NOTES AND NEWS

A NEW METHOD FOR MOUNTING SAMPLES FOR POWDER X-RAY SPECTROMETRY*

H. D. Holland, W. B. Head III, G. G. Witter, Jr., and G. B. Hess

During the course of an investigation of the effect of nuclear radiation on the structure of zircon, it became necessary to determine accurately the unit cell dimensions of crystals by means of a Norelco High Angle X-ray Spectrometer. Various smear techniques were tried, but it was found that errors in the measurement of 2θ usually were on the order of 0.01 to 0.02°. The same conclusion was reached by Adams and Rowe (1954) in their survey of the sample mounting techniques available at present. These authors also discuss a pressed-sample mounting technique developed by them but do not state in their paper the reproducibility attainable thereby. The method finally adopted in this laboratory has been used successfully during the past year; the average difference in 2θ between the values measured on two sample slides of the same material is 0.003°. It appears unlikely that additional refinements of the technique will decrease this error appreciably.

Sample Preparation

The samples of zircon were crushed and then ground in a Fisher Scientific Co. automatic grinder equipped with tungsten carbide mortar and pestle, using methyl alcohol as a grinding medium. The resultant slurry was pipetted into a vial, and the volume brought up to 35 cc. with additional methyl alcohol. The suspension was then poured into a 250 ml. beaker and permitted to stand for five minutes. After this length of time the supernatant liquid was pipetted into a second 250 ml. beaker and permitted to stand for 25 minutes. The sample still remaining in suspension was discarded or saved for other purposes and the material which had accumulated in the bottom of the beaker mixed with a small amount of methyl alcohol, was transferred to a glass vial. The concentration of zircon in this suspension was determined by evaporating 1 cc. on a watch glass and weighing the residue after heating at approximately 100° C.

The same procedure was followed in the preparation of a suspension of silicon metal (silicon metal powder, Fairmount Chemical Co. Inc., 600 Ferry Street, Newark, N. J.). Thus the settling velocity distribution

of the grains in the sample and reference suspensions was approximately the same. The desired volume of the two suspensions was then pipetted into the sedimentation cell shown in Fig. 1. The cell was made of brass and consisted of a base plate, A, ring, B, half-cylinder, C, and set screws, D. A brass planchet, E, whose surface had been polished on a diamond
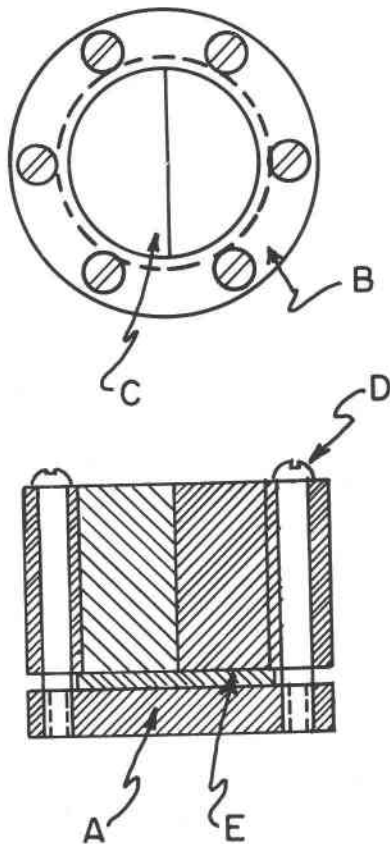

Fig. 1

lap, was introduced between the base plate and the ring and half-cylinder and clamped tightly by means of the set screws. After the two suspensions had been introduced, the holder was placed on a level shelf and covered with a 250 ml. beaker. At normal room temperatures the zircon and silicon powders settle out of the suspension in about 6 hours, and evaporation of the methyl alcohol is usually complete in 36 hours. The evaporation can be speeded up considerably by removing the beaker

after the first 6 hours of settling, but care should be taken to prevent the formation of convection currents, particularly near the end of the period of evaporation. After the methyl alcohol has evaporated completely, the sample planchet is removed from the holder and is then ready for introduction into the Norelco Spectrometer.

Recently a holder of the type shown in Fig. 2 has been put into use. The principle of operation is the same as that of the holder described
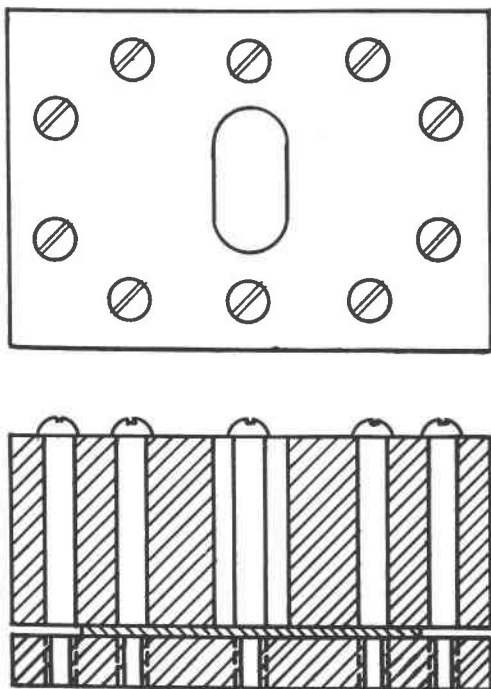

Fig. 2

above; however, two improvements have been made. The shape of the sample well approximates more closely that of the x-ray beam, and glass slides can be used as mounting planchets. This saves the expense of machining and polishing, permits one to observe the underside of the sample mount, and eliminates interference from x-ray reflections from the brass planchet itself.

The quantity of silicon and sample used in the preparation of the slides varies somewhat with the problem at hand. In the present work approximately 5 mg. of silicon and 10 mg. of zircon were used. It was found that the difference in 2θ values between the zircon peaks and the reference silicon peaks was insensitive to the ratio of the two components

and to the total weight of material used, which indicates that the mixing of the two components was adequate and that the silicon acted as a true internal standard.

MEASUREMENT OF 2θ VALUES

The sample was mounted in the head of the Norelco Spectrometer. The following program is typical of that used in the determination of the unit cell dimensions of the zircon samples:

1. The recorder pen was drawn across the strip chart at right angles to the long direction of the chart by means of the manual control in the rear of the recorder.

2. The spectrometer was set so that 2θ was slightly less than 28.000°.

3. The switch controlling the scanning motor on the spectrometer was turned on, and the clutch connecting the spectrometer with the scanning motor was thrown in.

4. The motion of the spectrometer was watched with a hand lens, and, as 2θ reached 28.000° the strip chart recorder switch was turned to the on position, starting the motion of the strip chart.

5. The (111) peak of silicon at approximately 28.45° was then scanned. After passage of the peak, the recorder chart switch was turned off at an accurately determined value of 2θ, usually 28.700°, and the 2θ value at this final point marked on the chart.

6. The pen was then drawn across the recorder strip chart as before.

7. The motion of the scanning motor and of the spectrometer were disconnected by releasing the clutch, and the spectrometer was set at 2θ slightly less than 19.700°.

8. The clutch was again thrown in, and the strip chart recorder switch turned on when 2θ was just equal to 19.700°. The (101) peak of zircon at approximately 20.00° was then scanned.

9. At an accurately determined value of 2θ near 20.300° the strip chart recorder switch was turned off, and the pen drawn across the paper as before.

10. The above procedure, steps 2 through 9, was carried out four more times so that the (111) peak of silicon and the (101) peak of zircon were each scanned five times.

11. The same scanning procedure was then used for obtaining reflections from the (200), (112) and sometimes the (312) peaks of zircon. A complete run of this type therefore consisted of twenty Si (111) peaks and five peaks each of the (101), (200), (112), and (312) reflections of zircon. On the strip chart zircon and silicon peaks thus alternate. A scanning speed of $\frac{1}{8}$° per minute and a chart speed of $\frac{1}{4}''$ per minute were used throughout. It was found that the measured 2θ values were

insensitive to changes in the scale factor setting, but that the time constant and multiplier settings should not be changed during a run.

After completion of the scanning program the strip chart was removed from the recorder. The height of each peak was measured from the base of the peak, and a point 15% from the top of the peak was marked off. The midpoint of the peak at this point was measured and the distance from the midpoint to the reference line drawn across the chart at the conclusion of the peak was determined to the nearest 0.001° with an engineer's rule and hand lens. It is preferable to use the line drawn at the conclusion of the scanning of each peak rather than at the beginning of the scan since errors are sometimes incurred due to lags in the motion of the strip chart motion just after the strip chart switch has been turned on.

From these measurements the 2θ values at the midpoints of the peaks are calculated. The five values thus obtained for each zircon are then averaged and a probable error is assigned to this average such that at least three of the five measured values fall within the average plus and the average minus, the assigned probable error. The same procedure is carried out for the Si (111) peaks associated with each of the zircon peaks. A probable error is assigned to this average in the same manner as to the average for each of the zircon peaks. The average for each zircon peak is then corrected by subtracting the difference between the measured average value for Si (111) and the standard value of 28.447° accepted for this angle. The probable error of the corrected value of 2θ for the zircon peaks is the sum of the probable error for the uncorrected average of the zircon peak, and the probable error for the average 2θ value for the Si (111) peak. A sample determination of the corrected value of a $ZrSiO_4$ (101) peak is shown in Table 1. The combined error in the two readings is usually between 0.002 and 0.004°. That this procedure is justified is shown by the fact that for a given zircon sample the four averages for the Si (111) peak determined in the manner shown above [one average each is determined in conjunction with the calculation of the corrected 2θ values of the $ZrSiO_4$ (101), (200), (112), and (312) peaks] rarely fall outside the limits determined by any one of the averages plus and minus, the assigned probable error.

RESULTS

In Table 2 the data on the reproducibility of duplicate sample slides studied during the past year have been summarized. This includes some data on slides which looked rather poor, having been disturbed by convection currents during the evaporation process. It can be seen that in most cases the difference $(2\theta_{ZrSiO_4} - 2\theta_{Si})$ between duplicate sample slides

TABLE 1. SAMPLE CALCULATION OF 2θ VALUE OF A $ZrSiO_4$ (101) PEAK

Sample: Zr 4-42H2

Peak No.	Si (111)	$ZrSiO_4$ (101)
1	28.452	
2		20.004
3	28.450	
4		20.003
5	28.449	
6		20.000
7	28.451	
8		20.001
9	28.451	
10		19.998
average	28.451 ± 0.001	19.999 ± 0.002

$$28.451 \pm 0.001$$
$$-28.447$$

correction factor: 0.004 ± 0.001

corrected value of 2θ for $ZrSiO_4$ (101)

$$19.999 \pm 0.002$$
$$- \ 0.004 \pm 0.001$$

$$19.995 \pm 0.003$$

TABLE 2. DIFFERENCES IN MEASURED VALUES OF $(2\theta_{ZrSiO_4} - 2\theta_{Si})$ FOR DUPLICATE SLIDES*

$(2\theta_{ZrSiO_4} - 2\theta_{Si})$	Number of cases in which this difference was found
0.000°	4
0.001	14
0.002	8
0.003	19
0.004	5
0.005	6
0.006	1
0.007	2
0.008	3
0.009	0

* In all of these measurements Si (111) was used as the reference peak; the zircon peaks most commonly measured were (101), (200), (112), and (312).

is less than 0.005°. In the present work this permitted the determination of the unit cell dimensions of zircon to approximately 1.5 parts in 10,000.

At the moment it appears doubtful that this technique can be improved appreciably. The main residual error now lies in the measurement of the 2 θ values on the strip chart. This in turn is probably controlled mainly by fluctuations in the count rate of the spectrometer. The present technique therefore probably represents the extreme of accuracy to which x-ray powder spectrometry can be carried with the Norelco instrument.

REFERENCE

ADAMS, L. H., AND ROWE, F. A. (1954), The preparation of specimens for the focusing-type x-ray spectrometer: *Am. Mineral.*, **39**, 215–221.

BEYRICHITE, A DISCREDITED SPECIES*

CHARLES MILTON AND JOSEPH M. AXELROD, *U. S. Geological Survey, Washington 25, D.C.*

Inasmuch as many museums and private collections possess specimens labeled beyrichite and there seems to have been no unambiguous statement in the literature concerning its status, it is hoped that this note may remove whatever uncertainty or confusion may exist in regard to beyrichite. To summarize the following data, the original description probably referred to what we now term violarite, and all specimens of so-called beyrichite which we have been able to examine have been shown to be well-known minerals or artificial substances.

Beyrichite was first described by K. Th. Liebe (1871) from "Lammrichs Kaul Fdgrb," Westerwald, Germany. Its specific gravity was 4.7 (millerite sp. gr. 5.9), color lead gray, and composition determined as $3NiS \cdot 2NiS_2$ or $2NiS \cdot NiS_2$. A loss of sulfur on heating was construed by Liebe as indicating change of beyrichite into millerite; he also held that beyrichite, by addition of nickel from solution, forms millerite. Liebe's views were adopted by Laspeyres (1892), who went so far as to assert that all millerite is an alteration product of beyrichite and that the change involves only the physical properties—color and density— with no chemical or cystallographic change. Hintze (1904) summarizes the early literature, and accepts beyrichite as a dimorph of millerite. He notes that unchanged beyrichite is known from only one locality— Altenburg near Oberlahr (Grube Lammerichskaule) in Rhenish Prussia.