

QUANTITATIVE DETERMINATION OF HEMATITE AND GOETHITE IN LATERITIC BAUXITES BY THERMODIFFERENTIAL X-RAY POWDER DIFFRACTION

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Abstract—An X-ray thermodifferential powder diffraction method for the quantitative determination of goethite and hematite in lateritic bauxites has been developed and consists of measuring the integrated intensities of the 012 line of hematite before and after heating the sample at 900°C and of correcting the obtained values by the X-ray mass absorption coefficient of either the untreated or heated matrix. From the corrected line intensities and the chemical analyses, the amounts of iron to be allocated to goethite and hematite in the untreated samples can be estimated. The actual content of goethite and hematite in a sample is calculated by taking into account the degree of Al substitution in each of these minerals. The method was tested on artificial mixtures of goethite and hematite and subsequently used to analyze 98 auger drill samples from lateritic bauxites of Guinea Bissau. The estimated precision of the determination of goethite and hematite content was $\pm 2\%$ (absolute). The method can not be applied to samples containing $<10\%$ Fe₂O₃ (on a whole weight basis) unless preconcentration is carried out.

Key Words—Bauxite, Goethite, Hematite, Iron, Mineral analysis, Thermal treatment, X-ray powder diffraction.

INTRODUCTION

Knowing the goethite and hematite content of soil or ore samples is of the utmost importance, for example, for predicting the chemical and physical properties of a soil or the behavior of an iron ore during an industrial process or for calculating nonavailable alumina in bauxite processing. The quantitative determination of both minerals in a given rock or soil sample can be achieved by means of several instrumental techniques; however, in recent years, two methods seem to have received special attention. Mössbauer spectroscopy (see e.g., Janot *et al.*, 1971) is probably the most precise and accurate, of these techniques but it is also time consuming and costly, and therefore poorly suited for the examination of large numbers of samples.

X-ray powder diffraction, on the other hand, can be applied either to natural bauxite samples (Black, 1953) or to soil samples rich in iron oxides (Kampf and Schwertmann, 1982a). It has some limitations, however, due to the nonlinear variation of goethite and hematite XRD line intensities in various reference samples and to the fact that the mass absorption coefficient used by some workers has been estimated rather than accurately calculated.

In the present study, a procedure for the quantitative mineralogical analysis of goethite and hematite in mixtures is described, for which chemical composition is known. This method, which requires that the chemical composition of the mixture be known, is simple and

convenient and is based on thermally induced dehydroxylation of goethite and its subsequent transformation into hematite. Measuring and comparing integrated hematite XRD line intensities before and after thermal treatment of a sample enable content of each mineral to be calculated.

PRINCIPLE OF THE METHOD

Intensity of an XRD line and concentration of the diffracting component

The intensity I_{ij} of a given diffraction line i of a crystalline component j present in a mixture is expressed by the formula proposed by Klug and Alexander (1974):

$$I_{ij} = \frac{K_{ij}x_j}{d_j[x_j(\mu/\rho_j - \mu/\rho_m) + \mu/\rho_m]}, \quad (1)$$

where K_{ij} = a constant; x_j = content of component j in the mixture, in wt. %; d_j = density of component j , in g/cm³; μ/ρ_j = mass absorption coefficient of component j for the wavelength (λ) of radiation used; and μ/ρ_m = mass absorption coefficient of the matrix.

If the mineral component j is present in different concentrations designated as x_j and y_j in matrices m_1 and m_2 of different chemical composition, and if the density d remains the same in both cases, the ratio of two considered concentrations may be written as:

$$x_j/y_j = \frac{I_{x_j} \cdot \mu/\rho_{m_1}}{I_{y_j} \cdot \mu/\rho_{m_2}} \quad (2)$$

If only one of the concentrations in Eq. (2), x_j or y_j , is unknown, it can be found, provided the chemical composition of both mixtures containing mineral j is known (a necessary condition for calculating μ/ρ).

Calculation of hematite content in a matrix containing goethite

For an ore or soil sample containing both goethite and hematite, after suitable thermal treatment (described in detail below), all iron in the sample will be in the form of α -Fe₂O₃. Therefore, if the chemical composition of this sample is known, the hematite (Hm) content after heating is also known and the conditions for the solution of Eq. (2) are fulfilled. The consequent measurement of a chosen hematite XRD line intensity before and after thermal treatment (designated Iⁿ and I^h, respectively) provides the data for the calculation of hematite content before heating, using the following equation:

$$\% \text{Hm} = \% \text{Hm}^h \cdot I_c^n / I_c^h, \quad (3)$$

where: $I_c^n = (I^n \cdot \mu/\rho^n)$; $I_c^h = (I^h \cdot \mu/\rho^h)$; μ/ρ^n and μ/ρ^h = the mass absorption coefficients of untreated and heated samples, respectively; and I^n and I^h = the intensities of the considered XRD line of the untreated and heated samples, respectively. The percentage of hematite (% Hm^h) can be calculated by correcting the Fe₂O₃ content in a sample for loss of H₂O after thermal treatment, which is assumed to be equal to the measured loss on ignition (L.O.I.):

$$\% \text{Hm}^h = \% \text{Fe}_2\text{O}_3 \cdot (1/100\% - \% \text{L.O.I.}) \quad (4)$$

For greater clarity of explanation, the aluminum substitution in hematite in both Eqs. (3) and (4) was not considered; the necessary corrections for Al are discussed below.

The necessary condition for the correct calculation according to Eq. (3) is a knowledge of the elemental composition (major components) of an examined sample, from which the iron content after thermal treatment can be calculated and the mass absorption coefficient (μ/ρ) can be computed for both the natural and the heated samples. The mass absorption coefficient is dependent on only two parameters: (1) elemental (chemical) composition of a sample, and (2) wave-

length (λ) of radiation used (Klug and Alexander, 1974), regardless of the mineralogical form the chemical components may take. The mass absorption coefficient of a bauxite sample composed of Al₂O₃, Fe₂O₃, SiO₂, TiO₂, and H₂O, for a given X-ray radiation wavelength, will be equal to the sum of individual coefficients of all specified components multiplied by their weight percentage content in the mixture. Hence,

$$\begin{aligned} \mu/\rho = & \% \text{Al}_2\text{O}_3 \cdot \mu/\rho_1 + \% \text{Fe}_2\text{O}_3 \cdot \mu/\rho_2 \\ & + \% \text{SiO}_2 \cdot \mu/\rho_3 + \% \text{TiO}_2 \cdot \mu/\rho_4 \\ & + \% \text{SiO}_2 \cdot \mu/\rho_5 + \% \text{H}_2\text{O} \cdot \mu/\rho_6. \end{aligned} \quad (5)$$

The elemental mass absorption coefficients for CoK α radiation used in the calculations below were taken from Klug and Alexander (1974). To illustrate this approach, the calculation of the hematite content (based on the intensity of the hematite 012 line) in sample 14m2 is given below; the relevant data are listed in Table 1. The recorded 012 line intensities actually correspond to Al-substituted mineral species, therefore, for calculations using Eq. (4), the Al content of the hematite must be added to the chemically determined ferric component. A study of Al substitution in hematites was beyond the scope of this research, but the value of this parameter was assumed to be equal to 15 and 8 mole % for heated and nonheated hematites, respectively (on the basis of the available data of Janot *et al.*, 1971; Nahon, 1976; Schwertmann *et al.*, 1979; Yariv *et al.*, 1981; Tardy and Nahon, 1985; and Ambrosi *et al.*, 1986). Consequently the amount of hematite in sample 14m2 after heating is:

$$\begin{array}{ccc} \text{Fe}_2\text{O}_3 & & \text{Al}_2\text{O}_3 & & \text{mole} \\ \text{comp.} & & \text{comp.} & & \text{ratio} \\ \downarrow & & \downarrow & & \downarrow \\ \% \text{Hm}^h = & 55.9\% + & [(55.9 \cdot 100/85) - & 55.9]0.64 \\ & & & & \\ & = & 62.2\%, & & \end{array} \quad (6)$$

where 0.64 is the Al₂O₃/Fe₂O₃ mole ratio used to convert mole % to wt. %. According to Eq. (4) the quantity of hematite in the untreated sample is:

$$\% \text{Hm}^n = 62.2\% \cdot 1876/4297 = 27.2\% \quad (7)$$

Calculation of goethite content

The amount of iron associated with goethite in the untreated sample is thus the difference between total

Table 1. Results of 900°C thermal treatment of the sample 14m2.

Sample	Chemical composition (wt. %)					μ/ρ^1	012 line int. (cts)	
	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	SiO ₂	H ₂ O		I ⁿ	I ^c · 10 ⁻²
Untreated	31.7	44.8	1.8	1.9	19.41	41.71	4490	1876
900°C	39.5	55.9	2.3	2.3	—	48.21	8913	4297

¹ Mass absorption coefficient.

² Measured intensity of hematite 012 X-ray powder diffraction line.

³ Corrected intensity of hematite 012 X-ray powder diffraction line.

Fe_2O_3 and Fe_2O_3 attributed to hematite (in the untreated sample):

$$\begin{array}{ccc} \text{Total Fe}_2\text{O}_3 & & \text{Fe}_2\text{O}_3 \text{ in hematite} \\ \downarrow & & \downarrow \\ \% \text{Fe}_2\text{O}_{3(\text{Gth})} = 44.8 - [27.2 - (27.2 \cdot 0.08) \cdot 0.64] & & \\ = 19.0\% & & \end{array} \quad (8)$$

The pure hydrated ferrous component of goethite is obtained by adding 11.25% water (stoichiometric ratio to Fe_2O_3). Thus:

$$\begin{array}{ccc} \% \text{FeOOH}_{(\text{Gth})} = 19.0 + (19.0 \cdot 11.25\% \text{H}_2\text{O}) & & \\ = 21.4\% & & \end{array} \quad (9)$$

Obviously, to transform the above calculated ferric iron content into α -FeOOH content, besides adding of stoichiometric water, corrections equivalent to mole % Al substitution must be made as well. For example, in sample 14m2 in which the Al substitution rate in goethite $\text{Al}/(\text{Al} + \text{Fe}) = 20\%$ (calculated according to Fitzpatrick and Schwertmann, 1982), the value calculated using Eq. (5) represents 80 mole % of total goethite wt. % in the sample. Thus, the final value is:

$$\begin{array}{ccc} \text{FeOOH} & & \text{M wt.} \\ \text{comp.} & \text{AlOOH comp.} & \text{ratio} \\ \downarrow & \downarrow & \downarrow \\ \% \text{Gth} = 21.4 + \{[(21.4 \cdot 100/80) - 21.4] \cdot 0.67\} & & \\ = 25.0\% & & \end{array} \quad (10)$$

where 0.67 is the AlOOH/FeOOH molar ratio used to convert mole % to wt. %.

MATERIALS AND METHODS

Sampling

The samples were taken from 20 boreholes along 5 lines in the ferruginous bauxite developed on a flat top hill or "bowal" in the Boe region, southeast Guinea Bissau, West Africa. The samples were taken using a UGB-50 mobile drilling rig equipped with auger drill. The sampling interval was determined by the length of auger segments, each 1.5 m long. The entire raw sample (about 30 kg) was ground and split to the desired volume. For all samples discussed here the first two alphanumeric characters indicate the borehole number and the third number indicates the sampling interval; thus, sample 14m2 is from borehole 14m, the second sampling interval (1.5–3.0 m). Duplicate samples were prepared in a quantity of about 100 g each and grain size <200 mesh. Ninety-eight samples were collected and analyzed mineralogically and chemically.

Methods

X-ray powder diffraction. The 012 X-ray powder diffraction (XRD) line at about 3.66 Å was chosen for

Table 2. Intensity of 012 X-ray powder diffraction line of hematite after heating of different durations in different temperatures.¹

Heating time (hr)	Intensity (cts)				
	1	2	4	8	12
600°C	—	3420	—	—	—
700°C	—	4140	—	—	—
800°C	—	4320	—	—	—
900°C	4380	4297	4420	4406	4392

¹ Sample 14m2.

the intensity measurements because it did not overlap with peaks of other minerals present in the bauxites. Although it is less intense than the 110 line, it gave more accurate results than did the latter during testing of the method on synthetic samples of known composition.

Self-supporting powder mounts were prepared by gentle-pressure back-filling of the powdered sample into aluminum sample holders placed against filter paper to minimize orientation (Kampf and Schwertmann, 1982a). XRD data were obtained using $\text{CoK}\alpha$ radiation (40 kV, 20 mA) and a Philips PW 1050 vertical goniometer equipped with a 1° divergence slit, a 0.2-mm receiving slit, a 1° scatter slit, a graphite monochromator, and a proportional detector. The 012 line width was recorded from the XRD pattern and a background value corresponding to that width was calculated. The 012 line of each treated and untreated sample was scanned three times at 0.5°/min; the integrated line intensity retained for the further calculations was the average of the three runs. The counting rate was 400 counts/s, so that no dead time correction was necessary.

To limit the errors caused by the instrumental drift (resulting from temperature, pressure changes, etc.) the measurements on natural and thermally treated samples were carried out successively.

Thermal treatment. Well-crystallized goethite dehydroxylates at 320°–390°C. For the very finely crystalline varieties this value may be much less than 300°C (Kelly, 1956; Schwertmann *et al.*, 1985). According to Yarov *et al.* (1981), after dehydroxylation, goethite is con-

Table 3. Results of tests on the synthetic samples of known composition (wt. %).

Standard	Gibbsite	Quartz	Anatase	Goethite	Hematite	Hematite calculated	
						(1)	(2)
S1	62.7	1.5	1.3	18.7	16.7	16.5	17.0
S2	45.0	2.9	2.0	35.0	15.0	14.5	15.4
S3	45.0	2.9	2.0	14.5	35.5	35.6	36.1

(1) = Hematite content found in the first series of synthetic samples (all minerals synthetic).

(2) = Hematite content found in the second series of synthetic samples (goethite natural).

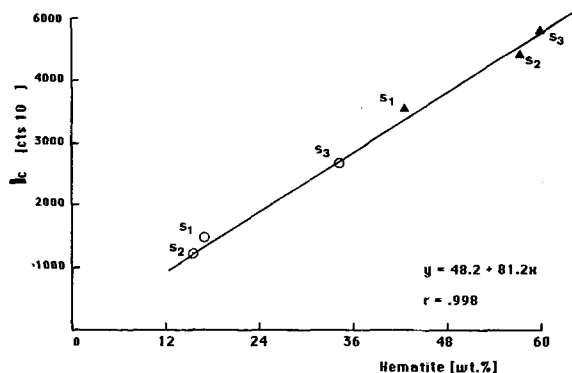


Figure 1. Hematite content vs. corrected 012 line intensity (I_c) in synthetic samples from series 1. \circ = sample before thermal treatment; \blacktriangle = sample after thermal treatment.

verted to "protohematite" which is stable to 600°C. The XRD pattern of protohematite differs from that of well-crystallized hematite by having broader and weaker lines. The XRD peaks of samples heated to >600°C become sharper and their width at half height (WHH) approached the values for well-crystallized hematite. In the present study, aliquots of a selected natural sample (14m2) were heated for 2 hr at 600°, 700°, 800°, and 900°C, and the 012 line intensities were recorded as shown in Table 2. From these data heating at 900°C appeared to ensure the stable intensity of the 012 XRD line and that no significant changes in line intensity would result on longer heating. Thus, heating for 2 hr at 900°C was the routine condition maintained for all analyses of all samples.

Peak position and geometry. For most samples, the thermal treatment caused the 012 peak to shift toward lower d values by 0.03 to 0.07 Å. According to Yariv *et al.* (1981) this shift on heating is due to greater Al substitution in the hematite after the heating, as a result of the incorporation of Al from Al-bearing minerals. Similarly, for most samples, the width at half height (WHH) of the hematite 012 peak increased 10 to 20% after heating, probably because of the small crystallite size of the hematite formed at the expense of dehydroxylated goethite.

Tests on synthetic mixtures of known composition

To check the validity of the theoretical premises (i.e., the linearity of $\alpha\text{-Fe}_2\text{O}_3$ concentration vs. 012 line intensity), two series of standards (three standards in each series) of the same compositions were prepared (see Table 3) and treated as described above. In the first series, all mineral components were "Merck" laboratory reagents, except the goethite, which was synthesized in the laboratory. In the second series of standards, the goethite was a natural material from a weathered pyrite vein. Its chemical analyses gave 88.8% Fe_2O_3 , i.e., 1.1% less than the theoretical formula.

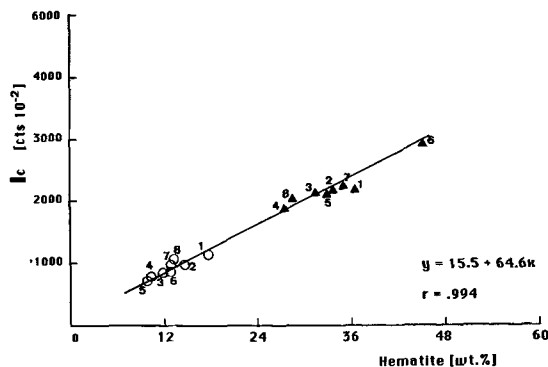


Figure 2. Hematite content vs. corrected 012 line intensity (I_c) in samples from borehole 5I. \circ = sample before thermal treatment; \blacktriangle = sample after thermal treatment.

EVALUATION OF THE RESULTS

All experimental data on the synthetic samples are listed in Table 3 and plotted in Figure 1. According to these results, the standard error of estimation for the hematite content is $\pm 0.4\%$ hematite. Given the insignificance of the error introduced during weighing of the synthetic standards, the source of error must be due to the measurement of the XRD line intensity and the calculation of the background intensity. The precision of the hematite determination in natural samples depends, however, on more parameters, namely: (1) errors in chemical analyses; (2) variation in the degree of Al substitution in Fe minerals and in hematite before and after the thermal treatment; and (3) variations in the crystallinity of the goethite which affects the crystallinity of hematite obtained by the thermal treatment (see Table 4). For the eight samples from borehole 5I (Figure 2), the standard error of estimation for hematite content is $\pm 1.2\%$ hematite.

The flatter slope of the regression line in Figure 2 compared with that in Figure 1 can be explained by the lower crystallinity of natural hematites compared with the synthetic varieties. This difference in crystallinity does not affect the calculation of hematite and goethite content in the natural samples, as in fact the "hematite calibration line" is derived from the proportionality between the hematite XRD line intensity before and after heating, considered *individually* for each sample (*vide supra*). Consequently the absolute error in the hematite determination using the present method is probably about $\pm 2\%$. This value is also applicable to the determination of goethite content, which, however, may also bear an additional error due to nonstoichiometric water. To illustrate results obtained from the analyses of 98 samples, nine examples representing the Fe_2O_3 variation range are listed in Table 4. The mean crystallite dimension of goethite, hematite, and hematite after the thermal treatment was calculated according to Scherrer formula (Klug and Alexander, 1974). The values obtained show a much small-

Table 4. Range of variation of total Fe₂O₃, hematite, and goethite contents and Al substitutions (mole %) in goethites from selected samples.

Sample	Fe ₂ O ₃ (wt. %)	Goethite (wt. %)	Al Sub (M %)	MCD ¹ (Å)	Hematite (wt. %)	MCD _n ² (Å)	MCD _h ³ (Å)
31e4	51.99	31.2	18.0	323	29.4	440	440
5j3	50.56	40.4	6.0	612	17.0	795	1069
14m2	44.76	24.8	20.0	246	27.2	795	795
14o5	41.30	17.0	16.0	269	29.3	795	521
25u4	36.94	30.7	17.0	233	13.7	521	440
14o2	31.68	24.5	17.0	290	11.9	400	400
14f1	25.35	11.2	20.0	270	17.7	521	440
5d1	19.20	14.0	16.0	233	8.6	521	368
29e1	12.35	7.9	20.0	185	6.6	650	521
Mean (n = 98)	31.7	22.0	16.0	254	17.3	613	511

¹ Mean crystallite dimension of goethite.

² Mean crystallite dimension of natural hematite.

³ Mean crystallite dimension of heated hematite.

er size of the goethite crystallites compared with the hematite, as well as a decrease in the mean crystallite dimension of the hematite after heating. Al substitution in goethite was calculated according to Fitzpatrick and Schwertmann (1982); the mean value (16 mole %) is within the threshold limits for ferruginous bauxites found by the latter workers.

Limitations of the method

To obtain reliable integrated line intensities, the hematite 012 XRD line should have a sufficiently high peak/background intensity ratio. This generally means that if the total Fe₂O₃ content in a sample is less than 7–10% (the actual limit depends on the XRD unit), the preconcentration of iron oxyhydroxides will be necessary (e.g., Kampf and Schwertmann, 1982b). In the studied samples the only iron minerals identified were well-crystallized goethite and hematite; thus, conditions for quantification of both minerals were optimal. If other ferric-ferrous minerals are present in a sample, their Fe content should be subtracted from total Fe₂O₃, to render the method fully applicable.

CONCLUSIONS

The high precision and linearity achieved in testing synthetic standards prove the technique to be reliable and permit the quantitative determination of goethite and hematite with precision of ±2% absolute. To calculate the mineral composition and mass absorption coefficient, however, the chemical composition of the examined sample must be known. The limiting conditions for the applicability of the method are: (1) the total iron content in the sample must not be less than 7–10% Fe₂O₃; and (2) other iron-bearing minerals must not be present.

REFERENCES

Ambrosi, J. P., Nahon, D., and Herbillon, A. J. (1986) The epigenetic replacement of kaolinite by hematite in laterite—

- Petrographic evidence and mechanism involved: *Geoderma* **37**, 283–294.
- Black, R. H. (1953) Analysis of bauxite exploration samples: *Anal. Chem.* **25**, 743–748.
- Fitzpatrick, R. W. and Schwertmann, U. (1982) Al-substituted goethite: An indicator of pedogenic and other weathering environments in South Africa: *Geoderma* **27**, 335–347.
- Janot, Ch., Gibert, H., de Gramont, X., and Biais, R. (1971) Etude des substitutions Al-Fe dans des roches latéritiques: *Bull. Soc. Fr. Mineral. Crystall.* **94**, 367–380.
- Kampf, N. and Schwertmann, U. (1982a) Quantitative determination of goethite and hematite in kaolinitic soils by X-ray diffraction: *Clay Miner.* **17**, 359–363.
- Kampf, N. and Schwertmann, U. (1982b) The 5 M NaOH concentration treatment for iron oxides in soils: *Clays & Clay Minerals* **26**, 401–408.
- Kelly, W. C. (1956) Application of d.t.a. to identification of natural hydrous ferric oxides: *Amer. Mineral.* **41**, 353–355.
- Klug, H. P. and Alexander, L. E. (1974) *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*: 2nd ed., Wiley, New York, 585 pp.
- Nahon, D. (1976) Cuirasses ferrugineuses et encroûtements calcaires au Sénégal et en Mauritanie: *Mem. Univ. Louis Pasteur, Strasbourg* **44**, 232 pp.
- Schulze, D. (1981) Identification of soil iron oxide minerals by differential X-ray diffraction: *Soil Sci. Soc. Amer. J.* **45**, 437–440.
- Schwertmann, U., Cambier, P., and Murad, E. (1985) Properties of goethites of varying crystallinity. *Clays & Clay Minerals* **33**, 369–378.
- Schwertmann, U., Fitzpatrick, R. W., and Taylor, R. M. (1979) The influence of aluminum on iron oxides. Part II. Preparation and properties of Al-substituted hematites: *Clays & Clay Minerals* **27**, 105–112.
- Tardy, Y. and Nahon, D. (1985) Geochemistry of laterites, stability of Al-goethite, Al-hematite, and Fe-kaolinite in bauxites and ferricretes: An approach to the mechanism of concretion formation: *Amer. J. Sci.* **285**, 865–903.
- Yariv, S., Mendelovici, E., and Vilalba, R. (1981) Interactions between the iron and aluminium during the heating of Venezuelan lateritic bauxites. II. X-ray diffraction studies: *Termochim. Acta* **45**, 339–348.

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