USE OF LONG-SPACING ALCOHOLS AND ALKANES FOR CALIBRATION OF LONG SPACINGS FROM LAYER SILICATES, PARTICULARLY CLAY MINERALS

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Abstract—Lattice spacings of layer silicates, particularly clay minerals, may exceed 20 Å. The errors in measuring lattice spacings increase rapidly for spacings greater than about 10 Å and diffraction angles 2θ less than about 10°. Long-chain organic compounds, such as normal alcohols, C_{14}–C_{20}, and normal alkanes (paraffins), C_{26}–C_{30}, provide useful calibrations for lattice spacings in the range 10–50 Å. The basal spacings of the calibrating substances are determined from their higher order reflections in the angular range where reflections from quartz and silicon are used as standards.

INTRODUCTION

The measurement of lattice spacings greater than about 10 Å in layer silicates, particularly in clay minerals, is subject to several sources of error, of which some arise in the conventional use of diffractometers, and others are related to the nature of the diffracting materials and the diffraction process itself. Kittrick (1960) emphasized that when X-ray diffractometers are adjusted by observing reflections from silicon or quartz powders, any lack of perfection in the adjustment or in the instrument itself becomes greatly magnified when measurements are made at small angles. If the Bragg equation, $n\lambda = 2d\sin\theta$, is written in the approximate form $n\lambda \simeq d.2\theta$, which is valid for small angles, then by differentiation $\Delta d/d = -\Delta(2\theta)/2\theta$, and an x per cent error in measuring 2θ becomes an x per cent error in d. To measure a 30 Å spacing correctly to 0·1 Å with CuKα radiation ($2\theta = 2·94°$), 2θ must be measured accurately to 0·01°. If the accuracy in measuring 2θ is no better than $\pm0·05°$, then d is known only to $\pm0·5$ Å.

To improve the accuracy of long spacing measurements, Kittrick (1960) recommended that diffractometers be adjusted with respect to an accurately known long spacing reflection and showed that the strong (010) reflection from cholesterol could be so used. Cholesterol has $d(010) = 33·6$ °A, $I = 100$, and $d(020) = 16·8$ Å, $I = 12$, (see *X-Ray Powder Data File*, Card 7–742, experimental data by P. M. de Wolff). No higher orders of $0k0$ occur but numerous weaker ref-

lections are listed. (In the 1972 edition of the *Organic Index of the X-Ray Powder Diffraction File*, cholesterol is not listed alphabetically, but appears in disguised form as 5-cholesten-3β-ol). Sudo and Hayashi (1955) previously used α-stearic acid, with $c \sin\beta = 39·8$ Å, as an internal standard but remarked that mechanical deformations must be avoided because 'the crystal configuration is easily collapsed by grinding'.

In recent personal correspondence with Dr. D. H. Fink of the U.S. Water Conservation Laboratory, Phoenix, Arizona, a letter from the late Dr. W. F. Bradley dated 30 March 1970, to Dr. Fink was brought to our attention, in which Bradley suggested the possible use of purified long-chain hydrocarbons for calibrating small angle reflections. Having already available a number of long-chain normal primary alcohols extending up to C_{20}, we have examined their suitability for calibrating long-spacing measurements. Some long-chain normal alkanes (paraffins) also have been obtained and examined.

USE OF LONG-CHAIN ALCOHOLS AND ALKANES AS CALIBRATING SUBSTANCES

These materials are waxy solids with low melting points. They crystallize with long basal spacings related to the number of carbon atoms in the chain molecules and furnish a sequence of strong and sharp basal reflections with no confusion from other reflections down to around 3 Å. Many of these compounds crystallize with more than one crystalline arrangement,

in triclinic, monoclinic and orthorhombic forms. Robertson (1953) summarized data for the long spacings of alkanes and more recent summaries have been given by Broadbent (1962) and by Nyburg and Potworowski (1973). We have not found any similar compilation for long-chain alcohols.

The basal reflections from these substances are strongly developed either by melting thin layers on glass slides or by crystallization from solutions. They are also strongly developed by pressing the waxy materials into a shallow cavity in a glass or metal slide, but this type of sample preparation has disadvantages, as discussed later. Kittrick emphasized that a standard substance should have a well-established spacing from whatever source it is obtained. However, this requirement is less critical with the long-chain compounds because their spacings are easily measured by direct comparison with quartz or silicon reflections. The fact that several polymorphic forms may occur appears at first sight to be a disadvantage, but actually may be useful because more calibration lines are provided.

For accurate calibration, the essential requirement is that the volume from which X-rays are reflected and its position relative to the diffractometer must be the same for the calibrating substance and for the material under investigation. This requirement can be achieved by using a mixture of the two substances, but this method has the disadvantage that the two diffraction patterns are superposed, and it is not always convenient to make such mixtures.

An alternative method is to calibrate the diffractometer using extremely thin layers of the organic materials on glass slides. The slides can be retained for quickly checking the calibration of the instrument at any time. Extremely thin layers are necessary because of the low absorption of X-rays in organic materials. The linear absorption coefficients of silicates and organic materials of the long-chain type for CuKα radiation are of the order of 75–100 for silicates, and about 4–5 for organic materials. Suitably thin layers are obtained by melting about 2 mg of the organic material in an area about 1.5×2 cm^2. If 0.83 g/cm^3 is taken as the average solid density of these organics, then the calculated layer thickness is of the order of 8×10^{-4} cm. These thin layers give an excellent series of basal reflections, and 15–20 orders can be measured. If the silicate mineral is dispersed in water and then dried as a similar thin layer on a glass slide, it can be taken that the X-ray reflections from the silicate and the calibrating substance come from essentially identical thin volumes. If the silicate powder is contained in a cavity, the penetration of the radiation is so small that the reflected radiation comes essentially from the surface.

RESULTS

A few results will be given to illustrate the use of long chain n-alcohols and n-alkanes for diffractometer calibration. Table 1 records data for n-tetradecanol, $C_{14}H_{29}OH$, taken with filtered CuKα radiation and recorded with a $1/4°$ slit system at $0.5°$ (2θ)/min with chart recording $1°(2\theta)$/in. Reflections were measured at half-maximum intensity, and 2θ values were estimated to $0.01°$.

Column 2, Table 1(a), gives the directly measured values of $d(00\,l)$ from $l = 1$ to $l = 18$. The values of $d(001)$, column 3, are seen to be nearly constant beyond $l = 6$.

Table 1(b) gives the quartz calibration data, where the measured spacings are compared with those of Keith (1955); the differences are mainly of the order of 0.05 per cent. From these results, the $d(001)$ values of tetradecanol are corrected from $l = 10$ to $l = 18$, i.e. in the range covered by the quartz reflections. The average corrected $d(001) = 39.63 \pm 0.02$ Å. This result is typical of those obtained with other alcohols and alkanes, i.e. the uncertainty is of the order of 0.05 per cent. Corrected values of $d(00l)$ and values of $\Delta d = d(\text{corrected}) - d(\text{observed})$ are given in columns 5 and 6 of Table 1(a).

These values of Δd for several long-chain compounds when plotted against 2θ enable a calibration curve for the diffractometer to be drawn. However, when spacings as long as 30 Å are involved, the ultimate accuracy depends on the measurement of 2θ, for an error of $0.01°$ in 2θ becomes an error of 0.1 in a 30 Å spacing when measured with CuKα radiation, i.e. the accuracy is of the order 0.3 per cent. The instrumental calibration is therefore somewhat more accurate than the limit imposed by the measurement of 2θ for spacings of the order of 30 Å. For spacings of about 15 Å, the limit imposed by the measurement of 2θ is about the same as that arising from the instrumental calibration.

Table 2 lists the measured spacings of normal alcohols with C_{14}, C_{16}, C_{18}, C_{20}, and alkanes C_{26}, C_{28} and C_{30}. These values are believed to be accurate to about 0.1 per cent. Two or three different sets of basal spacings are obtained for each substance corresponding to different angles of tilt of the molecules in the various structures. The alcohols were commercial grade samples from the Continental Oil Company and were labelled 'Alfols'. The spacing for hexadecanol, 37.06 Å, is close to the value 37.2 ± 0.15 Å given by Abrahamsson $et\ al.$ (1960). The alkanes were supplied by Dr. T. E. Daubert of the Chemical Engineering Department, Pennsylvania State University; they came from the Humphrey–Wilkinson Co., North Haven, Connecticut and were said to be better than 99

Table 1(a). Observed and corrected basal spacings (Å) of tetradecanol, $C_{14}H_{29}OH$, with quartz calibration

l (1)	Observed values $d(00l)$ (2)	$d(001)$ (3)	$d(001)$ after quartz calibration (4)	Corrected $d(00l)$ (5)	$\Delta d = d(\text{corr.}) - d(\text{obs.})$ (6)
1	38·41	38·41		39·63	1·22
2	19·59	39·18		$19·81_5$	$0·22_5$
3	13·11	39·33		13·21	0·10
4	9·89	39·56		$9·90_5$	0·015
5	$7·91_5$	39·57		7·926	0·011
6	6·598	39·59		6·605	0·007
7	5·660	39·62		5·661	0·001
8	4·948	39·58		4·954	0·006
9	*	—		4·403	---
10	3·963	39·63	39·59	3·963	0·000
11	3·604	39·64	39·61	3·603	−0·001
12	3·308	39·70	39·67	3·302	−0·006
13	3·050	39·65	39·62	3·048	−0·002
14	2·834	39·68	39·65	2·831	−0·003
15	2·645	39·67	39·65	2·642	−0·003
16	2·477	39·63	39·61	2·477	0·000
17	2·332	39·64	39·62	2·331	−0·001
18	2·203	39·65	39·63	2·202	−0·001

* Not observed. Average $39·63 \pm 0·02$.

Table 1(b). Quartz calibration data

hkl	d observed	d standard†	$\Delta d = d(\text{std.}) - d(\text{obs.})$	$\Delta d/d$ (%)
100	4·258 (3)	4·2544	−0·0039	−0·091
101	3·345 (2)	3·3428	−0·0024	−0·072
110	2·457 (7)	2·4563	−0·0014	−0·057
102	2·281 (9)	2·2809	−0·0010	−0·044
111	2·237 (0)	2·2361	−0·0009	−0·040
200	2·127 (0)	2·1272	+0·0002	+0·009
201	1·980 (7)	1·9794	−0·0013	−0·071
112	1·818 (6)	1·8176	−0·0010	−0·055

† Data of H. D. Keith (1955).

Table 2. Basal spacings (Å) of some long-chain alcohols and alkanes

	Present values (obs.)		From Nyburg and Potworowski (1973) (obs.)	(calc.)	Structure
(a) Alcohols					
$C_{14}H_{29}OH$	32·96	39·63			
$C_{16}H_{33}OH$	37·06	44·74			
$C_{18}H_{37}OH$	41·28	49·86			
$C_{20}H_{41}OH$	45·85	55·69			
(b) Alkanes					
$C_{26}H_{54}$	32·57		32·9	32·64	Triclinic
	30·86		31·0	30·95	Monoclinic
	34·78		34·95	34·87	Orthorhombic
$C_{28}H_{58}$	33·24		33·6	33·21	Monoclinic
	37·49		37·7	37·41	Orthorhombic
$C_{30}H_{62}$	35·74		35·8	35·47	Monoclinic
	39·88		40·0	39·25	Orthorhombic

per cent pure. The present observed values are compared with observed and calculated values given by Nyburg and Potworowski (1973).

While the present data in Table 2 are thought to be correct to about ± 0.1 per cent, they are given primarily to assist in selecting a suitable standard. It is not known if the values for the commercial grade alcohols are affected by impurities. It is recommended that an investigator using these materials should measure the basal spacings with respect to quartz or silicon data in the manner of Table 1. It is possible that samples from different sources may have somewhat different basal spacings.

OTHER SOURCES OF ERROR IN MEASURING LONG SPACINGS

In determining long spacings in clay minerals other sources of error can arise besides those arising from instrumental causes. At small 2θ angles, lattice spacing and peak position may not be related exactly by the Bragg equation. The X-ray intensity near a Bragg reflection angle depends on the variation of the lattice structure factor and the Lorentz-polarization factor with the diffraction angle 2θ, and also on the number of cooperating lattice planes. The combined structure and Lorentz-polarization factor increase very rapidly as 2θ diminishes towards zero. Consequently the intensity on the small angle side of a Bragg reflection angle is enhanced with respect to that on the high angle side; the reflected intensity peak is displaced towards smaller angles and the apparent spacing is increased. This effect is particularly important when the number of diffracting planes is small (less than about 10) and the peaks become broadened (small crystal broadening). When long spacings and small 2θ values are involved, this effect becomes still more important and corrections for the Lorentz-polarization–structure factor variations must be taken into account. Ross (1968) and Reynolds (1968) have considered these questions in detail.

It is observed in Table 1 that for tetradecanol $d(00l)_{\text{obs.}}$ for small values of l is displaced to *smaller* spacings than $d(00l)_{\text{corr.}}$, which is in the opposite direction to that discussed in the previous paragraph. The organic reflections give sharp peaks and the Lorentz-

polarization–structure factor effect therefore is quite small. Therefore, the organic reflections at small l are displaced mainly for reasons related to the adjustments of the diffractometer.

Long spacings are usually developed by an alteration of two layers of different kinds, as for example in mica–chlorite interstratifications. The position of a diffracted intensity peak may then depend on the degree of order (or disorder) in the layer succession.

These additional considerations are mentioned briefly here because it is important to recognize that calibration of the diffractometer in measuring small values of 2θ takes care only of instrumental sources of error. Further corrections may be required in going from a value of 2θ to a lattice spacing d.

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Résumé—Les espacements réticulaires des phyllosilicates, en particulier les minéraux argileux, peuvent dépasser 20 Å. Les erreurs commises dans la mesure de ces espacements augmentent rapidement pour des espacements supérieurs à 10 Å et des angles de diffraction 2θ inférieurs à 10° environ. Des composés organiques à longue chaîne tels que les alcools normaux de C_{14}–C_{20} et les alcanes normaux (paraffines) de C_{26}–C_{30}, constituent des étalons utiles pour les espacements réticulaires compris entre 10 50 Å. Les distances basales de ces substances étalons sont déterminées à partir de leurs ordres de réflexion supérieurs dans le domaine angulaire où les réflexions du quartz et de la silice sont utilisées comme standard.

Kurzreferat—Basisebenenabstände von Schichtsilicaten, besonders von Tonmineralen, können 20 Å übersteigen. Die Fehler bei der Messung nehmen bei Basisebenenabständen über 10 Å und Beugungswinkels 2θ kleiner als etwa 10° schnell zu. Langkettige organische Verbindungen wie normale Alkohole, C_{14}–C_{20}, und normale Alkane (Paraffine), C_{26}–C_{30}, stellen nützliche Eichsubstanzen für Schichtabstände im Bereich von 10–50 Å dar. Die Basisebenenabstände der Eichsubstanzen werden aus den Beugungslinen höherer Ordnung in dem Winkelbereich bestimmt, in dem die Reflexe von Quarz und Silicium als Standards benutzt werden.

Резюме — Периоды решетки слоистых силикатов, особенно глинистых минералов, могут превышать 20 Å. При измерении периодов решетки часто возникают ошибки, которые возникают даже чаще, если периоды решетки примерно более 10 Å, а углы отклонения при диффракции 2θ, менее приблизительно 10°. Органические соединения с длинными цепями, такие как стандартные спирты, C_{14}–C_{20}, и стандартные алканы (парафины), C_{26}–C_{30}, предоставляют приемлемую калибровку для периодов решетки в пределах 10–50 Å. Основные периоды решетки веществ применяемых для калибровки определяются по их более высокому порядку отражения в угловом радиусе, где отражения кварца и кремния используются в качестве эталонов.