Table 1. Salient features of the mass spectrometric cracking pattern of tetraphenylbenzidine and of the volatile product produced by heating the montmorillonite triphenylamine complex at 40°C in a vacuum better than 10^{-7} torr. The m-equiv. ratios, the empirical formula of the fragments and relative intensity ratios are tabulated for the significant peaks

m-equiv.		Relative intensities: Tetraphenylbenzidine	Relative intensities: Volatile products from montmorillonite–triphenylamine complex
490	$[(Ph_2NC_6H_4)_2H_2]^+$	40	40
489	$[(Ph_2NC_6H_4)_2H]^+$	170	130
488	$[(Ph_2NC_6H_4)_2]^+$	420	310
487	$[(PH_2NC_6H_4NPhC_6H_4]^+$	8	9
245	$[(Ph_2NC_6H_4)_2H_2]^{2+}$	64	45
244.5	$[(Ph_2NC_6H_4)_2H]^{2+}$	38	39
244	$[(Ph_2NC_6H_4)_2]^{2+}$	105	100
168	$[Ph_2N]^+$	13	21
167	$[PhNC_6H_4]^+$	20	38
166	$[(C_2H_4)_2N]^+$	7	19

or: (2) a direct coupling between the para positions of the benzene rings of two triphenylamine radical cations followed by elimination of two protons.

We further note that the production of tetraphenylbenzidine is almost quantitative as evidenced by the similarity of the intensity of fragments having a m-equiv. ratio less than 245 in the cracking patterns of the pure organic and of the volatile product from the clay–organic complex.

Other reactions, the study of which is facilitated by mass spectrometry, will be reported in more detail elsewhere.

Experimental

Suspensions of Wyoming montmorillonite in alcohol (sedimented fraction of < 0·02 μm equivalent spherical diameter of Ward's standard clay mineral No. 48W 1250) were allowed to react with an alcohol solution of triphenylamine for one week. The resulting green material thoroughly washed in alcohol, separated and dried over calcium chloride in a vacuum desiccator, to yield a reddish purple product. The N,N,N′,N′-tetraphenylbenzidine was prepared by a method described by Wieland (1913).

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QUANTITATIVE MINERALOGICAL ANALYSIS OF SOIL CLAYS CONTAINING AMORPHOUS MATERIALS: A MODIFICATION OF THE ALEXIADES AND JACKSON PROCEDURE

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The scheme for quantitative mineralogical analysis of the clays of soils and sediments based on physico-chemical determinations as proposed by Alexiades and Jackson (1966) can be applied successfully to the analysis of clays which are chiefly composed of crystalline minerals. Cation exchange capacity (CEC) and potassium fixation capacity analyses are used for quantitative determination of the smectite and vermiculite components. In the calculations (Alexiades and Jackson, 1966, equation 2) amorphous material, determined separately, is assigned a CEC value of 110 m-equiv./100 g only if its SiO_2/R_2O_3 molar ratio is greater than 3·0. Amorphous inorganic constituents having a ratio less than 3·0 are assumed to have no CEC. A further assumption that amorphous minerals do not fix potassium on drying is implicit in the calculation for vermiculite (Alexiades and Jackson, 1966, equation 1).

Recent studies (Raman and Mortland, 1970; De Villiers, 1971) have indicated that soil amorphous aluminosilicates with varying SiO_2/R_2O_3 molar ratios lower than 3·0 also have considerable CEC. Similarly, amorphous components have been reported by van Reeuwijk and De Villiers (1968) and Raman and Mortland (1970) to have considerable K^+-fixation capacity. The assumptions made in the Alexiades and Jackson procedure might, therefore, lead to considerable error in the determination of smectite and vermiculite in soil clays containing large amounts of amorphous material. However, Briner and Jackson (1970) assumed a CEC value of 20–160 m-equiv./100 g for allophanes (from basaltic soils of Australia) with SiO_2/Al_2O_3 molar ratios ranging from 2·4–4·0 for quantitative clay mineral analysis. It is difficult to assign CEC and K^+-fixation capacity values to amorphous minerals for eliminating such errors unless a

quantitative relationship between composition and properties is first established. A possible solution to the problem would be removal of the amorphous minerals followed by mineralogical analysis of the crystalline residue.

Hashimoto and Jackson (1960) extracted amorphous aluminosilicates from clays with negligible damage to the crystalline components, by boiling the samples in 0·5 N NaOH for 2·5 minutes and cooling the reaction mixture immediately. This procedure was adopted here for preparation of clays free of amorphous constituents. A larger sample was used, but the ratio of sample to solution was maintained approximately.

Twenty-seven samples representing eight tropical ferruginous soil profiles of the Mysore plateau, India, were taken for this study. The clay fractions (<2 μm) of the soils were obtained by the segregation procedure of Jackson (1956). About 1 g of each clay was treated with boiling 0·5 N NaOH as indicated above. The residue was washed free of NaOH with methanol and stored in NaCl solution. Quantitative mineralogical analysis was carried but by the Alexiades and Jackson (1966) procedure on aliquots of the amorphous-free clays. The amorphous material content of the original clays was determined by the Hashimoto and Jackson (1960) method. The crystalline mineral content of the cleaned clay fraction was recalculated to the original clay basis. The quantitative mineralogical composition of the clays is presented in Table 1.

The sum of the various components determined in the 27 soil clays averaged 100·4 ± 0·42 (±standard error of means). This total of very near 100 per cent (maximum range 96·3 to 103·7 per cent) for the analyses shows the suitability of the modified procedure for kaolinitic clays containing considerable amorphous material. The alkali pretreatment to remove amorphous aluminosilicates appears

Table 1. Mineralogical composition of the clay fractions

Horizon	AFAS* (%)	Kaolinite (%)	Smectite (%)	Mica (%)	Quartz (%)	Feldspars (%)	Rutile + anatase (%)	Chlorite (%)	Total
				Profile 1. *Nandi series*					
A	24·9	53·5	2·3	14·0	4·5	1·3	0·7	0	101·2†
B_t	27·0	55·9	2·4	8·9	3·5	1·3	0·7	0	99·7†
C	21·8	50·1	1·6	15·0	10·1	1·0	0·6	0	100·2†
				Profile 2. *Chikbalapur series*					
A_p	22·6	45·8	0·5	14·3	14·0	2·2	0·9	0	100·3†
B_{t1}	23·9	50·8	0·4	13·4	11·7	1·8	1·1	0	103·1
B_{2t}	25·2	54·5	1·3	9·8	9·6	1·4	1·0	0	102·8
B_{cn}	22·9	59·6	0·4	10·2	8·6	1·0	1·0	0	103·7
				Profile 3. *Muddhanahalli ravine cut*					
B_1	24·9	60·3	0·7	8·4	6·1	1·1	0·7	0	102·2
B_{cn}	23·8	57·8	0·1	9·3	6·0	1·6	0·7	0	99·3
BL_2	18·3	70·5	0·1	6·3	5·3	1·0	0·7	0	102·2
BL_k	9·7	72·7	0·3	7·9	4·9	0·4	0·4	0	96·3
C	12·2	73·6	0·5	7·6	1·9	0·4	0·4	0	96·6
BL_4	18·7	70·2	0	10·2	0·4	0·2	1·7	0	101·4
				Profile 4. *Vijayapur series*					
A	22·5	34·8	2·2	16·2	17·5	2·9	1·1	0	97·2
B_t	27·0	28·7	2·8	16·1	17·6	2·9	1·7	0	96·8
B_{cn}	22·8	51·2	3·1	9·1	10·0	2·1	1·1	0	99·4
				Profile 5. *Malmachanahalli series*					
A_p	19·5	39·7	8·6	12·9	15·6	4·0	0·7	0	101·0†
B_2	19·6	29·3	10·4	15·0	12·6	2·5	0·9	0	100·3†
B_g	10·8	23·5	26·9	16·9	16·0	5·2	0·7	0	100·0†
				Profile 6. *Koppali series*					
A_p	31·2	52·4	1·2	7·5	8·9	0·4	0·6	0	102·2
B_{t1}	35·4	49·3	1·5	6·4	8·6	0·3	0·5	0	102·0
B_3	31·9	53·1	1·6	6·0	8·0	0·3	0·5	0	101·4
				Profile 7. *Royalpad series*					
A_p	25·1	55·0	3·0	9·6	7·3	0·5	1·1	0	101·6
B_{2t}	27·6	50·2	5·2	6·8	9·3	0·3	0·6	0	100·0†
B_{23}	28·3	49·4	7·0	5·3	9·5	0·3	0·6	0	100·4†
				Profile 8. *Nandi Cross*					
A	29·9	49·7	0·2	12·0	9·0	1·6	0·6	0	103·0
BL_4-b	13·6	71·4	0·9	5·0	4·1	0·5	0·8	0	96·3
								Average	100·4 ± 0·42

* Amorphous ferro-aluminosilicate; standard error of means $s_{\bar{x}}$ = 0·42; standard deviation, s = 2·205; coefficient of variation, c.v. = 2·15%.

† Within fiducial limits at the 5% level, ±0·872 = 0·42 × t, when t = 2·056, for 26 deg of freedom.

to be quite compatible with the original analytical scheme. Incidentally, El-Attar and Jackson (1973) have observed considerable thermal decomposition at 550°C of Fe-rich layers and/or interlayers in montmorillonitic soils of Nile River alluvium.

Additional information that can be deduced from the above procedure is the CEC and K^+-fixation capacity of the amorphous constituents of the clays provided these values are determined for the original clays also. The present modification avoids the assignment of arbitrary, possibly erroneous, values of CEC and K^+-fixation capacity values to the amorphous inorganic constituents of soil clays.

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SOME EFFECTS OF GRINDING KAOLINITE WITH POTASSIUM BROMIDE

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In a significant note published recently in this journal, Miller and Oulton (1972) described effects of mixing–grinding of kaolinite with KBr on the ratio R of the absorbance values of the 3695 and 3620 cm^{-1} bands and the percentage changes P (percentage) in absorbance, for each of the two bands using the 1002 cm^{-1} band as a reference standard. They found an increase of R with increasing time of grinding principally due to a decrease in intensity of the 3620 cm^{-1} band and also, as they reported, due in part to an increase in the 3695 cm^{-1} band. Following Parker (1969) who was able to show a correlation between R values and the crystallinity and shape of the kaolinite, the authors concluded that their results are due in part to a delamination of the kaolinite particles (tactoids) by the KBr, possibly aided by intercalation of the kaolinite by the water sorbed during the grinding. Although this suggestion seems to be reasonable, it cannot be supported by their results. The observations reported here do provide strong evidence for the occurrence of that delamination.

According to Farmer and Russell (1966), delamination can be examined from the intensity and position of the vibration of the Si–O^- band which gives a dipole oscillation perpendicular to the plates. For delaminated kaolinite, an infrared absorption occurs when the radiation is perpendicular to the crystal plates. Due to a field which opposes the dipole vibration, the force constant increases causing a rise in the vibration frequency V_1. With laminated kaolinite (tactoid) absorbance and frequency of absorption depend on the angle between the optical axis and the normal to the lattice wave. Thus a broad shoulder having a range of values is obtained which corresponds to absorption by randomly oriented particles. The frequencies of these absorptions are always lower than that of the single layer kaolinite. The sharpness and position of this band can therefore give information on the delamination of kaolinite during grinding in the presence of KBr and is examined below.

A mixture of 5 mg kaolinite from Georgia (Oneal Pit, Macon, supplied by Ward's Natural Science Establishment, Inc.) and 500 mg of KBr (BDH suitable for i.r. spectroscopy) was ground in an automatic porcelain mortar for various time periods. To avoid grinding effects in the preparation of the discs, 15 mg of the mixture were gently mixed manually with 120 mg of KBr. I.R. spectra were recorded on a Perkin–Elmer spectrophotometer, model 237. To obtain the spectrum of an unground kaolinite, 0·4 mg of the clay was gently mixed manually with 135 mg of KBr. Some of the spectra are given in Fig. 1.

The following positions for the different bands of the unground samples are (in cm^{-1}): A, 3700; B, 3670 (shoulder); C, 3657 (weak); D, 3627; E, 1115; F, 1031; G, 1007; H, 937 (weak); I, 912. The assignment used here is that of Miller and Oulton (1970).

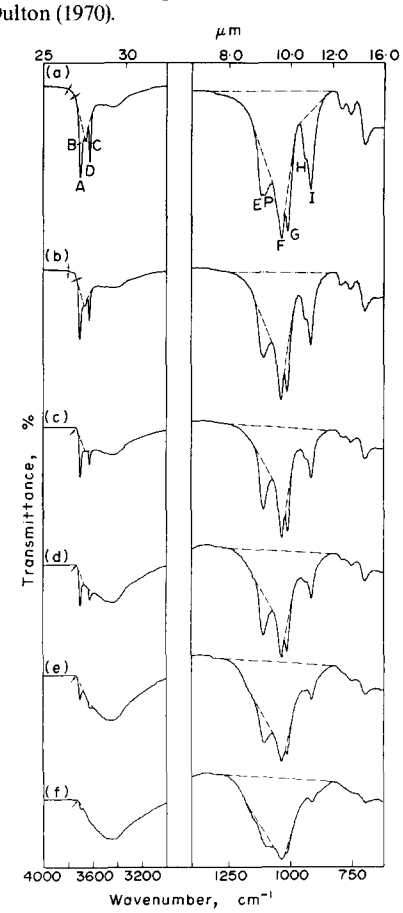

Fig. 1. The i.r. absorption spectra of kaolinite in KBr discs and the extrapolated base lines, (a) unground, (b) ground for 30 sec, (c) ground for 10 min, (d) ground for 20 min, (e) ground for 60 min and (f) ground for 120 min in the presence of KBr.