

Use of the Kubelka–Munk theory to study the influence of iron oxides on soil colour

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SUMMARY

The Kubelka–Munk theory, which is commonly applied to 'pigment mixtures', adequately predicted the colour of mixtures of synthetic haematite, synthetic goethite and deferrated soil powders. The theory illustrated the higher pigmentation effect of haematite compared with goethite. In mixtures containing haematite the calculated colour coordinates could be combined into simple 'redness' indices that were highly correlated with haematite content and were not appreciably influenced by goethite.

The theory was also applied to the study of the chromatic characteristics of 98 soils, differing widely in their origin but having an organic matter content <2% in which haematite or goethite was the dominant Fe oxide. The theory showed that the average 'soil' haematite and 'soil' goethite had colours similar to those of their synthetic counterparts, whereas the rest of the soil components could be considered as an essentially 'grey' matrix. It was also useful in predicting the haematite and goethite contents of soils either from several reflectance measurements of soil-white standard mixtures or from the indices of redness developed for the synthetic mixtures.

INTRODUCTION

Soils are mixtures of particles of mineral and organic compounds which interact with incident light and are usually neither completely transparent nor completely opaque: the particles partly absorb and partly scatter the incident light. This type of mixture has been called 'pigment mixture' (Duncan, 1949) and its properties can be studied by the theory of Kubelka & Munk (1931). This theory has been applied successfully to ceramic materials (Hogg & Noble, 1979) and kaolins used in paper filling (Jepson, 1985); that is, mixtures containing common soil minerals. However, to our knowledge, this theory has not yet been applied to soils.

The present study examines the application of the Kubelka–Munk approach to well drained soils with small amounts of organic matter; in such soils Fe oxides are generally the dominant pigments. Haematite, in particular, has a high pigmentation power and a good correlation has been found between its concentration in soils and 'redness' ratings based on usual colour parameters (Torrent *et al.*, 1983), from which the haematite content can be predicted. However, we felt that the use of the Kubelka–Munk theory could give a more general overview of the effect of ferric pigments on soil colour and would in turn offer the possibility of using soil colour as a source of information in soil mineralogical studies.

This paper reports on the usefulness of the Kubelka–Munk theory to predict the colour of the mixtures of soil minerals with synthetic haematite and goethite and the development of 'theoretical' soil colour indices related to the Fe oxide content and mineralogy. Then the chromatic characteristics of the haematites and goethites of a large group of soils are studied and the soil colour is used to estimate the content and nature of soil Fe oxides.

THEORY

The theory assumes that a pigment mixture layer of thickness U , capable of both scattering and

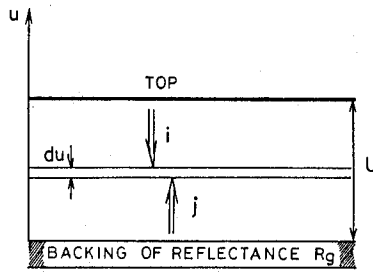


Fig. 1. Schematic diagram of a cross-section through a pigment mixture layer.

absorbing radiation of wavelength in the visible region, is irradiated in the u direction with a diffuse, monochromatic radiation flux (Fig. 1). This layer is very extensive in the plane normal to u compared with U and can be divided into a large number of elementary layers whose thickness (du) is small compared to U but is large compared to the diameters of the pigment particles comprising the layer. The model considers two diffuse light fluxes: one downward (i), and the other upward (j). The i flux in its passage through du is decreased by absorption by an amount $Ki du$ and is also decreased by an amount $Si du$ by scattering, which reverses the direction of some of the light rays. These rays belong then to j . The K and S values are called the absorption and the scattering coefficients respectively of the pigment mixture layer. In summary, the changes in the upward and downward fluxes can be written:

$$dj = -(S+K)j du + Si du \quad (1)$$

$$-di = -(S+K)i du + Sj du \quad (2)$$

dj and di showing different algebraic signs because of the different directions of the two fluxes.

Kubelka (1948) obtained explicit hyperbolic solutions for these equations. The most general solution is

$$R = \frac{1 - R_g(a - b \coth bSU)}{a - R_g + b \coth bSU} \quad (3)$$

where R is the reflectance of the layer over a background of reflectance R_g , $\coth bSU$ is the hyperbolic cotangent of bSU , U is the thickness of the layer, a is $(1 + K/S)$ and b is $(a^2 - 1)^{1/2}$.

In the limiting case of the film being sufficiently thick so that further increase in thickness does not change the reflectance (for pressed soil powders this occurs for thicknesses of a few tenths of a millimeter) the background has no influence and equation (3) becomes:

$$R = \frac{S}{K + S[K(K + 2S)]^{1/2}} \quad (4)$$

that can be simplified to:

$$\frac{K}{S} \frac{(1-R)^2}{2R} = \theta \quad (5)$$

Duncan (1940) showed that the coefficient of absorption of a pigmented system could be treated as a simple additive function of coefficients of absorption assigned to the constituent pigments, weighted in accordance with the proportion of each pigment present (and similarly for the scattering coefficients). That is:

$$K_M = C_1 K_1 + C_2 K_2 + \dots + C_n K_n \quad (6)$$

$$S_M = C_1S_1 + C_2S_2 + \dots + C_nS_n \quad (7)$$

where K and S are the values for the pigments specified by subscripts 1, 2, ... n , C is the proportion of the specified pigment in the mixture and K_M , S_M are the values for the layer. Equation (5) becomes then:

$$\theta_M = \frac{(1 - R_M)^2}{2R_M} = \left(\frac{K}{S}\right)_M = \frac{C_1K_1 + C_2K_2 + \dots + C_nK_n}{C_1S_1 + C_2S_2 + \dots + C_nS_n} \quad (8)$$

For many pigment mixtures most of the scatter is supplied by white pigment. This is the case of soils with low organic matter content where many of the constituent minerals such as feldspars, clay minerals or quartz are white and can be considered together as only one pigment: this is the white-grey usually observed when soils have been treated with dithionite to dissolve Fe oxides. If this assumption is valid, then equation (8) becomes:

$$\theta_M = \frac{1}{C_nS_n} (C_1K_1 + C_2K_2 + \dots + C_nK_n) \quad (9)$$

where subscript n refers to the white-grey matrix and the other subscripts (1, 2, ...) to other pigments. Thus, a simple linear relationship exists between θ and the concentration of the pigments. From equations (5) and (9) it can be shown that the addition of small amounts of a pigment to a 'white' mixture causes a sharp decrease of the reflectance (R) values as seen, for instance, in the addition of haematite, to a haematite-free soil (see review by Torrent *et al.*, 1983).

To make colour predictions it is necessary to determine the values of K and S of the pigments by using equation (8). For the simplest case a pigment is mixed with a standard 'white' whose reflectance, R_s is 1 and to which an arbitrary value of $K_s = 0$ is assigned. Equation (8) becomes:

$$\theta_M = \frac{C_pK_p + C_sK_s}{C_pS_p + C_sS_s} \quad (10)$$

and, if $K_s = 0$, it can be written:

$$\frac{1}{\theta_M} = \frac{S_s}{K_p} \times \frac{C_s}{C_p} + \frac{S_p}{K_p} = \frac{2R_M}{(1 - R_M)^2} \quad (11)$$

where R_M is the reflectance of the mixture.

According to equation (11), if $1/\theta_M$ is plotted against C_s/C_p for different binary mixtures the slope of the line gives S_s/K_p and the intercept gives S_p/K_p . For the sake of simplicity a value of $S_s = 1$ can be adopted whereby relative (rather than absolute) scattering values are obtained for the pigment. Then equation (11) gives the K_p and S_p values.

MATERIALS AND METHODS

Synthetic goethites and haematites

In most experiments four goethites (G12, G31, G612 and G51) were used. They were obtained by precipitating 10 mmole of $(\text{Fe} + \text{Al})^{3+}$ (as nitrate) with 2 M KOH to a final pH of 8 and storing the resulting protoferrihydrite precipitate in 200 ml of a KOH solution. The mole % Al, storage time, temperature and final KOH concentration were: 7.4%, 76 days, 25°C and 1 M for G12; 0%, 73 days, 70°C and 0.3 M for G31; 0%, 62 days, 25°C and 0.03 M for G612 and 0%, 65 days, 70°C and 1 M for G51. After storage the products were washed free of salts and treated with ammonium oxalate at pH 3 to remove non-crystalline material. The resulting products were found to contain only goethite by X-ray powder diffraction.

Four synthetic haematites were generally used: H21, H42, H32 and Merck. Haematite H21 was obtained by heating a goethite similar to G31 at 400°C for 1 day; haematite H42 was produced by precipitating $(\text{Fe} + \text{Al})^{3+}$ (1.7 mole % Al) as above and storing the precipitate in 0.01 M oxalate at

pH 6.1 and 100°C for 16 days; haematite H32 was produced by storing the precipitate (1.2 mole % Al) in 0.1 mM tartrate at pH 10 and 100°C for 8 days. The Merck haematite was a reagent grade $\alpha\text{-Fe}_2\text{O}_3$ (Merck reagent no. 3924).

Soil samples

This study was carried out on samples of 98 soils from Spain, Portugal, France, Germany, Nigeria, Madagascar, Brazil, New Zealand and the United States. They included, according to the FAO-Unesco system (Food and Agriculture Organization, 1974), luvisols, nitosols, acrisols and ferralsols from which either A or B horizons or both were examined; some C horizon samples were included. Most of the samples had less than 1% organic C and their dithionite-soluble iron (Fe_d) ranged from 0.7 to 11.5%. The Munsell hue (measured as described below) ranged from 1.40YR to 1.19Y. Most soils had very low amounts of oxalate-extractable Fe (Fe_o).

Iron-free soil samples

Several soil samples were ground to $< 50 \mu\text{m}$ and 2 g placed in 60 ml polyethylene bottles containing 50 ml of 0.26 M sodium citrate and 0.11 M sodium bicarbonate solution to which 1 g of sodium dithionite was later added. The bottles were tightly stoppered and shaken in a reciprocating shaker (200 cycles min^{-1}) for 16 h at 25°C. The method is similar to that of Mehra & Jackson (1960) except for the longer time at lower temperature, which usually provides a more complete extraction of free Fe oxides. Four soils were subjected to this iron removal or 'deferration' treatment: a loamy Bt horizon of a chromic luvisol containing illite, kaolinite and vermiculite (sample MB-3); a clayey Bt horizon of a chromic luvisol containing kaolinite, illite, vermiculite and smectite (CB-1); a clay loamy Ap horizon of an eutric nitosol containing kaolinite (20054) and a clayey B21 horizon of an eutric nitosol containing kaolinite and illite (20056).

Mineralogical analyses

The haematite and goethite concentrations in the soils were obtained from conventional X-ray diffraction after concentrating the Fe oxides by a boiling NaOH treatment (Norrish & Taylor, 1961) or by using differential X-ray diffraction (DXRD) on the untreated clay fraction (Schulze, 1981). Details of the procedures used are given by Peña & Torrent (1984). No other crystalline Fe oxides were identified in any of the soils studied.

Colour measurement and analysis

To prepare powders suitable for colour measurement about 10 g of $< 2 \text{ mm}$ soil or dithionite treated soil were ground in an agate ball mill, of 80 cm^3 capacity, with four agate balls of 2 cm diameter. In the first few minutes of grinding the colour changed rapidly but subsequent changes were very slow, with negligible change after 40–60 min. A standard grinding time of 1 hour was adopted. The same colour was obtained after grinding, by hand, 0.5 g of soil in an agate mortar for about 10 min. This last procedure was adopted for samples for which less than 10 g was available.

Colour measurements were carried out only on dry powders as opposed to the more common field practice of measuring moist soil colours. Spectrophotometric colour measurements of moist powders give less consistent results because of small moisture changes during measurement. In addition, moisture films cause unwanted specular reflection that creates problems in the application of the Kubelka–Munk analysis.

The samples used for colour measurement were different types of mixtures (soil-white standard, synthetic Fe oxides-white standard, etc.) that were made by grinding gently a total amount of about 250 mg of powder in an agate mortar until no further change in colour was observed: usually 5–10 minutes. The reflectance values of the mixtures were measured from 400 to 700 nm at 10 nm intervals in a double beam, Perkin-Elmer Lambda 3 spectrophotometer equipped with a reflectance (integrating sphere) attachment. The white standard was BaSO_4 Din 5033 (Merck no. 1748) whose reflectance was taken to be 100%. Both sample and standard (as dry powders) were back-filled into 8 × 17 mm aluminium frames and then gently pressed against filter paper to minimize preferred orientation (and specular reflection). These powder mounts were self supporting and allowed reflectance measurements without the use of cover glasses.

The reflectance measurements were converted to tristimulus values (X, Y, Z) according to the 1931 CIE colour-matching spectral energy distribution weighted for CIE Source C (Judd & Wyszecki, 1975). The X, Y, Z values were converted to the Munsell hue (H), value (V) and chroma (C) using the method given by the ASTM (1980). These X, Y, Z values were also converted to the CIE L^*, a^*, b^* values defined by the CIE (1978). The (L^*, a^*, b^*) space is supposed to be a 'uniform' colour space thus permitting a better colour discrimination than the Munsell notation.

The absorption and scattering coefficients at different wavelengths of the Fe oxides, the iron-free soils, and their mixtures were obtained by thoroughly mixing a sample with the BaSO_4 white standard in different proportions, measuring the reflectance and calculating the slope and intercept of the regression line fitted to equation (11), assuming that $S_{\text{BaSO}_4} = 1$. Thus, the calculated K and S values are relative rather than absolute. The same procedure was adopted for the ground soil samples.

Since no procedure is available for the quantitative separation of soil haematite and goethite from the associated non-Fe soil the K and S coefficients of soil-derived haematite and goethite cannot be measured. However, if the K and S of a number of soils are known, we can estimate average values of the K and S of these two minerals as follows. For any wavelength the absorption and scattering coefficients of a soil, K_M and S_M respectively, can be written, according to equations (6) and (7) as:

$$K_M = K_{hm} C_{hm} + K_{gt} C_{gt} + K_{df} C_{df} \quad (12)$$

$$S_M = S_{hm} C_{hm} + S_{gt} C_{gt} + S_{df} C_{df} \quad (13)$$

where C are concentrations and the subscripts hm, gt and df denote, respectively, haematite, goethite and the Fe oxide-free 'matrix'; this 'deferrated' soil includes the rest of the soil minerals plus the organic matter.

If the concentrations of haematite and goethite are determined (by DXRD) and K_M and S_M are measured, the unknowns, in equations (12) and (13) are, respectively, the K and S for the three components. If we consider for any of these equations a number of samples, m , higher than three (i.e. the number of unknowns) we can find, using a minimization technique, the 'best' average values for K and S . Such a method was used for $m = 98$, minimizing by a least-squares procedure, and the K and S values were obtained for 'soil haematite' and 'soil goethite' that are discussed below.

RESULTS AND DISCUSSION

Absorption and scattering coefficients of Fe-oxides and deferrated soils

The K and S coefficients of synthetic haematites differed widely from one sample to another (Fig. 2). These differences were also evident from their Munsell colour which indicated more purple hues for the samples prepared at high temperature (H21 and Merck), a common observation in laboratory synthesis experiments. The range of variation of chromatic properties was narrower when only low temperature ($< 100^\circ\text{C}$) haematites (H42, H32 and some others not described in detail here) were considered.

The four goethites described above differed in their K and S values (Fig. 3); differences were more marked for S than for K . Measurements of the colour of these samples and other goethites (not described in detail here) showed that the range of chromatic properties was lower than in haematite.

The dithionite-treated soils showed grey (low Munsell chroma) colours and widely different K and S values (Fig. 4) although the spectral distribution of each coefficient was similar from one sample to another.

Predicted versus measured colours of mixtures of Fe oxides and deferrated soils

The reflectance, R , from 400 to 700 nm, of different mixtures of haematite, goethite and iron-free soil was: (i) measured, as indicated above, (ii) calculated by using equation (8) (in which both the proportions and the K and S values of those three components were known). Predicted and measured values agreed well, especially for mixtures with less than about 20% of haematite +

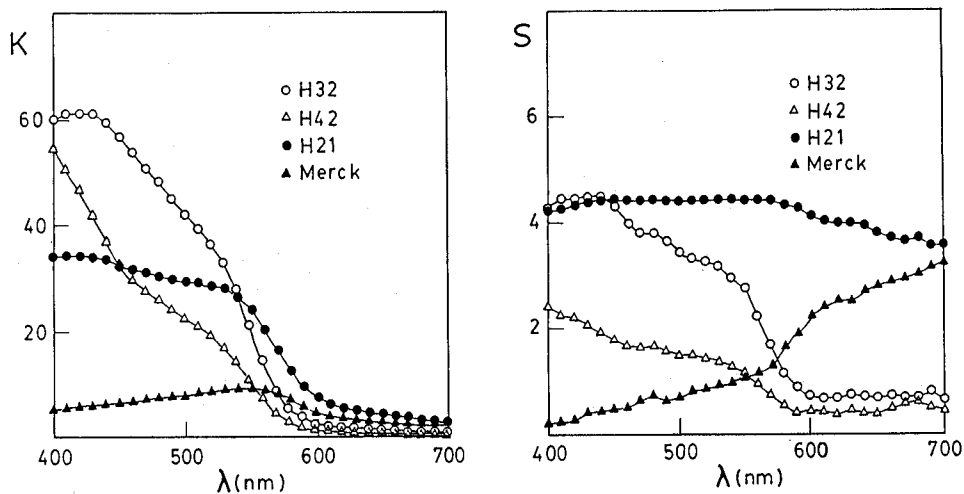


Fig. 2. Absorption (K) and scattering (S) coefficients of four synthetic haematites for the 400–700 nm wavelength range.

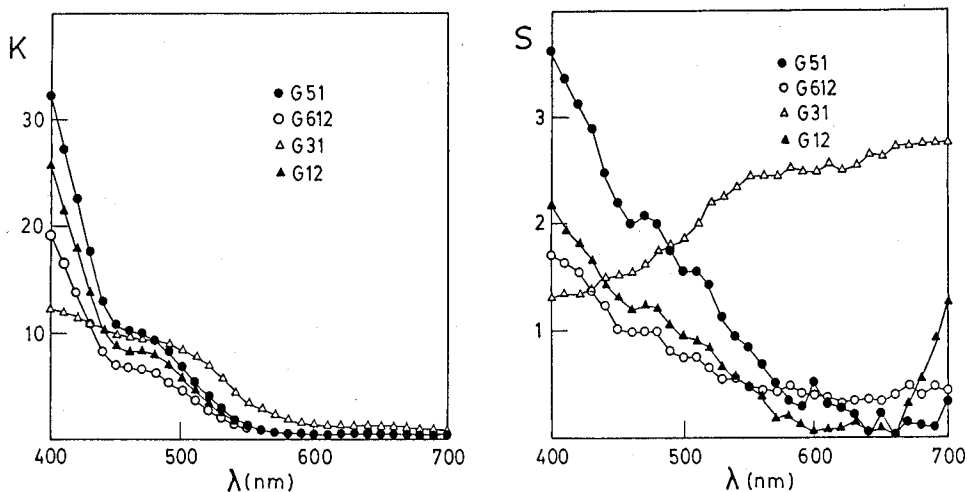


Fig. 3. Absorption and scattering coefficients of four synthetic goethites.

goethite (Fig. 5). Thus, the Kubelka–Munk approach can be safely used for predicting the colour of that type of mixture.

Pigmenting effects of haematite and goethite

Inasmuch as the Kubelka–Munk approach is essentially valid, we can visualize the pigmenting effects of haematite and goethite by inserting in equation (8) the K and S values of these minerals, and converting the resulting reflectance figures from 400 to 700 nm into the coordinates of a point in a suitable colour space. Fig. 6 shows the colour of binary haematite-deferrated soil and goethite-deferrated soil mixtures in the CIE (L^* a^* b^*) colour space (where L^* measures lightness; a^* measures redness when positive, grey when zero and greenness when negative; b^* values measure yellowness, grey when zero and negative values indicate blueness). Even at very low percentages, haematite causes a marked change in colour, contrasting with the lower pigmenting effect of goethite. In neither binary mixture does much further change in colour occur above a certain

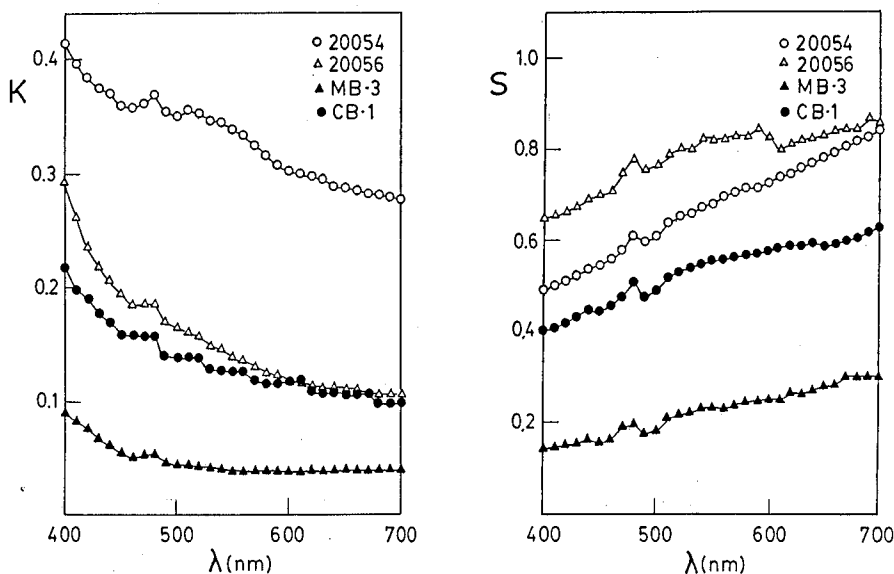


Fig. 4. Absorption and scattering coefficients of four dithionite-treated (deferrated) soils.

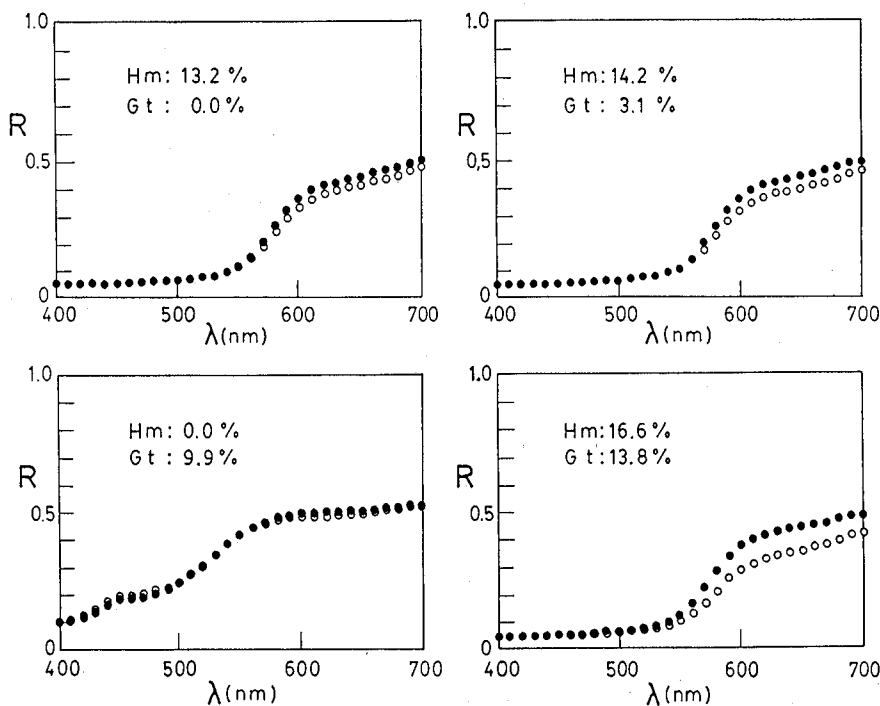


Fig. 5. Measured (●) versus predicted (○) values of the reflectance of several mixtures of haematite H32 (Hm), goethite G612 (Gt) and deferrated soil CB1. Haematite and goethite percentages of the mixtures are indicated.

'saturation' percentage (about 10% for haematite and 30% for goethite); in the case of haematite a decrease in the degree of redness is observed when the proportion is $> \sim 15\%$; in goethite, yellowness decreases above 50%. These effects can also be appreciated in terms of the more familiar Munsell system: Fig. 7 shows the projection of the points representing the mixtures in the CIE Yxy space on the plane of Munsell value $V=7$ (this plane shows the isolines for hue and for chroma).

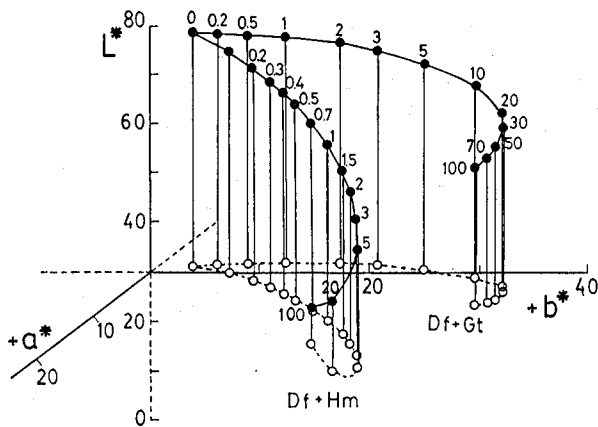


Fig. 6. Calculated positions (●), and their projections on the a^*-b^* plane (○) of haematite-deferrated soil (Hm + Df) and goethite-deferrated soil (Gt + Df) mixtures in the CIE ($L^* a^* b^*$) colour space (L^* = lightness, a^* = redness, b^* = yellowness). Numbers refer to percent haematite or goethite.

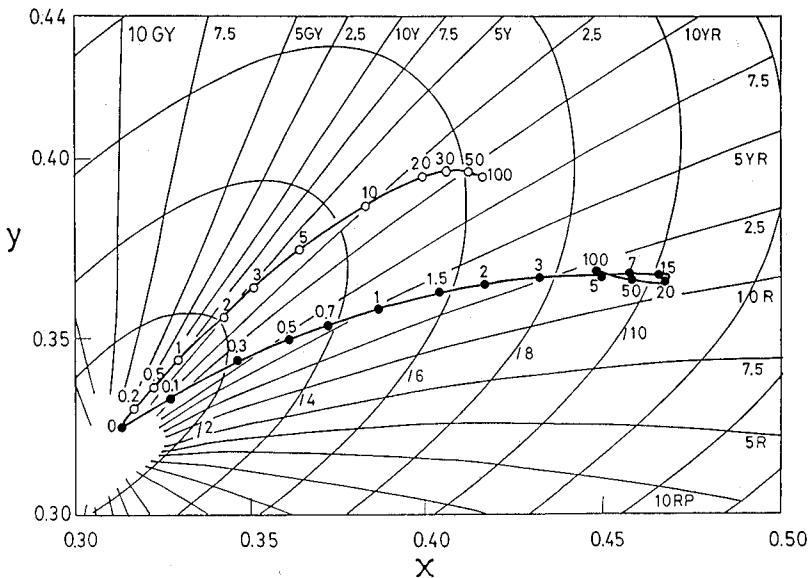


Fig. 7. Projection, on the plane of Munsell value = 7, of the calculated position, in the CIE $Y x y$ space, of the haematite-deferrated soil (●) and goethite-deferrated soil (○) mixtures. Numbers refer to percent haematite or goethite. The figure shows the isolines for Munsell hue and chroma.

Development of redness indices

The obvious reddening effect of haematite has led several authors to develop 'redness' indices which would allow estimation of the haematite content in soils. Torrent *et al.* (1983) summarized some of these efforts and suggested two empirical indices based, respectively, on the Munsell notation and the CIE chromaticity coordinates (Y, x, y). Both indices were useful although saturation effects were present. It is now clear that tests of new (and better) indices can be carried out without long series of measurements because the Kubelka–Munk theory provides a good technique to calculate the colour of haematite-containing mixtures.

For practical purposes, indices must be developed in one of the colour notation systems used by commercial colorimeters and spectrophotometers. In this study we used: (i) the CIE chromaticity coordinates (Y, x, y); (ii) the Munsell hue, value and chroma (H, V, C) and (iii) the CIE 1978

(L^*, a^*, b^*) space. We used a simple multiplicative index in which each variable was given an exponent. Different exponents were tested until the maximum correlation was obtained between index and haematite content of the artificial binary (haematite + deferrated soil) mixtures. For the CIE system the best index was:

$$R_{\text{CIE}} = \frac{(x-0.34)^2 10^4}{(y-0.34) Y^2} \quad (14)$$

in which Y , x , y are the chromaticity coordinates, the 0.34 values correspond to the x and y coordinates of an average iron-extracted soil and 10^4 is used to avoid the use of decimal values. For the Munsell system the best index was:

$$R_{\text{Munsell}} = \frac{(10-H)^3 C 10^3}{V^6} \quad (15)$$

where H is the figure preceding YR in the Munsell hue and C and V the chroma and value, respectively.

And for the $L^* a^* b^*$ space:

$$R_{\text{Lab}} = \frac{a^* (a^{*2} + b^{*2})^{\frac{1}{2}} 10^{10}}{b^* L^{*6}} \quad (16)$$

where L^* , a^* , b^* have the usual meaning.

Table 1 shows the good correlations found between the redness indices of artificial mixtures and their haematite content up to 15% haematite. For higher percentages there is a quick 'saturation' in redness as expected from the results shown in Figs 6 and 7.

All the redness indices defined above are essentially insensitive to the goethite content. Table 1 shows the small effect of adding 15% goethite in the regression line of calculated R_{Lab} against haematite content. This is due, obviously, to the much lower pigmenting effect of goethite.

Table 1. Relationships between several calculated redness indices of haematite-deferrated soil mixtures and haematite content

| Index | Regression equation hm = haematite (%) | r^2 |
|-------------------------------------|---|-------|
| R_{CIE} | $y = 1.86 hm - 0.52$ | 0.996 |
| R_{MUNSELL} | $y = 34.8 hm - 25.7$ | 0.995 |
| R_{Lab} | $y = 2.35 hm - 0.29$ | 0.997 |
| $R_{\text{Lab}(15\% \text{ gt})}^*$ | $y = 2.00 hm + 0.15$ | 0.997 |

* R_{Lab} for mixtures having 15% goethite.

The natural pigment mixtures found in soils and sediments usually contain <15% haematite and <15% goethite, falling, therefore, within the effective range of our indices. The use of such indices in soils will be examined after considering the chromatic properties of soil Fe oxides.

Properties of the soil haematites and goethites and Fe oxide-free matrix

The calculated K and S values in the λ 400–700 nm range for the haematite and goethite in soils and for the Fe oxide-free matrix (Fig. 8), were similar to those of synthetic haematite and goethite and dithionite-treated soils (Figs 2, 3 and 4). Better agreement was found for wavelengths between 400

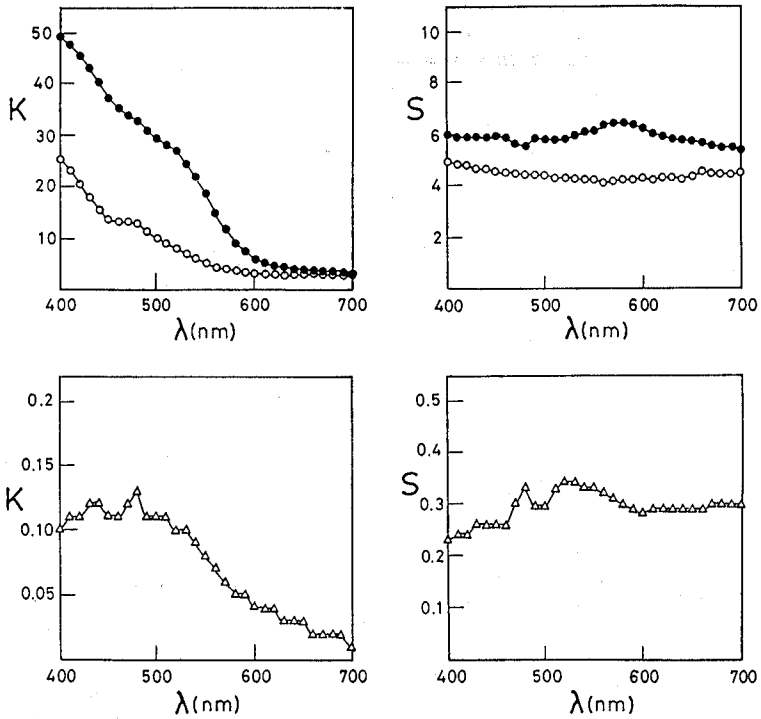


Fig. 8. Calculated absorption (K) and scattering (S) coefficients of the average 'soil' haematite (●), 'soil' goethite (○) and Fe oxide-free matrix (△) for the 400–700 nm wavelength range.

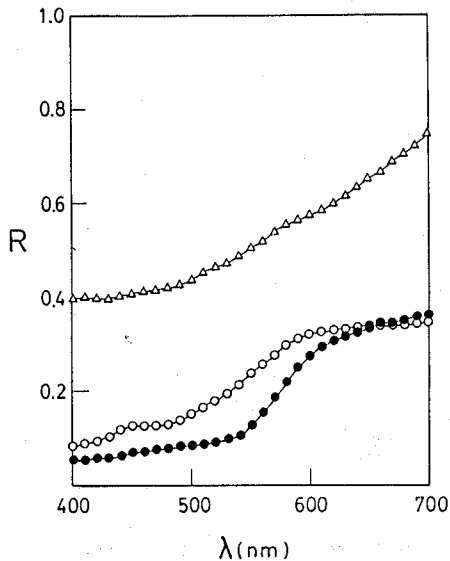


Fig. 9. Calculated reflectance curves of the soil haematite (●), 'soil' goethite (○) and Fe oxide-free matrix (△).

and 550 nm and for the absorption rather than for the scattering coefficients. The reflectance curves (calculated from equation (5)) are shown in Fig. 9 and correspond to the following Munsell colours: 3.4YR 4.6/6.6 for haematite, 9.2YR 5.5/4.5 for goethite and 6.7YR 7.5/2.2 for the Fe-free residue. Thus, soil haematite appeared slightly yellower and lighter than most of the synthetic haematites

Table 2. Relationships between measured redness indices of soils and haematite content

| Index | Regression equation $hm = \text{haematite (\%)}$ | r^2 |
|----------------------|---|-------|
| R_{CIE} | $y = 1.37 hm + 0.28$ | 0.86 |
| R_{Munsell} | $y = 18.5 hm - 10$ | 0.67 |
| R_{Lab} | $y = 1.97 hm + 0.54$ | 0.87 |

prepared at low temperature (Barron & Torrent, 1984). Soil goethite was slightly redder and had lower chroma than most of the synthetic goethites described by Kosmas (1984) or studied by ourselves (unpublished results). Finally, the Fe oxide-free matrix was pinkish grey, i.e. slightly more coloured than the real grey dithionite-treated samples.

Estimating the haematite and goethite contents of soils

For any soil the concentrations of haematite and goethite (C_{hm} , C_{gt}) can be obtained by feeding into equations (12) and (13) the K_M and S_M values (obtained from reflectance measurements of several soil-white standard mixtures) and the K and S values for soil haematite and goethite and Fe oxide-free matrix discussed above. This gives, both for equation (12) and for equation (13), two unknowns, i.e. C_{hm} and C_{gt} (because $C_{df} = 1 - C_{hm} - C_{gt}$). Therefore, data for only one wavelength are sufficient to solve the system. In practice, however, we found that the best results were obtained using only equation (12) for two or more different wavelengths. Obviously when more than two wavelengths are used the number of equations exceeds that of unknowns. In that case a least-square minimization can be used to obtain the best values for C_{hm} and C_{gt} . By means of this procedure, for 31 wavelengths (400–700 nm in 10 nm steps), we found a good correlation ($r^2 = 0.82$, $n = 98$) between predicted and measured (DXRD) haematite contents. The correlation was, however, not so good for goethite ($r^2 = 0.70$).

The use of the above estimation procedure requires measuring the reflectance of several (usually 4–5) mixtures of soil plus white standard. In practice it would be more convenient (and faster) to make predictions from the reflectance measurements of only one sample. In connection with this, Torrent *et al.* (1983) showed how two different 'redness' indices derived from the colour of a soil sample were correlated with haematite content. Table 2 shows that the indices developed above were also highly correlated with the haematite content of the group of 98 soils. The best correlation was found with the R_{Lab} index ($r^2 = 0.87$). Up to about 10% haematite there was no saturation effect in any of the indices. To avoid saturation problems, soils suspected to contain excess haematite can be diluted with a known amount of dithionite treated soil. If dithionite-soluble iron (Fe_d) is known, the amount of goethite can be estimated indirectly by subtracting from the Fe_d the Fe in the associated haematite (i.e. % haematite/1.43) and the oxalate extractable Fe (Fe_o) and multiplying the difference by 1.59 (i.e. the stoichiometric goethite/Fe ratio). For our 98 soils there was a good correlation between the goethite estimated by this procedure and the goethite determined by DXRD ($r^2 = 0.81$).

Calcining a soil transformed the Fe oxides into haematite, the amount of which may be estimated by measuring the redness index. This provided a quick method for estimating the Fe oxides. The correlation between the R_{Lab} index and Fe_d , which is a reasonably good measurement of the free Fe oxides present, was good ($R_{\text{Lab}} = 1.17 + 2.01 (\text{Fe}_d \times 1.43)$; $r^2 = 0.78$). The slope of the regression line (2.01) was very similar to the one found for the untreated soils (1.97) which suggested that essentially all the dithionite-soluble Fe mineral species had been converted to haematites with similar characteristics to those of the untreated soils.

The difference between the redness indices of untreated and calcined soil samples was related to the goethite content but the correlation was relatively poor ($r^2 = 0.51$). This was to be expected because the errors in the estimations of haematite of the two samples were additive.

CONCLUSIONS

The methods predicted the haematite and goethite contents in soils and gave better results than previous ones (Torrent *et al.*, 1983). Some remarks, however, need to be made. Firstly, colour (and colour indices) depend on degree of grinding; consequently the procedures described in the 'Materials and Methods' section should be carefully followed. Secondly, accurate reflectance measurements are necessary. Most commercial reflectance spectrophotometers are adequate if they are properly calibrated. The use, for instance, of several matte Munsell colour standards (obtainable from the Munsell Color Company) in the colour range expected for soils permits the accuracy of the calibration to be checked.

Reflectance spectrophotometers yield a reflectance curve whose values are applicable in any of the above methods to estimate haematite and goethite. In contrast, colorimeters give only three colour coordinates in one or more of the colour systems, usually CIE (Y, x, y) or CIE $L^* a^* b^*$, thereby restricting the prediction procedures to those based on the redness ratings. This is not a major inconvenience inasmuch as the R_{Lab} index gives a very good estimation (and only one colour reading is needed for its calculation).

Only a few minutes were required for application of any of the above methods, apart from the time recommended for sample grinding. Preparation of the powder mount and measurement required only a short time and, if computerized, direct goethite and haematite readings may be obtained, thus making the method suitable for use on a routine basis.

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