40°C for 200 h). Cell parameters by least-squares from 130, 021, 111 and 140 reflections.

(iii) Synthetic lepidocrocite (prepared by Dr Z. Karim by neutralization of FeCl₂ with NaOH under N₂ followed by oxidation by air). Cell parameters by least-squares from 130, 111, 022 and 151 reflections.

$$(iv) R\text{-factor} = \Sigma \frac{|I_{\text{obs}} - I_{\text{calc}}|}{\Sigma I_{\text{obs}}} \times 100$$

Dixon, 1981; Schulze, 1984). The mass fractions determined by X-rays are in error by up to 0.024, which, although quite acceptable for analytical purposes, is far outside the range of statistical error. The reason for this is not clear, especially as very close agreement was obtained for two of the four samples examined and the profile *R*-factors for all four are similar. The difference between the true mass attenuation coefficients and those calculated from the structural formulae are unlikely to be sufficiently large to account for the disagreement and the most likely source of the error is that the mixtures were not weighed accurately enough nor sufficiently mixed to be truly homogenous on the scale required by the X-rays. Although of no significance in terms of the soil-clay analyses this discrepancy does suggest that systematic errors are likely to be significant and that caution should be exercised in the interpretation of the probable errors quoted.

Fig. 1a illustrates the analysis of a soil clay containing approximately 7% extractable iron (sample 86c). The measurements from the untreated sample are shown as points and the calculated pattern as a continuous line. The four components used in the

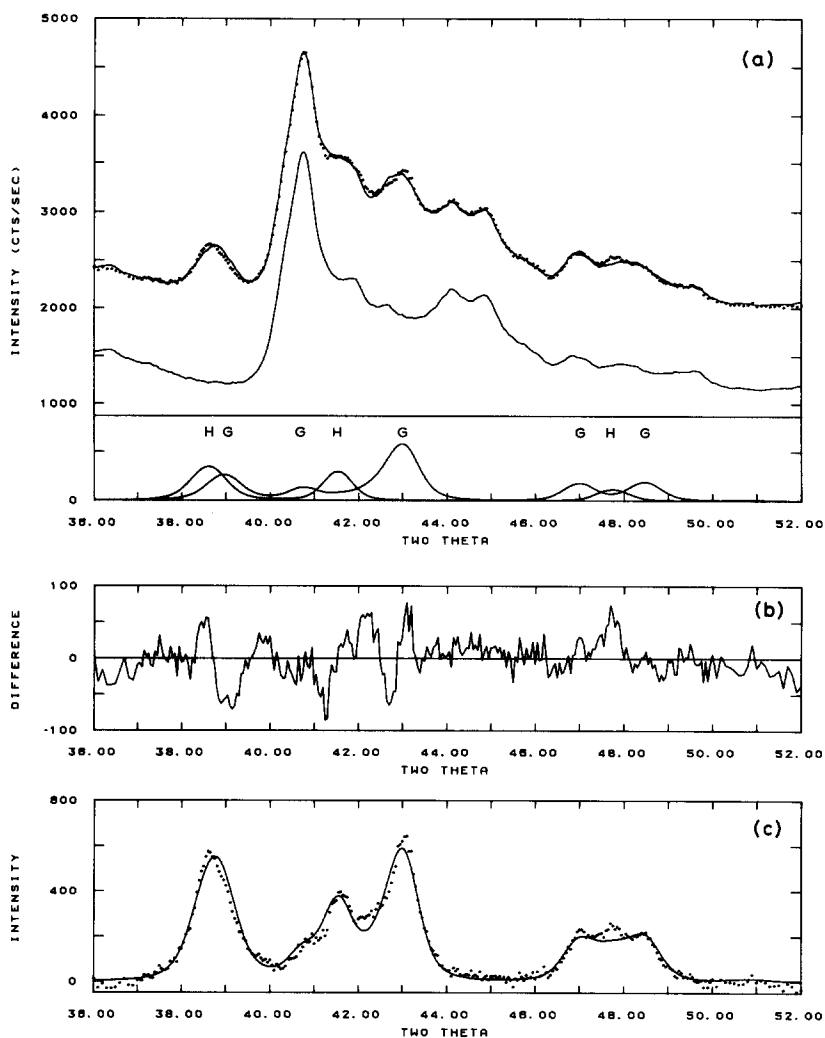


FIG. 1. (a) Profile refinement of a soil clay containing ~7% dithionite-extractable Fe (sample 86c). The observed pattern from the untreated clay is shown as points and the calculated pattern as a smooth line. The four individual components of the calculation—'clay' (dithionite-treated sample), hematite, goethite and fluorescence term (horizontal line) are also shown. The principal hematite and goethite peaks are marked with the letters H and G respectively. (b) Final difference ($I_{obs} - I_{calc}$) at a magnification $\times 7.5$. (c) Observed (points) and calculated pattern of iron oxide components obtained by subtraction of the clay and fluorescence terms.

calculation—treated clay, hematite, goethite and fluorescence term (no lepidocrocite was detected in this sample)—are also shown. Fig. 1b gives the final difference pattern ($I_{obs} - I_{calc}$) with vertical scale magnified $7.5\times$ and Fig. 1c the observed and calculated patterns of the iron oxides. It can be seen that the observed and calculated patterns agree well, although some features are observable in the difference pattern around the positions of the iron oxide peaks. This point will be discussed further below.

Table 2 lists the results obtained from 12 palaeosol horizons from south-east England.

TABLE 2. Results of analyses of 12 palaeosol horizons from south-east England.

Sample ⁽ⁱ⁾	Extractable iron ⁽ⁱⁱ⁾		Ratios by mass ⁽ⁱⁱⁱ⁾		Percentage by mass ^(iv) assuming (Fe _d - Fe _o)				Percentage by mass ^(v) from X-rays alone				Profile R-factor %	
	Fe _d	Fe _o	Hematite	Goethite : Lepidocrocite	'Clay'	Hematite	Goethite	Lepidocrocite	'Clay'	Hematite	Goethite	Lepidocrocite		%
9	13.30 (22)	0.53	4.4 (4)	: 95.6 (4)	—	79.8 (4)	0.90 (8)	19.3 (3)	—	76.4 (2)	1.0 (1)	22.5 (2)	—	1.1
23	20.83 (27)	1.46	3.7 (4)	: 96.3 (4)	—	69.3 (5)	1.1 (1)	29.6 (4)	—	70.2 (3)	1.1 (1)	28.7 (3)	—	1.5
42a	5.93 (13)	0.34	14.3 (5)	: 85.7 (5)	—	91.2 (2)	1.25 (5)	7.5 (2)	—	91.2 (1)	1.25 (5)	7.5 (1)	—	0.8
42b			13.5 (5)	: 86.5 (5)	—	91.2 (2)	1.18 (5)	7.6 (2)	—	90.3 (1)	1.31 (6)	8.4 (1)	—	0.9
48 ^(vi)	0.80 (12)	0.19	11.5 (2.5)	: 88.5 (2.5)	—	99.0 (2)	0.11 (3)	0.9 (2)	—	98.0 (1)	0.22 (5)	1.7 (1)	—	0.9
49a	7.53 (13)	1.19	37.9 (7)	: 48.9 (8)	: 13.3 (6)	90.3 (2)	3.7 (1)	4.7 (1)	1.28 (9)	90.0 (2)	3.77 (7)	4.9 (1)	1.32 (9)	0.8
49b			38.1 (6)	: 46.0 (7)	: 15.8 (5)	90.3 (2)	3.7 (1)	4.5 (1)	1.53 (8)	88.9 (2)	4.23 (7)	5.1 (1)	1.76 (8)	0.8
86a	6.95 (15)	1.05	27.4 (6)	: 72.6 (6)	—	90.9 (2)	2.49 (8)	6.6 (2)	—	90.3 (1)	2.66 (6)	7.1 (1)	—	0.8
86b			26.3 (6)	: 73.7 (6)	—	90.9 (2)	2.39 (8)	6.7 (2)	—	88.8 (2)	2.94 (7)	8.3 (1)	—	0.9
86c			27.6 (5)	: 72.4 (5)	—	90.9 (2)	2.51 (8)	6.6 (2)	—	90.5 (1)	2.61 (6)	6.9 (1)	—	0.8
89a	5.69 (13)	0.84	18.4 (4)	: 81.6 (4)	—	92.4 (2)	1.39 (5)	6.2 (2)	—	92.18 (8)	1.44 (4)	6.38 (8)	—	0.7
89b			17.2 (5)	: 82.8 (5)	—	92.4 (2)	1.30 (5)	6.3 (2)	—	92.2 (1)	1.34 (4)	6.45 (9)	—	0.8
117a	3.88 (13)	0.33	36.5 (9)	: 63.5 (9)	—	94.6 (2)	1.98 (9)	3.4 (1)	—	94.6 (1)	1.97 (5)	3.43 (9)	—	0.8
117b			37.9 (7)	: 62.1 (7)	—	94.6 (2)	2.05 (8)	3.4 (1)	—	93.5 (1)	2.45 (5)	4.03 (9)	—	0.7
117c			38.8 (7)	: 61.2 (7)	—	94.6 (2)	2.09 (9)	3.3 (1)	—	94.77 (8)	2.03 (4)	3.20 (7)	—	0.7
120a	2.29 (13)	0.09	13.8 (7)	: 86.2 (7)	—	96.6 (2)	0.47 (4)	3.0 (2)	—	96.81 (6)	0.44 (2)	2.76 (5)	—	0.5
120b			12.8 (8)	: 87.2 (8)	—	96.6 (2)	0.44 (4)	3.0 (2)	—	95.60 (9)	0.55 (4)	3.84 (8)	—	0.6
120c			10.5 (8)	: 89.5 (8)	—	96.5 (2)	0.36 (3)	3.1 (2)	—	95.96 (8)	0.42 (3)	3.62 (8)	—	0.6
130	17.49 (22)	0.78	3.6 (3)	: 77.6 (5)	: 18.8 (4)	73.5 (3)	0.96 (9)	20.6 (3)	5.0 (1)	68.1 (3)	1.2 (1)	24.7 (2)	6.0 (2)	1.1
167	5.98 (14)	0.97	8.1 (6)	: 91.9 (6)	—	92.1 (2)	0.64 (5)	7.3 (2)	—	90.7 (1)	0.75 (5)	8.6 (1)	—	0.8
184	9.63 (18)	1.28	7.3 (5)	: 79.5 (10)	: 13.1 (8)	86.8 (3)	0.97 (7)	10.5 (3)	1.7 (1)	84.9 (3)	1.11 (8)	12.0 (2)	2.0 (2)	0.9

(i) Samples 9 and 23; Valley Farm Soil from Ipswich Airport, Suffolk (Kemp, 1984b). Samples 42, 48, 49, 86, 89; Valley Farm Soil from Stebbing, Essex (Kemp, 1984a). Samples 117, 120; Valley Farm Soil from Great Blakenham, Suffolk (Kemp, 1984a). Sample 167; Paleo-argillic horizon from Hornchurch, Essex (Kemp, 1984a). Sample 184; Paleo-argillic horizon from Clapton Common, NE London (Kemp, 1984b).

(ii) Fe_d: dithionite-extractable iron (difference in total iron content, determined by ICPAES, of the untreated and dithionite-treated samples). Fe_o: oxalate-extractable iron (determined colorimetrically).

(iii) Ratios by mass determined by X-rays with estimated standard deviations in parentheses (the number shown refers to the least significant figure). The numbers are normalized so that their sum = 100.

(iv) Calculated assuming ratios by mass (iii) and chemical analyses (ii) and normalizing to 100%. Estimated standard deviations in parentheses (the number shown refers to the least significant figure).

(v) Calculated solely from X-ray results assuming $\Sigma g_j = 1.0$ and calculating mass attenuation coefficients from the elemental analyses. Estimated standard deviations in parentheses (the number shown refers to the least significant figure).

(vi) Halfwidth parameter not refineable. Value fixed at 0.7° (see text).

For six of the samples replicate X-ray specimens were prepared, and the results from these are also given, with the distinguishing letter 'a', 'b', etc. The table lists the percentage by mass of dithionite-(Fe_d) and oxalate-(Fe_o) extractable iron (determined chemically) followed by the ratios by mass of the different iron oxides present (determined by X-rays). The amount of oxalate-extractable iron, generally assumed to give a measure of the non-crystalline components present, is small in all the samples examined. The total amounts of iron oxides are then calculated in two ways:

- (i) by apportioning the amount of extractable iron from crystalline components ($\text{Fe}_d - \text{Fe}_o$) in the ratio determined by X-rays;
- (ii) solely from the X-ray experiment (using mass attenuation coefficients calculated from the chemical analyses).

In both cases the totals are normalized to 100% and the term 'clay' is taken to encompass all components except crystalline iron oxides. It can be seen that very good agreement is obtained both between the replicate specimens and between the combined chemical and X-ray method and that using X-rays alone. In particular, the results for the replicates using chemical knowledge are all consistent with their statistically determined standard deviations. Perhaps not surprisingly, if X-rays alone are used systematic errors appear to be of greater importance and in some cases differences outside the statistical range occur.

Probably the largest potential source of systematic error in this type of experiment is differences in the preferred orientation of the crystallites in the sample before and after chemical treatment. In this respect the agreement between replicate samples is very encouraging, especially as the different sets of data were collected over a period of two months and it is unlikely that reproducible artifacts could be prepared consistently over such a long period. In the present work we found little evidence for any dissolution of the layer-silicates by the dithionite treatment as mentioned by Bryant *et al.* (1983). It can be seen from Fig. 1 that in regions of the pattern where the iron oxide contribution is small (e.g. $40-41^\circ$ and $44-46^\circ$) an especially good fit is obtained.

The second major source of error arises from defects in the calculation of the diffraction patterns of the iron oxides. The present simple calculation is adequate for the purpose of quantitative analysis but will be valid for only a limited range of Bragg angle. It does, however, have the advantage of requiring, at most, two parameters (zero shift and broadening term) for each oxide. The cell parameters of the iron oxides in the soil clay, particularly those of goethite, will vary with the degree of aluminium substitution (hence it is preferable to use an aluminous goethite as the standard). Since only Bragg angles between 18 and 26° are considered, a simple alteration of the zero point of the iron oxide pattern is sufficient to accommodate this effect for the present purpose of quantitative analysis. If accurate cell parameters of the soil clay material are required or if the range of Bragg angle is increased, the refinement model could be extended to include, for example, a term describing the degree of aluminium substitution. Aluminium substitution can also strongly affect the line profiles (Schwertmann *et al.*, 1977). The results shown in Table 2 were obtained using a single broadening parameter, but refinements were also carried out for some samples using separate halfwidth parameters for each oxide. For the two-component mixtures (hematite and goethite) this resulted in almost identical mass percentages to those listed in Table 2, the differences between the two refinements being similar to that between the replicate specimens. For the soils containing lepidocrocite (samples 49, 130 and 184) it was found that changes in halfwidth did not seriously affect

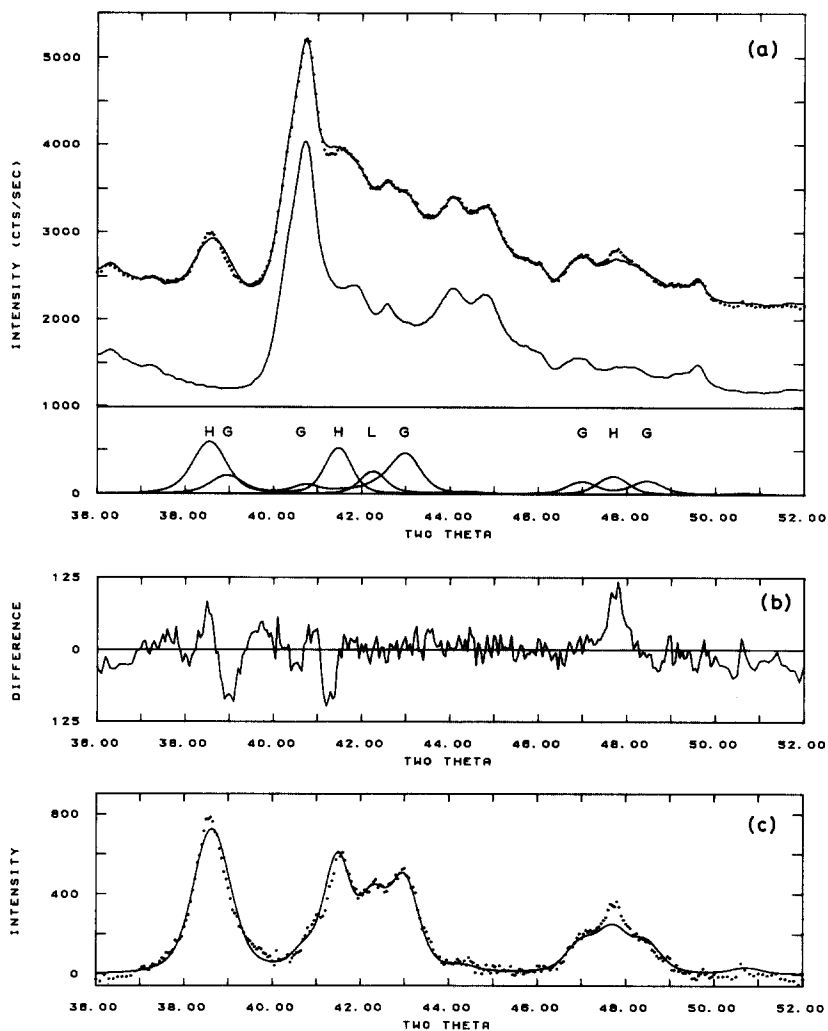


FIG. 2. (a) Refinement of a soil clay containing hematite, goethite and lepidocrocite (sample 49b: total dithionite-extractable Fe \sim 7.5%). Note that only one lepidocrocite peak (L) of appreciable intensity occurs in the 2θ range considered and that a slight improvement in fit could be obtained by sharpening the hematite peaks relative to those of goethite (see text). (b) Final difference ($I_{\text{obs}} - I_{\text{calc}}$). Magnification $\times 6.6$. (c) Observed and calculated pattern of iron oxide components.

the amount of hematite or of (goethite + lepidocrocite) but that the relative amounts of goethite and lepidocrocite were sensitive to the model used. The reason for this can be seen from Fig. 2, which shows the results of the refinement (parameters as listed in Table 2) of sample 49b. The 2θ -range used, chosen primarily for the analysis of hematite and goethite, contains only one lepidocrocite peak (at $2\theta \approx 42.2^\circ$) of significant intensity and this peak itself is seriously overlapped by a strong goethite reflection. Attempts to refine a halfwidth and zero-point shift for lepidocrocite are therefore unlikely to be successful unless the data are of very high quality. The problem, however, should be readily solved by extending the scan range to 55° (2θ) so as to include additional lepidocrocite reflections.

Having discussed the limitations of the technique it is appropriate to conclude by stressing its advantages. Firstly, we have shown, at least for the limited range of Bragg angle considered, that differences in preferred orientation between treated and untreated samples can be virtually eliminated by careful specimen preparation. Even in conventional powder diffraction, preferred orientation is often troublesome with Bragg-Brentano parafocusing diffractometers; in differential diffraction experiments differences in orientation between treated and untreated samples must be minimized and ideally eliminated. Secondly, we have shown that profile refinement techniques similar to the Rietveld method for conventional powder diffraction (Rietveld, 1969) can be combined with differential diffraction methods. This approach is particularly suitable for the analysis of patterns with broad and partially overlapped reflections. By using the minimum number of parameters possible to describe each iron oxide component, stable refinements have been achieved for samples containing as little as 2% extractable iron. For example, Fig. 3 shows the observed and calculated iron oxide patterns of a sample (120b) containing only 2.3% dithionite-extractable iron. It can be seen that a very good fit to the data has been obtained. It has even been possible to analyse samples with smaller extractable iron concentrations (sample 48), although in this case the halfwidth parameter could not be refined (refinements with a range of halfwidth parameters led to similar values for the oxide concentrations). Very good agreement has been obtained between the total amounts of iron oxides in the soil sample determined using chemical methods and by X-rays alone. This is most encouraging as it suggests that the results are free from systematic error. A further check is provided by evaluating the sum of the component concentrations determined by X-rays without normalization to 100%. The present data were collected using an X-ray source whose output declined considerably over the set of experiments and so there was some uncertainty in the relative scales of the soils and iron oxide standards. However, for the data sets that were collected immediately before the standards (e.g. samples 89a and 86c) and which could therefore be considered as reliably scaled, totals

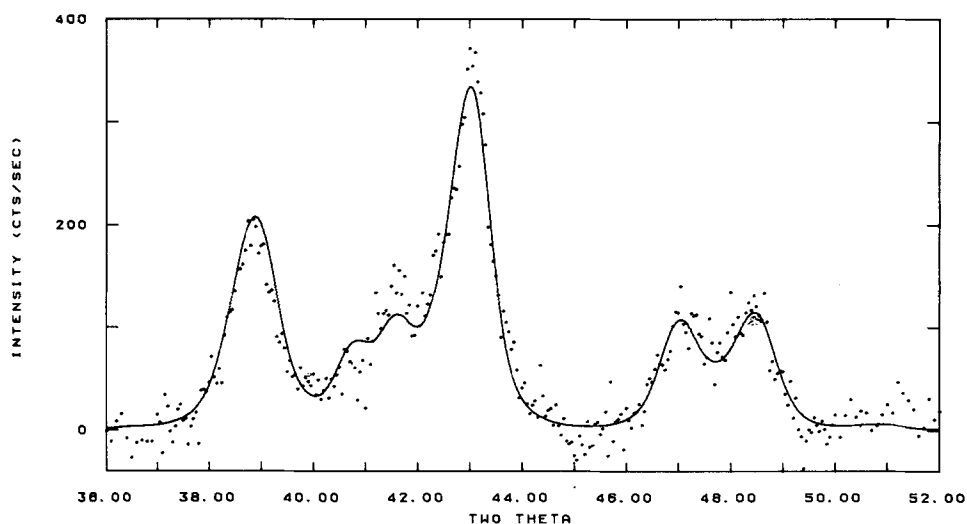


FIG. 3. Observed and calculated pattern of iron oxide components for a sample (120b) containing 2.3% dithionite-extractable iron.

very close to 100% were obtained (100.7(3) and 99.4(3) respectively). Thus it is apparent that the profile refinement method can provide information not only about the relative amounts of iron oxides present but also about their absolute amounts. This may be of value, for example, in assessing the proportions of 'crystalline' and 'non-crystalline' components extracted by different chemical treatments.

In future work it is hoped to extend the analysis to determine accurately the cell parameters and average particle size and shape of each of the oxide components as well as to include, if required, phases such as magnetite and maghemite. The crystallinity of iron oxides may itself be an important variable in pedogenic studies (Kühnel *et al.*, 1975) and in studies of sorption of ions such as phosphorus on soil particle surfaces (Jones, 1981). The present work using the range of *d*-spacings between 2.9 Å and 2.04 Å provides a method suitable for the quantitative estimation of hematite and goethite and which can also provide some information (though less reliably) about the amount of lepidocrocite present. Although ideally it requires an automatic diffractometer and computer analysis of the data, useful information can be obtained with more modest resources. The two data sets required for each sample can be collected manually in about 5 h. If only an approximate analysis is required, we have found that for samples containing more than about 5% extractable iron it is possible to estimate the relative amounts of hematite and goethite visually to within about $\pm 10\%$ by comparing the region of the patterns from 46° to $48^\circ 2\theta$ (Co-K α) of the treated and untreated samples with a set of calibration patterns collected from mixtures of the hematite and goethite standards.

The present study has been concerned solely with analyses of soil clays but it should be pointed out that differential diffraction methods, which are not widely used in crystallography, would appear to offer considerable potential for increasing the sensitivity of analyses of multi-component mixtures in which some of the components are selectively extractable. Alternatively, if no suitable extractant can be found, it may be possible in certain cases to exploit the anomalous scattering of atoms such as iron so as to produce difference patterns from data collected at different wavelengths.

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REFERENCES

- AVERY B.W. & BASCOMB C.L. (1974) *Soil Survey Laboratory Methods*. Soil Survey Technical Monograph No. 6, Harpenden.
- BIGHAM J.M., GOLDEN D.C., BOWEN L.H., BUOL S.W. & WEED S.B. (1978) Iron oxide mineralogy of well-drained Ultisols and Oxisols: I. Characterisation of iron oxides in soil clays by Mössbauer spectroscopy, X-ray diffractometry, and selected chemical techniques. *Soil Sci. Soc. Am. J.* **42**, 816–825.
- BRINDLEY G.W. (1980) In: *Crystal Structures of Clay Minerals and their X-ray Identification* (G. W. Brindley & G. Brown editors). Mineralogical Society, London.
- BROWN G. (1980) In: *Crystal Structures of Clay Minerals and their X-ray Identification* (G. W. Brindley & G. Brown, editors). Mineralogical Society, London.
- BRYANT R.B., CURI N., ROTH C.B. & FRANZMEIER D.P. (1983) Use of an internal standard with differential X-ray diffraction analysis for iron oxides. *Soil Sci. Soc. Am. J.* **47**, 168–173.

- FEY M.V. & DIXON J.B. (1981) Synthesis and properties of poorly crystalline hydrated aluminous goethites. *Clays Clay Miner.* **29**, 91–100.
- FYSH S.A. & FREDERICKS P.M. (1983) Fourier transform infrared studies of aluminous goethites and hematites. *Clays Clay Miner.* **31**, 377–382.
- GOLDEN D.C., BOWEN L.H., WEED S.B. & BIGHAM J.M. (1979) Mössbauer studies of synthetic and soil-occurring aluminium-substituted goethites. *Soil Sci. Soc. Am. J.* **43**, 802–808.
- GOODMAN B.A. & LEWIS D.G. (1981) Mössbauer spectra of aluminous goethites (α -FeOOH). *J. Soil Sci.* **32**, 351–363.
- INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY (1968) Vol. III Physical and Chemical Tables. Kynoch Press, Birmingham, England.
- JONES R.C. (1981) X-ray diffraction line profile analysis vs. phosphorus sorption by 11 Puerto Rican soils. *Soil. Sci. Soc. Am. J.* **45**, 818–825.
- KÄMPF N. & SCHWERTMANN U. (1982a) The 5-M-NaOH concentration treatment for iron oxides in soils. *Clays Clay Miner.* **30**, 401–408.
- KÄMPF N. & SCHWERTMANN U. (1982b) Quantitative determination of goethite and hematite in kaolinitic soils by X-ray diffraction. *Clay Miner.* **17**, 359–363.
- KEMP R. (1984a) The Valley Farm soil in southern East Anglia. In: *Quaternary Soils and Landforms* (J. Boardman, editor). J. Wiley and Sons, Chichester, Sussex, U.K.
- KEMP R. (1984b) *Quaternary soils in southern East Anglia and Lower Thames Basin*. PhD Thesis, Univ. of London.
- KLUG H.P. & ALEXANDER L.E. (1974) *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. Wiley, New York.
- KÜHNEL R.A., ROORDA H.J. & STEENSMAN J.J. (1975) The crystallinity of minerals—A new variable in pedogenic processes: A study of goethite and associated silicates in laterites. *Clays Clay Miner.* **23**, 349–354.
- MCKEAGUE J.A. & DAY J.H. (1966) Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* **46**, 13–22.
- MEHRA O.P. & JACKSON M.L. (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* **7**, 317–327.
- NUMERICAL ALGORITHMS GROUP (1983) NAG FORTRAN Library Manual—Mark 10. Numerical Algorithms Group, Mayfield House, 256 Banbury Road, Oxford, England.
- NORRISH K. & TAYLOR R.M. (1961) The isomorphous replacement of iron by aluminium in soil goethites. *J. Soil Sci.* **12**, 294–306.
- RIETVELD H.M. (1969) A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst.* **2**, 65–71.
- SCHULZE D.G. (1981) Identification of soil iron oxide minerals by differential X-ray diffraction. *Soil Sci. Soc. Am. J.* **45**, 437–440.
- SCHULZE D.G. (1984) The influence of aluminium on iron oxides. VIII Unit-cell dimensions of Al-substituted goethites and estimation of Al from them. *Clays Clay Miner.* **32**, 36–44.
- SCHULZE D.G. & DIXON J.B. (1979) High gradient magnetic separation of iron oxides and other magnetic minerals from soil clays. *Soil Sci. Soc. Am. J.* **43**, 793–799.
- SCHWERTMANN U., FITZPATRICK R.W. & LE ROUX J. (1977) Al substitution and differential disorder in soil hematites. *Clays Clay Miner.* **25**, 373–374.
- SCHWERTMANN U., FITZPATRICK R.W., TAYLOR R.M. & LEWIS D.G. (1979) The influence of aluminium on iron oxides. Part II. Preparation and properties of Al-substituted hematites. *Clays Clay Miner.* **27**, 105–112.
- SCHWERTMANN U. & TAYLOR R.M. (1972a) The transformation of lepidocrocite to goethite. *Clays Clay Miner.* **20**, 151–158.
- SCHWERTMANN U. & TAYLOR R.M. (1972b) The influence of silicate on the transformation of lepidocrocite to goethite. *Clays Clay Miner.* **20**, 159–164.
- SCHWERTMANN U. & TAYLOR R.M. (1977) Iron oxides. Pp. 145–180 in: *Minerals in Soil Environments* (J. B. Dixon, S. B. Weed, J. A. Kittrick, M. H. Milford and J. L. White, editors). Soil Science Society of America, Madison, Wisconsin USA.