

## RAPID, QUANTITATIVE ILLITE DETERMINATION IN POLYCOMPONENT MIXTURES<sup>1</sup>

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### ABSTRACT

Angular line broadening of illites decreases linearly the (001) intensity of reflection. The factor ( $F_{mi}$ ) by which observed (001) peak heights of illitic muscovite should be multiplied are expressed by the equation:  $F_{mi}=0.494 D$ , where  $D$  is the total angular peak spread measured in degrees.  $F_{mi}$  varies from 1.0 at  $D=2.5$  degrees for pegmatitic muscovite to 27.5 at  $D=57$  degrees for purified Fithian illite. Line broadening does not appear to be significantly influenced by particle size; broadening may be related to a decrease in  $K_2O$  content. This procedure for quantification of illite is rapid, is based entirely on quantitative  $x$ -ray methods, and does not depend upon the intensity shape factors for other minerals present in the mixture.

### INTRODUCTION

During the course of a clay-shale utilization project jointly conducted by the U. S. Bureau of Mines and the Pennsylvania Geological Survey, quantitative  $x$ -ray mineral analysis of clays and shales was initiated. The major problems requiring solution were:

1) a rapid method of sample preparation to accommodate several hundred samples in a relatively short length of time, 2) accurate quantitative identification of five major components: 14–15Å minerals (chlorite, vermiculite, and montmorillonite), illite, kaolinite, quartz and feldspar, and 3) adjustment of the variable intensities of illite resulting from its differential  $x$ -ray reflectivity characteristics.

Several methods have been devised and summarized by Freas (1962, p. 1343) to correct for illite percentage error. They have been based upon either theoretical structural calculations, or upon curves determined empirically utilizing standard mixtures or a comparison with other methods of quantitative mineral determination. Freas (1962) found that the area under the kaolinite (001) peak was three times the area under the illite (001) peak. However, Freas' method presupposes the separation of other 7Å reflections from the contribution of kaolinite, and also yields a relative illite intensity factor (relative to the shape factor for kaolinite), rather than an absolute measure of the reduction in illite intensity. As a consequence, a more generally applicable intensity factor was desired.

### TECHNIQUE

Crushed samples ground for 15 minutes (or until the quartz was approximately finer than 250 mesh) were backfilled in a standard aluminum sample holder. Slide sedimentation was not used because of the time

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involved and because non-layer lattice minerals were to be quantified simultaneously with layer lattice silicates. The samples were *x*-rayed on a Norelco diffractometer at 1 degree  $2\theta$  per minute at a scale factor of 8, a multiplier of 1.0 and a time constant of 4. Peak height was averaged from three runs per sample. Illite line broadening was determined by drawing tangents from the peak to the baseline juncture on both sides of the peak and measuring the total angle. The angles were averaged for each of the three runs. Where an obvious low angle peak occurred at 11.5 to 12.5Å indicating a regular interstratification with a 14–15Å component, this secondary peak was excluded from the angular peak measurement. The angular range for the same sample approximates 2.5 degrees for small angles and 6 degrees for large angles. However, peak intensity varies directly with this range so that the error in angular measurements is actually less than the 2.5 to 6 degree variation.

Initial quantification of the 5 major components was made from a series of artificial mixtures. The 14–15Å component was composed of a 3:2 mixture of vermiculite:chlorite. Crystalline pegmatitic muscovite with a peak breadth of 2.5 degrees was used for the 10Å component. A minimum of 9 runs was averaged for all standard samples. Two standard graphs were prepared: one, directly from averaged peak intensities at a constant scale factor of 8 and multiplier of 1.0, and another, a fraction of the sum of all the peak intensities calculated to 100 per cent. The resultant curves were slightly non-linear as a result of matrix absorption.

#### ILLITE INTENSITY FACTORS

Quantitative mineral per cent of unknowns determined from the two standard graphs vary considerably. Because this variation was considered to be largely the result of a reduction in the intensity of illite (001) reflection (other clay minerals constituted less than ten per cent of the unknowns) and because quartz should be relatively unaffected both by orientation and structural strain, the observed mica peak intensity was multiplied by a factor necessary to bring the quartz intensities from the two standard curves into agreement. The resultant mica value was then added to the intensities for the other mineral components and recalculated proportionately to 100 per cent.

Although this method was thought to be reliable, measurement of angular peak breadth was used first as a check and second in the hope of arriving at a simpler method for calculating the illite factor. The effect of grain size on peak breadth was investigated by grinding pegmatitic mica for periods from  $\frac{1}{2}$  hour to 36 hours by several methods: hand mortar and pestle, automatic mortar and pestle, ball mill, and rotary plate grinder. Although there was a complete gradation in (001)

intensity from 2400 c.p.s. to 20 c.p.s. at 36 hours in the rotary plate grinder, no appreciable line broadening was observed. Consequently, the illite factor determined by the agreement of quartz percentages from the two quartz curves was plotted against the (001) angular peak breadth (Fig. 1). The curve is linear with a very small scatter, supporting the theory that structural strain, rather than grain size, is the significant cause of broadening. Similarly, the linearity and minor point scatter reinforces the assumption that quartz is an accurate quantitative internal

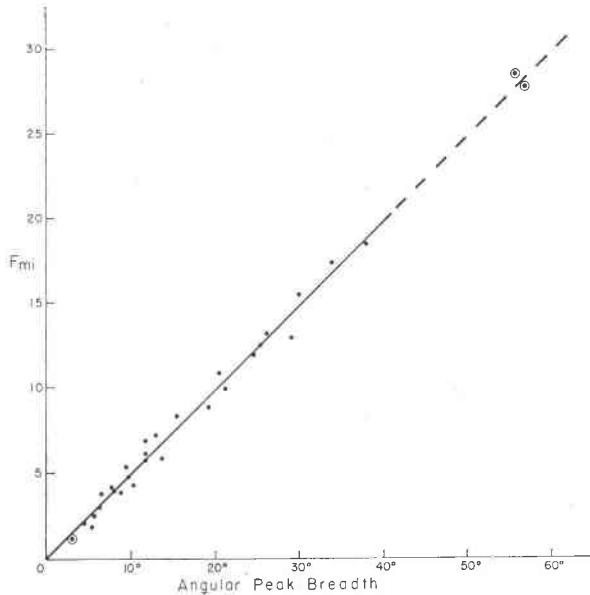


FIG. 1. Intensity factor ( $F_{mi}$ ) vs. angular line broadening in illitic mica.

standard. Purified Fithian illite and the crystalline pegmatitic muscovite used in the standards form the two end-points of the curve (Fig. 1, open circles). Their intensities were determined by counting at fixed time.

The equation of the curve in Fig. 1 is:

$$F_{mi} = 0.494 D$$

where  $F_{mi}$  is the multiplier factor for illite, and  $D$  the total degrees angular peak breadth. Maximum variation of  $F_{mi}$  from the curve is 0.6. Some line broadening variation may be due to interlayer expansion resulting from cation or hydroxyl substitution, or from variable water interlayers. However, for most samples the  $F_{mi}$ - $D$  points plot quite close

to the empirical curve. The accuracy of illite determination by this method is approximately  $\pm 6\%$  between 25% and 55% mica content for the 5-component mixtures, and will be higher for mixtures with fewer components or with no 14–15 Å clay minerals.

Because structural strain in illites may be, at least in part, a function of bond angle distortion resulting from a deficiency of  $K_2O$ , the  $K_2O$  content from bulk sample chemical analyses may vary proportionately with peak breadth. A small amount of  $K_2O$ , corresponding to one-half

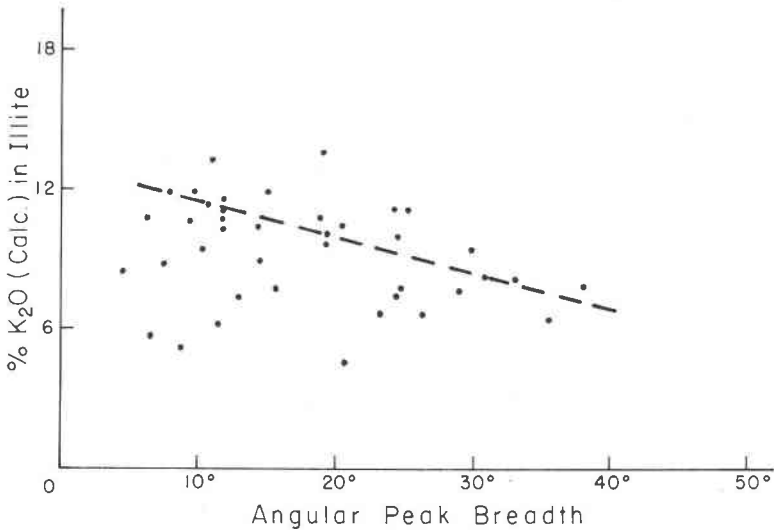


FIG. 2. Per cent  $K_2O$  in illites vs. angular line broadening.

the graphically determined total feldspar content, was subtracted from chemical analyses provided for the clay-shale project. This  $K_2O$  content was then recalculated to compare with the stoichiometric 11.9% of theoretically saturated muscovite, and plotted against peak breadth in Fig. 2. A tendency for parallelism between  $K_2O$  decrease and increased line broadening can be seen between 12% and 6%  $K_2O$ .

#### CONCLUSIONS

Illite can be quantitatively determined by measuring the angular peak breadth of the (001) reflection and graphically reading the corresponding multiplier factor which should then be multiplied by the observed peak height. This method obviates the necessity of measuring half height peak widths, which are inaccurate for very narrow or irregularly broad reflections. This intensity factor is independent of the intensity

shape factor of other minerals present, with the exception of matrix absorption corrections. Enhancement of basal reflections by the standard slide sedimentation technique, a procedure which would decrease the peak intensity of non-layer lattice components in complex mixtures, is not necessary for rapid and reasonably accurate mineral analysis (a maximum error of  $\pm 6\%$ ).

Line broadening appears to be primarily the result of structural strain within the mica, rather than the result of a decrease in grain size. It is directly proportional to decrease in peak intensity and very crudely proportional to a decrease in  $K_2O$  content of the mica.

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#### REFERENCE

- FREAS, DONALD H. (1962) Occurrence, mineralogy, and origin of the lower Golden Valley kaolinitic clay deposits near Dickinson, North Dakota, *Geol. Soc. Am. Bull.* **73**, 1341-1364.

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