NOTES

LONG-SPACING ORGANICS FOR CALIBRATING LONG SPACINGS OF INTERSTRATIFIED CLAY MINERALS

Key Words—Alcohols, Calibration, Interstratification, Long spacings, X-ray powder diffraction.

The calibration of X-ray diffractometers for measurements of d-spacings greater than 20 Å, such as occur in regularly interstratified clay minerals, requires standards with similar long spacings. The usual calibrations based on reflections from quartz or silicon do not extend below $2\theta \simeq 21°$ or $28°$ (CuKα radiation) respectively, and extrapolations to $2\theta \simeq 2°$ to cover d-spacings up to or even beyond 30 Å are not reliable. It follows from the Bragg equation that any error in measuring 2θ at small angles ($2\theta < 10°$) leads to the same percent error in d-spacings. Micas and chlorites can be used to calibrate spacings up to 10 and 14 Å, but these fall short of the long spacings of interstratified minerals; the reflections from these minerals also must be calibrated with respect to quartz or silicon reflections. Brindley and Wan (1974) advocated the use of long-spacing alcohols and alkanes for long-spacing calibrations. Although these substances with known basal spacings (Brindley and Wan found good agreement between their data based on quartz calibrations and those of other investigators) can probably be used as primary standards, it will be a useful precaution to compare such standards with either quartz or silicon. The alternative procedure to determine long spacings accurately is to measure higher order reflections. The higher orders, however, may be confused by reflections from other components in a mixed sample, and they may be weak or broadened. In any case, when long spacings are recorded from clay minerals it is useful to be able to measure them directly with reasonable accuracy, hopefully to 0.5%.

The present note (1) emphasizes the previous recommendations of Brindley and Wan (1974), (2) illustrates the very sharp reflections obtainable from long-spacing organics which are eminently suitable for low-angle calibrations, and (3) shows that with good adjustment of the goniometer small and nearly constant corrections to 2θ (observed) are obtained down to $2\theta \simeq 2°$.

Preparation of a standard slide

Samples are prepared very easily by melting a few mg of the organic material on a glass slide and allowing the melt to cool and crystallize. The preparation *must* be thin because of the low attenuation coefficients of these materials. Good orientation of the organic crystals is automatically achieved, and a long series of integral orders is obtained.

Figure 1 reproduces the pattern taken with CuKα radiation for tetradecanol, $C_{14}H_{29}OH$; similar patterns are obtained with C_{16}-, C_{18}-, and C_{20}-alcohols, and with C_{26}-, C_{28}-, and C_{30}- alkanes as described previously. The many sharp and strong reflections between $2°$ and $20°2\theta$ should be noted, as well as the weaker but easily measured reflections between $20°$ and $50°2\theta$. This pattern was recorded with a Philips Norelco instrument of 1960 vintage with a $\frac{1}{4}°$ incident slit and a scanning rate of $1°2\theta/\text{min}$. For convenience and accuracy in measuring 2θ, the pattern was recorded at a chart speed of $1°2\theta/\text{inch}$, but for reproduction in Figure 1, $2°2\theta/\text{inch}$ was preferred.

Evaluation of data

Table 1 records values of 2θ (observed) for 00ℓ reflections, $\ell = 1–21$. The basal spacing of the material is determined from reflections in the range $26°–48°2\theta$, where the observed values
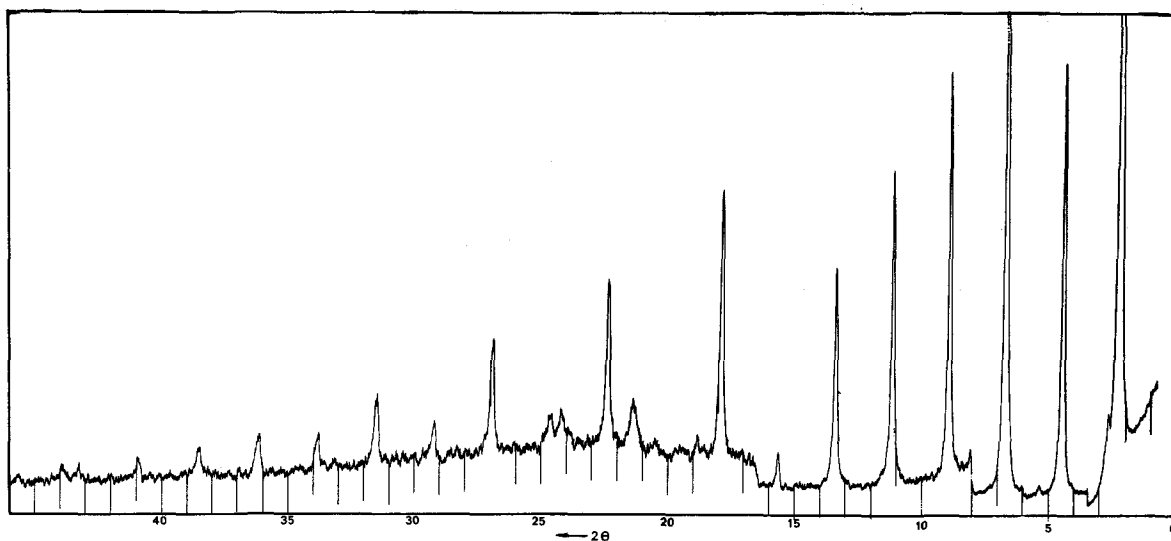

Figure 1. Diffractometer pattern of thin, oriented layer of tetradecanol, $C_{14}H_{29}OH$. Operating conditions: $\ell = 1$, 25 kV, 10 mA; $\ell = 2–19$, 40 kV, 15 mA. Recording conditions: $\ell = 1–3$, (16-1-4); $\ell = 4–7$, (8-1-4), $\ell = 8–19$, (4-1-4), where numbers in parentheses signify scalar setting, multiplier, and time constant, respectively. For other conditions, see text.

Table 1. Calibration of an X-ray diffractometer using CuKα radiation to measure d-spacings of tetradecanol.

ℓ	(00ℓ) observed (°2θ)	(00ℓ) corrected (°2θ)	d(00ℓ) (Å)	d(001) (Å)	d calculated (Å)	°2θ corrected	$\Delta(2\theta) =$ 2θ(cor.) − 2θ(obs.)
1	2.24 (5)				39.681	2.235	−0.01
2	4.44				19.840	4.45	0.01
3	6.67				13.227	6.68	0.01
4	8.89				9.920	8.91	0.02
5	.11.14				7.9362	11.15	0.01
6	13.37				6.6135	13.39	0.02
7	15.59				5.6687	15.63	0.04
8	17.85 (5)				4.9601	17.88	0.03
9	—				4.4090	—	—
10	22.38 (5)				3.9681	22.40	0.01 (5)
11	24.65				3.6074	24.68	0.03
12	26.94	26.97	3.3058	39.670	3.3067	26.96	0.02
13	29.22	29.25	3.0531	39.690	3.0524	29.26	0.04
14	31.54	31.57	2.8339	39.675	2.8343	31.56	0.02
15	33.87	33.90	2.6442	39.663	2.6454	33.89	0.02
16	36.20	36.23	2.4793	39.669	2.4800	36.22	0.02
17	38.52	38.55	2.3353	39.700	2.3342	38.57	0.05
18	40.93	40.96	2.2033	39.659	2.2045	40.94	0.01
19	43.26	43.29	2.0900	39.710	2.0885	43.32	0.06
20	—	—	—	—	1.9840	—	—
21	48.12	48.14	1.8901	39.692	1.8896	48.15	0.03

Avg. 39.681 ± 0.015

of 2θ are corrected on the basis of similarly recorded silicon reflections. From these corrected values of 2θ, the mean value of d(001) for the organic material is 39.68 ± 0.01(5) Å, and the ± variation is the mean deviation from the average. Brindley and Wan previously gave 39.63 ± 0.02 Å. From this value, calculated values of d(00ℓ) and hence of 2θ are obtained for the full range of reflections. Finally, values of $\Delta(2\theta) = 2\theta$ (corrected) − 2θ (observed) are obtained. When $\Delta(2\theta)$ is positive, this amount is to be added to 2θ (observed). A smoothed correction curve indicates that $\Delta(2\theta)$ is 0.01° in the range 2°–7°2θ, 0.02 in the range 8°–15°2θ, and 0.03 in the range 16°–40°2θ. Corrections at higher angles can be based directly on quartz or silicon data.

Before the data in Table 1 were recorded, the goniometer was adjusted so that the incident X-ray beam with ¼° incident slit was centered on a fluorescent screen mounted in the usual specimen position and also centered at 0°2θ. With these adjustments and with the calibration as described, 2θ values can be obtained correctly to about 0.01°2θ and d-spacings of the order of 30–40 Å can be measured directly to about 0.5%; higher orders can be measured to 0.1%.

In conclusion, the main point of this note is to emphasize that the many sharp reflections provided by thin layers of recrystallized long-spacing alcohols and alkanes, of which tetradecanol is typical, provide excellent calibrations for measurements of d-spacings up to 50 Å.

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REFERENCE

Brindley, G. W. and Wan, Hsien-Ming (1974) Use of long-spacing alcohols and alkanes for calibration of long-spacings from layer silicates, particularly clay minerals: *Clays & Clay Minerals* **22,** 313–317.