

A CLASSIFICATION OF KAOLINITES BY INFRARED SPECTROSCOPY

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ABSTRACT: A method is described for plotting and comparing measurements made on kaolinite clays. In this the ratio of the two strongest bands in the OH-stretch region of the spectrum (band maxima at $3695\text{--}3700\text{ cm}^{-1}$ and $3620\text{--}3625\text{ cm}^{-1}$) of an oriented preparation at 45° incidence is plotted against the corresponding ratio from the spectrum of a randomly oriented preparation. Both ratios are affected by the shape of the kaolinite particles and methods for minimizing this are given. The position of a kaolinite upon a plot so prepared gives information on the following points: (a) the type of kaolinite, (b) the degree of crystallinity of the kaolinite, (c) the shape of the kaolinite particles.

INTRODUCTION

In the infrared spectra of kaolinites there are two strong absorption bands in the OH-stretch region with maxima at $3695\text{--}3700\text{ cm}^{-1}$ $3620\text{--}3625\text{ cm}^{-1}$; the relative intensities of these bands depend not only upon the nature of the kaolinite but also upon the shape of the particles, their orientation and the angle of incidence of radiation upon the preparation examined in the spectrometer. Two of the standard methods of sample preparation are used to produce known orientations of kaolinite particles. In the first a dilute, deflocculated suspension is allowed to sediment onto a supporting surface whilst slowly evaporating. A glass disc is a suitable support in this range of wavenumbers. The kaolinite crystals in a film produced in this way are oriented, to a degree depending upon the particle shape, with the *c*-axis roughly perpendicular to the supporting surface. In the second method a very small proportion of kaolinite is ground in potassium bromide and the mixture compressed to a disc, in which the particles are in random orientation.

When a number of kaolinites are examined and the ratios A_{3695}/A_{3625} of the absorbancies of samples prepared by the two methods are plotted, concentrations of points occur in certain areas. Within each area a single type of kaolinite (fireclay type, china clay type, etc.) is dominant. A trend line for each type can be drawn through the points in the appropriate area (see Fig. 1).

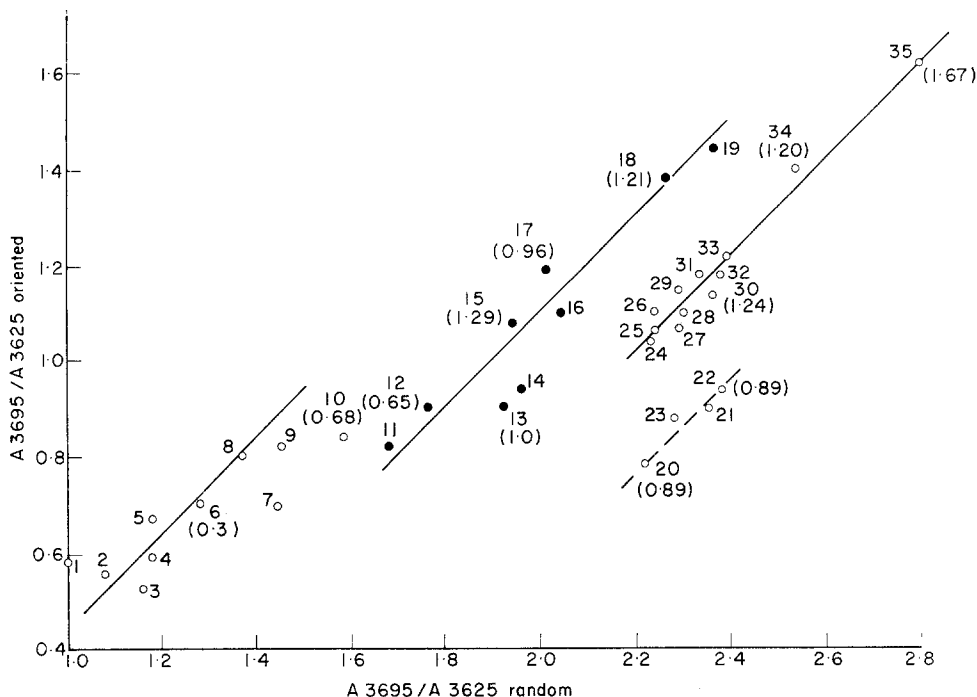


FIG. 1. A 3695/A 3625 ratio chart, with Hinckley crystallinity index figures in parentheses.

EXPERIMENTAL

Examples of the spectra from various types of kaolinite in different orientations have been given by Serratos, Hidalgo & Vinas (1962), Wolff (1963) and Farmer & Russell (1967). The procedure for measurement of band intensities in spectra, by the tangent base-line method, is well known. If numerical comparisons between spectra are to be made it is necessary to standardize the conditions under which they are produced and to apply corrections to some of the measurements.

To avoid distortion by the Christiansen effect in the spectrum from an oriented preparation the particle size should be finer than $1\ \mu$, and in order to reduce the absorbed water band with clays containing much fine mineral the finest part of the clay should be separated. Consequently monodisperse fractions, either $0.5\text{--}1\ \mu$ or $0.25\text{--}0.5\ \mu$, are usually preferable to whole clay samples. An incidental advantage of fractionation is that in many clays these fractions contain the highest proportion of kaolinite.

The spectra from oriented preparations are recorded at an angle of incidence of 45° , since the intensities of the bands at 3695 cm^{-1} and 3625 cm^{-1} are most nearly equal at this angle. In these spectra the ratio A 3695/A 3625 increases with

sample weight and the extent of this increase is dependent upon particle shape. Figures of change in A_{3695}/A_{3625} are given in Table 1 for four clays of known aspect ratio.

TABLE 1. Increase of A_{3695}/A_{3625} with A_{3625}

Clay, origin and number on Fig. 2.		Aspect ratio (0.5–1 μ)	Increase in A_{3695}/A_{3625} per 0.1 increase in A_{3625}
Zettlitz	(20)	16.6 : 1	0.04
Cornwall	(22)	12 : 1	0.06
Devon	(33)	8.2 : 1	0.07
Georgia	(14)	6 : 1	0.085

The measured ratio A_{3695}/A_{3625} should be adjusted to zero sample weight ($A_{3625}=0$). The correction can be estimated from Table 1 if the type of kaolinite has been identified, or, if the sample weight is small, the average correction factor, $-0.065 (A_{3695}/A_{3625})$ per 0.1 A_{3625} , can be used. Orientation in sedimented preparations is seldom perfect and there is a tendency for a majority of the particles to be slightly tilted in one direction. Compensation for this can be made by rotating the sample in its own plane between each of a number of readings and averaging the figures.

In spectra from randomly oriented samples the intensities of the absorption bands are linear with sample weight, but for kaolinites of high aspect ratio A_{3695} is enhanced. Examples of this effect of particle shape are given in Fig. 2, in which the ratios A_{3695}/A_{3625} are plotted against mean particle diameters of monodisperse fractions of a china clay and a Georgia kaolin. The aspect ratios of both these clays decrease with increase in particle size, since there is a progressive change from particles consisting of single plates towards particles composed of stacks of plate-shaped crystallites. The enhancement of A_{3695} is observed in the spectra from randomly oriented preparations, since it is only in these that a plate-shaped particle is edge-on to the incident radiation. In this position the absorption of the dipole producing the band at 3695 cm^{-1} is near maximum and the path length of the refracted ray within the crystal is also maximum.

The slope of the curve of the china clay is increased by mica. There is a concentration of mica-type mineral in the finest fraction. The remainder of the clay finer than $1\text{ }\mu$ is almost mica-free and there is a progressive increase in mica content with increase in particle size in the larger fractions. The principal mica found in china clay, of muscovite type, has an absorption band overlapping the kaolinite band at 3625 cm^{-1} but no absorption at 3695 cm^{-1} , so that mica decreases the ratio A_{3695}/A_{3625} . The Georgia kaolin is almost mica-free throughout the particle size range.

The effect of particle shape upon the measured ratio A_{3695}/A_{3625} is opposite

in spectra from samples prepared by the two methods so that it can be recognized and used to estimate differences in particle shape between clays, or the change in shape produced by mechanical treatment in a single clay.

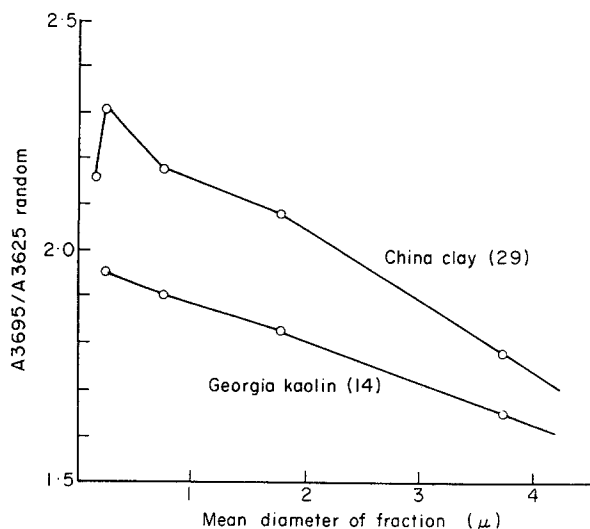


FIG. 2. A_{3695}/A_{3625} random against mean diameter of fraction.

THE A_{3695}/A_{3625} RATIO CHART

The A_{3695}/A_{3625} ratios of thirty-five clays are plotted in Fig. 1. On this chart the horizontal scale is the ratio from samples in random orientation (KBr disc preparation) and the vertical scale the ratio from oriented samples (sedimented film preparation) at 45° incidence. The clays are identified by numbers which are listed with their origin, particle size and X-ray crystallinity index figures in Table 2. On the chart three trend lines are drawn through the areas of greatest concentration of values for each of three types of kaolinite, fireclay (ball clay), Georgia kaolin and china clay. A similar but broken line is drawn through an area of lesser concentration of china clays, on the lower right-hand side. The four kaolinites which plot on the broken line have particles of high aspect ratio; the displacement of this group from the main trend line can be ascribed to the enhancement of the absorption at 3695 cm^{-1} by thin, plate-shaped particles in random orientation. Smaller displacements consequent upon particle shape differences are probable with many of the kaolinites.

Two of the clays on the chart have been described by previous workers. The first of these, No. 8, is Pugu D, a sedimentary clay from East Africa (Robertson, Brindley & MacKenzie, 1954). This is exceptional amongst the fireclay type clays since it is an almost pure kaolinite. The other clays in this group contain silica, as

quartz or amorphous, and mica. Silica does not affect the position of a clay but mica depresses it down the trend line; this displacement is not large. Sample 8 contains no mica, Sample 6 about 30% and Sample 4 about 12%. Sample 11, a Georgia type kaolinite from the South Devon ball clay area, has 17% of mica.

TABLE 2. Description of samples

No.	Origin	Fraction μ	Hinckley index
<i>Fireclay type kaolinite</i>			
1	Dorset Ball clay	0.5 -1	
2	Dorset Ball Clay	0.5 -1	
3	Dorset Ball Clay	0.5 -1	
4	Dorset Ball Clay	0.25-0.5	
5	S. Devon Ball Clay	0.25-0.5	
6	N. Devon Ball Clay	0.25-0.5	0.3
7	France, Provins	0 -1	
8	E. Africa, pugu D	0.5 -1	
9	N. England, Fireclay	0.5 -1	
10	S. Devon Ball Clay	0.5 -1	0.68
<i>Georgia kaolin type</i>			
11	S. Devon Ball Clay area	0.5 -1	
12	Georgia, U.S.A.	0.5 -1	0.65
13	Spain, Cuenca Province	0 -1	1.0
14	Georgia, U.S.A.	0.5 -1	
15	Venezuela, Bolivar State	0.5 -1	1.29
16	Georgia, U.S.A.	0.5 -1	
17	India, Kerala State	0.5 -1	0.96
18	Spain, Cuenca Province	0 -1	1.21
19	Georgia, U.S.A.	0.5 -1	
<i>China Clay Type</i>			
20	Czechoslovakia, Zettlitz	0.5 -1	0.89
21	Cornwall	0.5 -1	
22	Cornwall	0.5 -1	0.89
23	Cornwall	0.5 -1	
24	Wiltshire, Upper Chalk	0 -1	
25	Synthetic, hydrothermal	0 -0.5	
26	Lincolnshire, Oolite	0 -2	
27	Cornwall	0.5 -1	
28	Cornwall	0.5 -1	
29	Cornwall	0.5 -1	
30	Cornwall	0.5 -1	1.24
31	Cornwall	0.5 -1	
32	Cornwall	0.5 -1	
33	Devon	0.5 -1	
34	Mexico	0 -0.5	1.2
35	Russia	0 -0.5	1.67

The second described sample is No. 28; this clay is similar to that used by Brindley & Robinson (1945) for their X-ray study of the crystal structure of kaolinite. It is a Cornish china clay and on the chart is adjacent to a group of clays of similar type, Nos. 29–33, from Devon and Cornwall. Two samples having higher A 3695/A 3625 ratios, Nos. 34 and 35, are from Mexico and Russia respectively.

The central trend-line runs through the Georgia kaolin-type clay (distinguished by solid circles). This name has been used because it is in that part of North America that this type of clay is exploited on the largest scale. However, it is widely distributed. Of the samples on the chart only four are from North America, the remainder are from South America, Asia and Europe. The four kaolinites on the broken trend-line on the lower right-hand side of the chart are characterized by thin crystals; these are plastic china clays. Opposite, on the lower left-hand side, are the highly plastic ball clays, also characterized by thin crystals. The kaolinites on the main china clay trend-line and the Georgia kaolin line are of medium to low aspect ratio; in both, samples having thicker crystals are found towards the top of the chart.

All the samples along the two china clay trend lines and the Georgia kaolin line are (as tested) substantially pure kaolinite, except No. 11 which has been described above. They are, with three exceptions, either used in industry or are potentially useful. The three exceptions are: No. 24, the residue from solution in acid of a sample of the Upper Chalk, from Wiltshire; No. 25, a synthetic kaolinite prepared hydrothermally in this laboratory; No. 26, a fine fraction from a sandstone overlying the Upper Chamosite in the Lincolnshire iron-ore field.

CRYSTALLINITY INDEX

There is a general relationship between the Hinckley X-ray crystallinity index and the A 3695/A 3625 oriented ratio so that this index increases from bottom to top of the chart; however, there is no agreement in detail. The relationship is best seen when the crystallinity index figures are marked at the appropriate levels. This has been done on Fig. 1.

DISCUSSION

The principal features of the A 3695/A 3625 ratio chart are the lateral displacements of the trend lines along the A 3695/A 3625 random scale and the vertical displacement of kaolinites of each type on the A 3695/A 3625 oriented scale; these are connected with the degree of disorder in the crystal, as is shown by the crystallinity index figures. The displacements on the random scale are caused by the change in the angles of the dipoles relative to the basal surface of the crystal consequent upon the transition from the triclinic form (china clay type) to the pseudo-monoclinic form (fireclay type). On the oriented scale, at 45° incidence, the relative absorptions of the dipoles are independent of the dipole angles, so that differences between kaolinites are most probably attributable to changes in the numbers of protons participating in the two vibrations.

The absorption band at 3625 cm^{-1} is produced by hydroxyls which lie wholly within the kaolin layers with the proton-end directed towards the octahedral vacancy, that at 3695 cm^{-1} by hydroxyls in which the dipoles are directed nearly perpendicular to the basal surface of the crystal (Wolff, 1963; Fripiat & Toussaint, 1963; Ledoux & White, 1964). There is a general relationship between the $A\ 3695/A\ 3625$ oriented ratio and crystal shape. The kaolinites in which thin crystals predominate are found in the lower part of the chart, the plastic china clays along the short, broken trend line on the right, and the highly plastic ball clays in the lower left-hand part. The hydroxyls responsible for the absorption band at 3695 cm^{-1} are oriented so that hydrogen bonding to the oxygens of the adjacent kaolin layer is possible and it is suggested that the $A\ 3695/A\ 3625$ oriented ratio is a measure of the extent to which this interlayer bonding occurs in any particular kaolinite.

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