The identification of transition aluminas from X-ray data

There are well recognized difficulties in distinguishing between the transition aluminas and interpreting the conflicting nomenclature used by different authors [1]. As most of the evidence for the differentiation of these forms of alumina is X-ray data, it was thought of interest to analyse the data using cluster analysis [2]. This statistical method has been used with considerable success in areas such as geology [3] and bacteriology [4] where similar classification problems have been encountered. The technique is used to investigate data where there are many samples and many characteristics; in the present instance 24 sets of X-ray data each consisting of many *d*-spacings and their intensities [5–12].

Using the data reported by Rooksby for the gamma-form [5] (sample A), the seven strongest lines were selected and their positions noted. The X-ray data for the other 23 samples (labelled B to Y) were inspected and in each case the seven *d*-spacings closest to those of the gamma-form were selected. For some samples there was uncertainty over which of two adjacent lines to use and in those cases both sets of data were included. This was indicated by the use of subscripts, i.e. $N_1 \ldots N_4$, a procedure which increased the number of data sets to 36.

TABLE I Table of sample similarity coefficients

Samples	Samples			
	N_2	K	T	Q_1
N_2	000			
K	147	000		
T	222	303	000	
Q_1	430	157	402	000

A similarity coefficient (S) was then calculated between each pair of data sets by summing the differences between the corresponding *d*-spacing values taking all the differences as positive. The range of the similarity coefficients was adjusted to 0 to 1000 by multiplying the values by 10^3:

$$S = \Sigma |x_1 - y_1| \times 10^3$$

where x_1 and y_1 are the corresponding *d*-spacings for the pair of samples.

Comparing each sample with every other sample resulted in 1260 similarity coefficients, examples of which are given in Table I. The importance of these samples N_2, K, T and Q_1 will be explained later. Examination of the results indicated that most of the samples occurred in three groups with low inter-group similarity values and high intra-group similarity values. Models of the distribution of the groups and isolated samples were constructed in both two and three dimensions. With the exception of sample Y, alpha-alumina, all the other samples could be satisfactorily positioned in the three-dimensional

TABLE II Details of the groups and isolated samples

Group or sample	Forms in group	Number of samples	Number of data sets	Comments
One (N_2)	Gamma + eta	4 3	7 3	Two forms occur at random within group
Two (K)	Delta + theta	4 4	7 4	Two forms at opposite ends of group
Three (T)	Chi	5	5	
Q	Kappa	1	4	These two samples difficult to position in models
R	Kappa	1	4	
X	Iota	1	1	Remote from other samples
Y	Alpha	1	1	Could not be placed in models

TABLE III d-spacings for the identification of unknown samples (Å)

(a) Limits for selection of d-spacings

Upper	1.410	1.550	2.150	2.340	2.572	2.880	4.660
Lower	1.388	1.500	1.956	2.240	2.380	2.720	4.470

(b) d-spacings for comparison with those of unknown sample

Sample								Group	Range
N_2	1.395	1.520	1.990	2.284	2.397	2.770	4.600	1	120
K	1.392	1.543	1.989	2.311	2.457	2.737	–	2	90
T	1.394	–	2.126	–	2.404	2.848	–	3	60
Q_1	1.393	1.543	2.011	2.323	2.572	2.730	4.470	–	–
R_1	1.400	1.550	2.130	2.340	2.430	2.720	4.520	–	–
X	1.410	1.550	2.150	2.240	–	2.720	–	–	–

Where a d-spacing is missing the comparison of that particular line is ignored and the summation is of less than seven comparisons. The similarity coefficients between N_2, K and T are given in Table I and may be used for checking the method of calculation.

model. This and other relevant information is given in Table II.

In all the instances where alternative d-spacings have been used the samples always occur in the same group, i.e. $N_1 \ldots N_4$ are all found in Group One.

The demonstration that three separate groups can be differentiated by cluster analysis of the X-ray data does not, in itself, throw any light on the basis for the difference between the groups. They may belong to different crystal systems or merely have differing amounts of lattice disorder associated in some cases with a very small particle size.

In the initial stages of the calculations the intensities of the X-ray lines had also been included to give 14 characteristics rather than 7. However, better results were obtained with the d-spacings alone probably indicating the known unreliability of intensity data.

From the results of these calculations it was possible to derive a simple method for the assignment of aluminas to the appropriate group. A central sample was chosen for each group and the largest similarity value to that sample from the group members taken as an indication of the extent of the group. This value, 120 for Group One, is given as the "range" in Table III.

For any unidentified alumina the seven d-spacings which fall within the limits given in the first section of Table III are selected. Using these values three similarity coefficients are calculated between the unidentified sample and the representative samples of the three groups, N_2, K and T. If the calculated similarity value is less than that indicated in the "range" column of Table III for a particular group then the unknown sample is a member of that group.

The appropriate spacings for the kappa and iota forms have also been included in the table for those cases where the unknown alumina does not belong to one of the three main groups; three out of twenty-three in the present study. Where a d-spacing is missing the comparison of that particular line is ignored and the summation is of less than seven comparisons. The similarity coefficients between N_2, K and T are given in Table I and may be used for checking the method of calculation.

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Estimation of dolomite mineral in limestone by infra-red spectroscopy

Dolomite, $CaMG(CO_3)_2$, occurring as an impurity in limestone mineral has been observed to be the major contributor to the ultimate MgO content of cement clinker. Further, the recent investigation [1] on the high magnesia clinker up to at least 10% MgO makes it necessary to assess the mineral forms in which MgO occurs in limestone. As such the detection and estimation of dolomite in limestone is important. Earlier infra-red study [2] was limited to the estimation or calcite using the 975 cm^{-1} band. However, this band is not unique since other carbonates (dolomite, etc) contribute to it and in general the band is split. In this communication, we are reporting an infra-red spectral technique for rapid estimation of dolomite and the results of the analysis have been compared with other existing techniques.

The infra-red spectra of calcite and dolomite are characterized by bands at 711 and 727 cm^{-1},

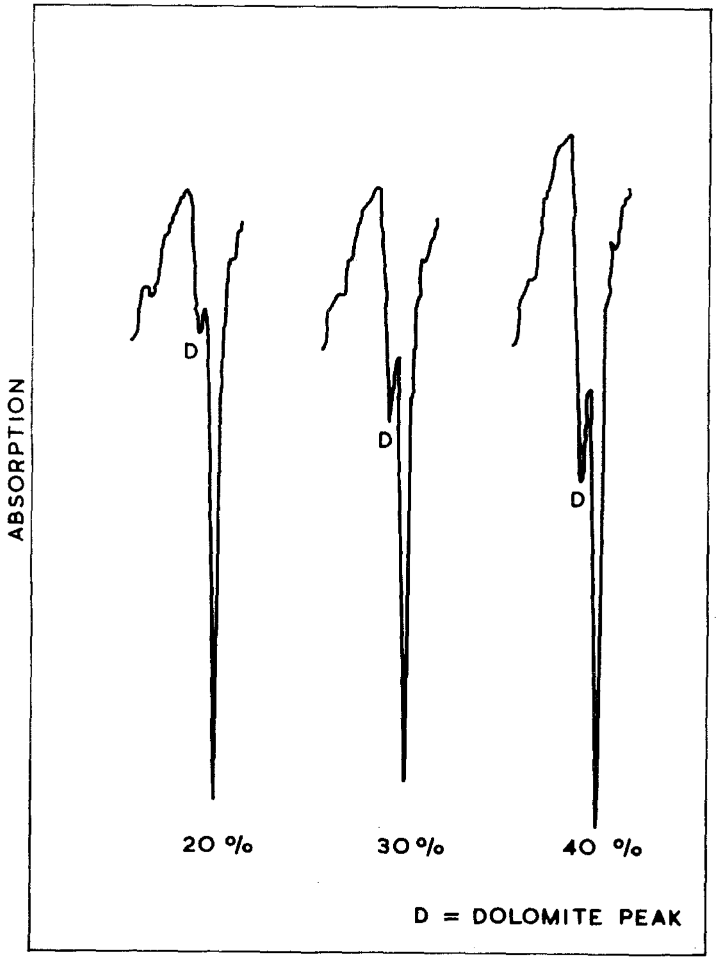

Figure 1 Infra-red spectra of standard mixes.