

ASSESSMENT OF GIBBSITIC MATERIAL IN SOIL CLAYS
BY DIFFERENTIAL THERMAL ANALYSIS
AND ALKALI DISSOLUTION METHODS

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Precision differential thermal analysis (DTA) equipment provides a sensitive and accurate means of detecting and estimating gibbsite in soil clays. A combination of DTA and sodium carbonate dissolution procedures enables well-ordered gibbsite to be distinguished from poorly-ordered aluminous material.

Pedologists have produced numerous correlations between particular macro-morphological features of the soil profile and the nature and amount of free** silica, alumina and iron oxide present. Properties such as aggregate stability, macroporosity and particle size distribution have been thought for some considerable time to be associated with the cementing properties of free iron oxides. Recent studies by Saini et al. [1] and Desphande et al. [2] have indicated, however, that correlations of soil structural properties with free iron oxides may involve some other factor and both groups of workers suggest that free aluminium oxides may play a more important role in the aggregation of soil particles than do free iron oxides.

In lateritic and related soils free hydrated crystalline oxides of aluminium (normally gibbsite) are frequently characteristic components. There are few accounts in the literature of the occurrence of free alumina, amorphous to X-rays in soils, although some laboratory studies on the ageing of these materials indicate that there is slight crystallization under mild acid conditions. The paucity of reports of particulate amorphous aluminium oxides in soils may be due to the difficulties in establishing their presence. It is considered, however, that aluminium oxides have a specific affinity for silica in solution and indeed Rich and Thomas [3] suggest that the lack of amorphous alumina in soils may result from it being stabilized by silica in allophane.

At the Macaulay Institute crystalline hydrated oxides of aluminium are normally detected in soil clays by DTA. Gibbsite, for example, is detected and estimated from the endothermic peak at approximately 300° on the DTA curve (Fig. 1,

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** The term free oxide is used to denote the oxides of iron, aluminium and silicon not present in the crystal lattice of any of the component aluminosilicate clay minerals.

curves A and B), recent developments in thermal analysis equipment enable determination of < 1 per cent of this component in a soil clay to be made.

Treatment of gibbsitic soil clays with cold 5 per cent sodium carbonate solution alters neither the shape nor the size of the endothermic peak at about 300° on the DTA curve. However, treatment with hot sodium carbonate solution markedly reduces the size of this peak indicating the removal of clay-size gibbsite and gibbsite-

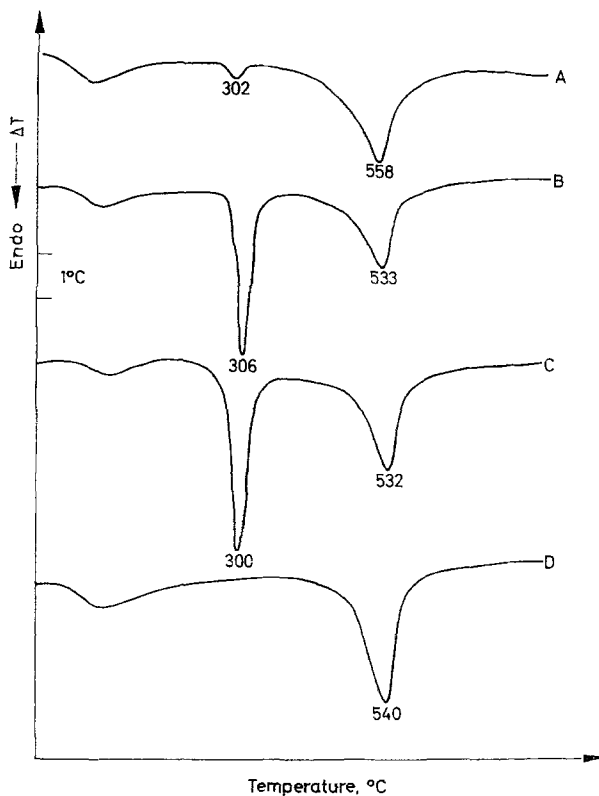


Fig. 1. DTA curves for soil clays: A — Longraw, untreated; B — Tanganyika (II), untreated; C — Tanganyika (II) after treatment with cold sodium carbonate solution; D — Tanganyika (II) after treatment with cold and hot sodium carbonate solution*

like material (pseudo-gibbsite) and not simply the extraction of poorly-ordered aluminous components. This combined DTA and sodium-carbonate-dissolution procedure has been employed in the investigation of a wide range of soils con-

* Heating rate 10°/min; integral 2-well inconel block; chromel-alumel thermocouples, temperature thermocouple in reference; sample weight 100 mg diluted with 100 mg calcined kaolinite, reference 200 mg × 2 calcined kaolinite; oxygen free nitrogen over sample and reference 200 ml/min.

taining free hydrated oxides of aluminium and provides an arbitrary means of differentiating free crystalline aluminous material from poorly-ordered assemblages containing alumina.

Materials and methods

Samples from the B horizon of sixteen gibbsite-containing soils representative of tropical and subtropical lateritic and temperate podzolic soils were examined. The clay fraction ($<1.4 \mu\text{m}$) was obtained by dispersing the soil with ammonia according to the method of Mackenzie [4]. Before treatment with 6 per cent hydrogen peroxide to remove organic matter, the clays were saturated with ammonium to prevent calcium oxalate formation [5]. The thermal characteristics of the clays were determined in nitrogen using a controlled-atmosphere DTA apparatus. X-ray diffraction patterns were obtained with a modified Debye–Scherrer powder camera using a Newton Victor generator as well as on a Philips 2KW diffractometer. The readily-soluble and less-readily-soluble silica and alumina were determined by treatment with 5 per cent sodium carbonate solution at room and at steam bath temperature, respectively [6]; these are hereafter referred to as cold carbonate treatment and hot carbonate treatment. The free iron oxide content of the clays was assessed by the dithionite procedure of Mitchell and Mackenzie [7].

Results and discussion

From X-ray examination, gibbsite is the only crystalline aluminium oxide hydrate present in the clay fraction of the soils studied. Hematite was noted in all samples and in five instances, namely Costa Rica (I) and (II), Ghana (II), Hong Kong and Australia, goethite was observed. However, the amount of goethite in the soil clays studied is very small and its dehydration in the $300\text{--}400^\circ$ range has little effect on the size of the gibbsite dehydroxylation peak. Assuming, therefore, that the endothermic peak between $270\text{--}310^\circ$ on the DTA curves of the soil clays (e.g. curves A and B, Fig. 1) is due to the dehydroxylation of gibbsite, the amount of this component in the clays varies from approximately 2 to 20 per cent.

Three successive treatments of the clays with cold carbonate treatment remove from 0.4 to 6.2 per cent (3.5 to 60.6 mmole/100 g) alumina and 0.1 to 2.1 per cent (1.8 to 34.8 mmole/100 g) silica (Table 1). The silica to alumina molar ratios of the extracts cover an appreciable range (0.2 to 4.0). In general, this cold alkali treatment neither alters the shape nor reduces the size of the 300° endothermic effect on the DTA curve (curves B and C; Fig. 1, curves D and E, Fig. 2). Furthermore, no measureable change is observable in the X-ray diffraction pattern or the infrared absorption spectrum.

In one instance, however, namely the clay fraction of the B₃ horizon of a peaty podzol (Drumboy, II) developed on a glacial till derived from basic to inter-

Table 1

Amounts of SiO₂ and Al₂O₃ removed by cold

Source of sample	Cold carbonate extract					
	No. of extractions	%SiO ₂ *	mmole/100 g SiO ₂	%Al ₂ O ₃ *	mmole/100 g Al ₂ O ₃	SiO/Al ₂ O ₃ molar
Longraw	3	0.5	8.7	0.4	3.8	2.3
Drumboy (I)	3	0.8	13.7	0.4	3.5	3.9
Tanganyika (I)	3	0.8	12.7	0.4	3.6	3.5
Dunkeld	3	1.0	17.0	2.1	20.8	0.8
Drumboy (II)	3	2.1	34.8	6.2	60.6	0.6
Ghana (I)	3	0.1	2.3	0.6	6.2	0.4
Glentanar (I)	3	1.1	18.3	2.1	20.1	0.9
Ghana (II)	3	0.1	2.0	0.8	8.7	0.2
Costa Rica (I)	3	1.2	20.6	1.2	12.1	1.7
Foodie Farm	3	1.9	32.3	1.9	18.6	1.7
Glentanar (II)	3	1.2	15.2	3.9	47.1	0.3
Costa Rica (II)	3	0.1	1.8	0.9	8.9	0.2
Ghana (III)	3	0.5	8.3	1.3	12.7	0.7
Hong Kong	3	0.5	13.7	0.3	3.4	4.0
Australia	3	1.1	18.3	1.0	9.9	1.8
Tanganyika (II)	3	0.8	14.3	1.7	18.2	0.8

* Percentages are expressed on basis of amount originally present.

mediate lavas, treatment with cold carbonate reduced the size of the 270–310° endothermic peak (compare curves A and B, Fig. 2). The reduction in peak area is equivalent to 2 per cent gibbsite or 25 per cent of the alumina extracted by the cold alkali solution. Following this treatment gibbsite was, according to X-ray diffraction evidence, still present in the residue although it was not detectable by infrared absorption spectroscopy. Hematite was the only crystalline iron oxide noted in this sample but following dithionite treatment, which removed 5.7 per cent iron oxide, the 300° endothermic peak was reduced in size to an extent comparable with that resulting from the carbonate treatment. Again gibbsite was detectable in the residue by X-ray diffraction but not by infrared absorption.

The results for samples of other peaty podzols investigated, namely those of the clay from the B₃ horizons of Glentanar (I) and (II) profiles developed on a granitic till, follow the trend mentioned above. That is, the 300° endothermic peak is not affected by either cold carbonate treatment or by the removal of the free iron oxide by dithionite treatment (curves E and I, Fig. 2). It would appear, therefore, that the clay from the Drumboy (II) profile contains, in addition to gibbsite, a pseudo-gibbsite component which is closely associated with iron oxide – possibly a ferruginous gibbsite.

As to the nature of the components preferentially dissolved by cold carbonate solution from the other clays, one can merely postulate and then only in general

and hot sodium carbonate solutions

No. of extractions	Hot carbonate extract					% gibbsite from chemical analysis	% gibbsite from DTA
	%SiO ₂ *	mmole/100 g SiO ₂	%Al ₂ O ₃ *	mmole/100 g Al ₂ O ₃	SiO ₂ /Al ₂ O ₃ molar		
2	2.1	35.6	1.3	12.8	2.8	2.0	2.4
2	2.6	43.0	1.6	15.7	2.7	2.7	2.5
2	2.5	41.0	2.0	19.6	2.1	3.1	3.2
2	2.1	35.0	2.5	24.5	1.4	3.8	3.0
4	2.4	39.8	3.4	33.6	1.2	5.2	4.8
3	4.0	66.9	5.2	51.2	1.3	8.0	8.6
3	3.8	63.3	5.3	52.0	1.2	8.1	7.6
2	1.9	31.6	4.8	47.1	0.7	7.3	7.8
2	3.7	61.6	4.3	42.2	1.5	6.6	5.8
3	4.9	80.9	5.0	49.1	1.6	7.7	8.6
3	2.9	48.3	7.4	72.6	0.7	11.3	10.5
3	5.7	95.2	8.9	87.1	1.1	13.6	12.1
4	4.4	73.9	7.9	77.5	1.0	12.1	12.2
3	3.0	50.0	9.0	88.3	0.6	13.8	14.8
4	3.1	51.9	11.6	112.8	0.5	18.0	19.7
4	3.6	59.9	12.2	119.7	0.5	18.7	18.6

terms. The total amounts of silica and alumina dissolved by three alkali treatments are very small, the averages being 14.7 and 12.4 mmole/100 g of silica and alumina, respectively. These values could represent free silica and free alumina and/or aluminosilicate in poorly ordered and/or finely particulate forms [8, 9].

Following the cold sodium carbonate treatment the soil clays were given successive treatments with hot sodium carbonate solution until the alumina content of the extract was low and constant (Fig. 3), from 2 to 4 treatments being required. One treatment with hot sodium carbonate solution reduces the size of the 300° endothermic peak on the DTA curve (curve F, Fig. 2) and successive treatments result eventually in its disappearance (curve D, Fig. 1, curves C and G, Fig. 2), except on the curves for the six soils that contain a small amount of goethite. On the curves for these clays a small broad endothermic peak in the 300° region remains even after the alumina content of the carbonate extract has attained a low value. This small endothermic effect is consistent with the presence of 1–2 per cent goethite. In general, the number of hot sodium carbonate treatments required to remove the 300° endothermic effect on the DTA curves of the clays or to reduce it to minimum size is the number of extractions necessary to attain a low and constant value for alumina in the carbonate extract. Assuming that the alumina in the sodium carbonate extract results essentially

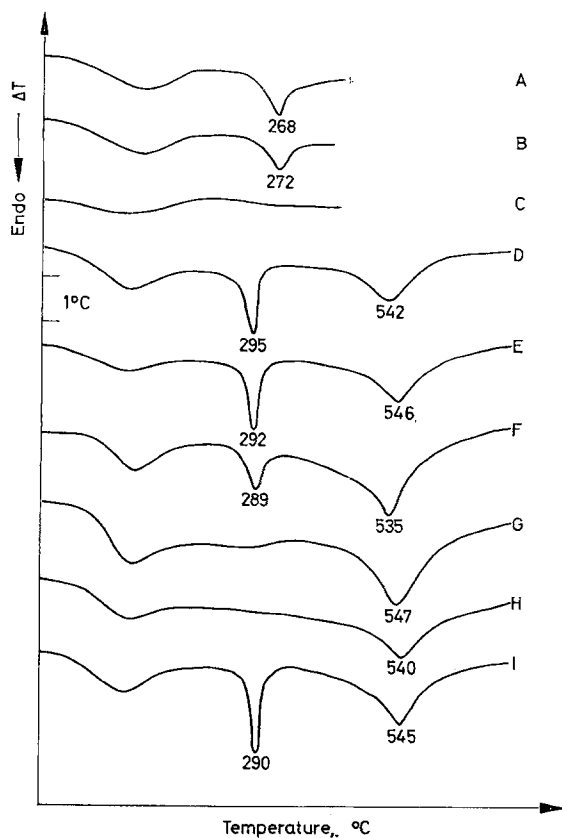


Fig. 2. DTA curves for soil clays: A – Drumboy (II), untreated; B – Drumboy (II) after treatment with cold sodium carbonate solution; C – Drumboy (II) after treatment with cold and hot sodium carbonate solution; D – Glentanar (II), untreated; E – Glentanar (II) after treatment with cold sodium carbonate solution; F – Glentanar (II) after treatment with cold sodium carbonate solution and *one* treatment with hot sodium carbonate solution; G – Glentanar (II) after treatment with cold sodium carbonate solution and *three* treatments with hot sodium carbonate solution; H – Glentanar (II) after treatment with hot 0.5 N caustic soda; I – Glentanar (II) after dithionite treatment*

from the dissolution of gibbsite in the clays, it can be seen from Table 1 that six clays with a gibbsite content of 2 to 7 per cent required two treatments; six, containing from 8 to 14 per cent gibbsite, had to have three treatments, and four clays with 5, 12, 18 and 19 per cent gibbsite required a fourth treatment before the 300° endothermic peak was markedly reduced or removed.

* Heating rate 10°/min; integral 3-well inconel block; chromel-alumel thermocouples, temperature thermocouple in reference; sample weight 100 mg diluted with 100 mg calcined kaolinite, reference 200 mg × 2 calcined kaolinite; oxygen free nitrogen over sample and references 200 ml/min.

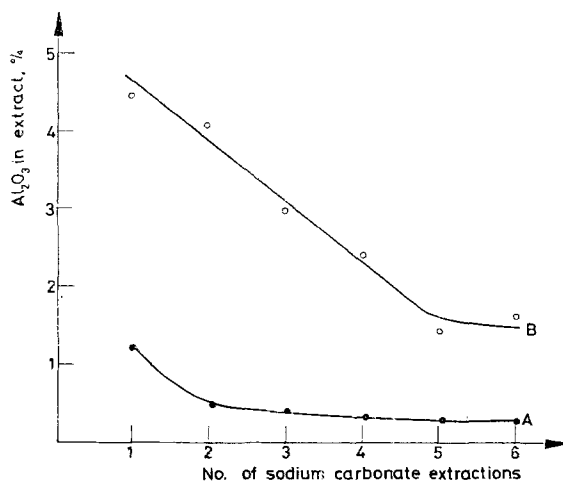


Fig. 3. Hot sodium carbonate solution extraction curves for: A — clay from B horizon of Longraw profile; B — clay from B horizon of Tanganyika (II) profile

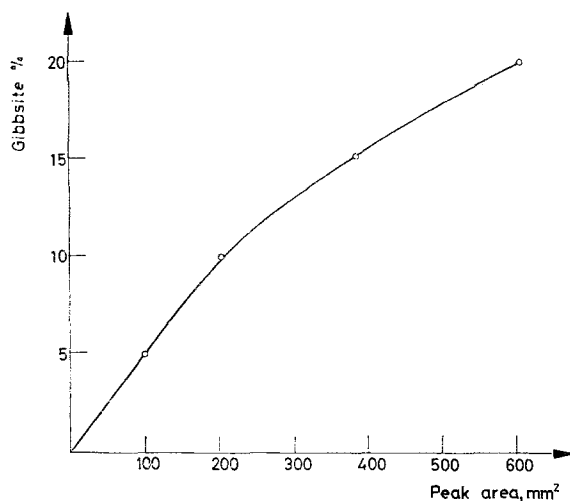


Fig. 4. Calibration curve for peak area against gibbsite content

In order to test this general correlation, the area of the 300° endothermic peak on the DTA curves for the clays was measured, a small correction being applied for these clays containing goethite, and the gibbsite content assessed from a calibration curve for peak area against gibbsite content (Fig. 4). This calibration curve was obtained by measuring the area of the 300° endothermic peak on the DTA curves of mixtures prepared from known amounts of high purity gibbsite from Suriname [10] and calcined kaolinite, 200 mg of a mixture being used for each determination.

In Fig. 5 the gibbsite percentage determined by DTA is plotted against gibbsite percentage calculated from the amount of alumina dissolved by hot sodium carbonate. By statistical analysis the following regression equation was found

$$y = -0.32 + 1.04x$$

with standard errors: ± 0.38 and ± 0.037 , respectively (y = per cent gibbsite from DTA, x = per cent gibbsite from carbonate dissolution). Since the intercept is not significantly different from zero, the assumption that the line passes through the origin would be acceptable. The equation for this line was found to be $y = 1.015x$ with a standard error of the slope of ± 0.019 . Thus, the slope

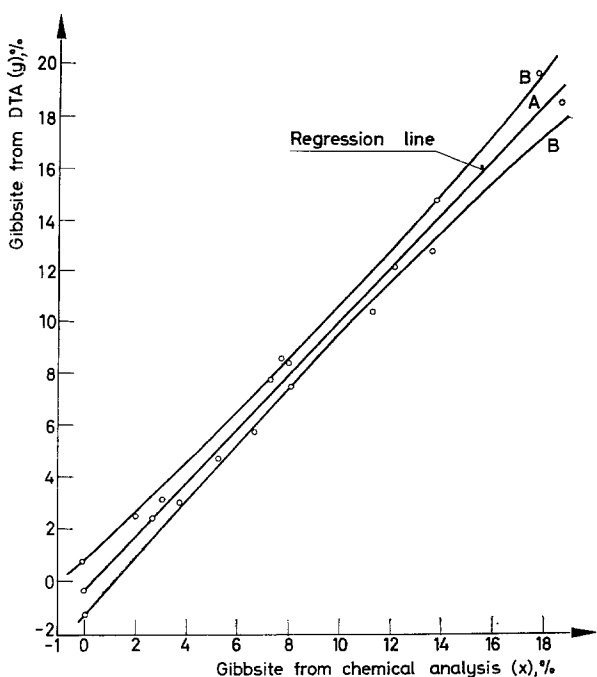


Fig. 5. Regression curve: $A - y = -0.32 + 1.04x$; $B - 99$ per cent confidence limits

does not differ significantly from unity, the relationship $y = x$ being consistent with the data; in other words, the same percentage of gibbsite is found by either method. One may then conclude that the greater part of the alumina dissolved by hot sodium carbonate solution results from the dissolution of gibbsite.

There was no evidence from X-ray examination of the residue to indicate that crystalline clay minerals had been adversely affected by hot carbonate treatment. Evidence of the lack of appreciable attack on these minerals was also provided by DTA, since the dehydration endothermic peak at about 100° and the

dehydroxylation peak in the 500° to 600° region were not significantly altered, in contrast to the effect on these peaks produced by sodium hydroxide treatment of the clays (curve H, Fig. 2). A large dehydration peak on the DTA curve of a soil clay can be indicative of an appreciable content of amorphous aluminosilicate (Mitchell and Farmer [10]). The dehydration peaks of the soil clays investigated varied from small to medium, providing no indication of a poorly-ordered aluminosilicate component. If material of this nature is present the amount must be small and it can only account for a small quantity of the silica and alumina in the hot carbonate extracts [10]. From 1.9 to 5.7 per cent (31.6 to 95.2 mmole/100 g) silica was removed from the soil clays with hot sodium carbonate and, from the above considerations, it would seem that much of this silica is free and is most likely a cryptocrystalline phase probably resembling a disordered cristobalite-tridymite intergrowth [8]. It is noteworthy that the Costa Rica (II) soil clay, which is representative of a soil in the final stage of laterization has the highest hot-carbonate-soluble silica value (5.7 per cent, 95.2 mmole/100 g).

This investigation has shown that poorly-ordered aluminous material and silica in varying amount are removed from soil clays by treatment with cold sodium carbonate solution. In one instance this treatment removed a gibbsite-like component closely associated with iron oxide. Treatment with hot sodium carbonate solution removes clay-size gibbsite and free cryptocrystalline silica without obvious destruction of the crystalline aluminosilicates. Although surface characteristics of the components of soil clays are probably of prime importance in determining their "alkali reactivity", degree of order and particle size are factors that must also be considered. In these experiments one has the dissolution not only of the surfaces of primary soil particles but also — and quantitatively more important — of soluble and sparingly soluble new phases formed by pedogenic processes. Temperature of extraction appears to be the principal experimental factor determining the success of a differential dissolution analysis with sodium carbonate solution, but other variables such as solid : solution ratio and the duration of extractions may also be important.

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RÉSUMÉ — Un équipement d'analyse thermique différentielle de précision a permis de déceler et d'estimer d'une manière sensible et précise la gibbsite dans les argiles du sol. En procédant à la dissolution du carbonate de sodium, combinée avec l'étude par ATD, on peut distinguer la gibbsite bienordonnée dans une substance alumineuse peu-ordonnée.

ZUSAMMENFASSUNG — Eine Präzisions-DTA-Einrichtung gestattet den empfindlichen und genauen Nachweis sowie die Bestimmung von Gibbsit in Tonmineralien. Wird die Methode mit einem Natriumkarbonat-Auflöseverfahren kombiniert, so ist es möglich, den gutgeordneten Gibbsit von schlechter geordneten aluminiumhaltigen Verbindungen zu unterscheiden.

Резюме. — Описан специальный прибор для дифференциального термического анализа (ДТА), являющийся чувствительным и точным для обнаружения и оценки гипсита в глине почвы. При сочетании ДТА и процедуры растворения с карбонатом натрия возможно отличать благоустроенный гипсит от гипсита слабо устроенного.