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EXPERIMENTAL ERROR IN DETERMINING CERTAIN PEAK LOCATIONS AND DISTANCES BETWEEN PEAKS IN X-RAY POWDER DIFFRACTOMETER PATTERNS

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ABSTRACT

The random errors inherent in two common types of x-ray diffractometer measurement have been estimated. Most of the error is apparently associated with operations contingent upon setting up the specimen and getting the instrument in motion. Although significant mean differences were detected between mounts of different type, different mounts of the same type gave agreement well within experimental error. Results obtained at scale factor 4 were indistinguishable from those obtained at scale factor 2. Scanning direction exerts a small but significant effect on estimates of distances between peaks. The exact numerical results apply strictly only to the specific operator-instrument combination which generated the data. The evaluation procedures should be widely applicable.

INTRODUCTION

Most of the routine quantitative use of the x-ray diffractometer is still concerned largely with the positions of the various reflections. Measurements made with the now standard automatic recording arrangement are subject to numerous systematic errors, many of which, as formulated by Parrish and Wilson (1954), evidently decrease with increase in 2θ. Although in principle one should always apply a correction to eliminate a systematic error of known size, in practice there is usually little point in doing so unless the size of the bias is of at least the same order as the random error of the measuring process.

There is surprisingly little published experimental information about the random error of results obtained in high-grade routine work. This note provides some, along with evaluation procedures which should permit others to procure as much as is necessary in any specific situation.

Our estimates of random error were developed in order to permit appraisal of the results one of us (W.S.M.) obtained in a particular problem. They are not intended to provide a general guide to expectable experimental error in work of this sort. Indeed, a very different and considerably more elaborate schedule of testing would be required before we could tell whether they are applicable even to the work of others in our own laboratory.

The measurements for which we required estimates of random error are of two types. In the first we are concerned simply with whether a series of x-ray diffraction patterns can or should be distinguished from

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each other. The "unknowns" were all samples of glasses of identical composition ($NaAlSi_3O_8$) crystallized at varying temperatures and for varying times; significant differences in a particular apparent interplaner distance could only be interpreted as responses to differing crystallization conditions. In the second we are concerned with the error attached to estimates of 2θ for various reflections given by Lake Toxaway quartz, a material much used both as an internal standard and as a means of calibrating an instrument.

Recording and Measuring Technique

The *x*-ray diffraction patterns were obtained on a Norelco wide-angle diffractometer, using Al-filtered copper radiation. The divergence and scatter slits were 1°, the receiving slit 0.006 inch.

All patterns were prepared and measured by one of us (W.S.M.). Each pattern was measured once with a specially designed ruler on which the vernier reads to 0.005 inch; individual readings were recorded to 0.005 inch. A point midway between the edges of the peak at $\frac{2}{3}$ of the peak height was taken as the peak location, both coordinates being judged by eye. For differences between the positions of two peaks ($\Delta 2\theta$), the variable in the first set of observations described below, the distance between the appropriate points was measured by ruler. For direct estimation of 2θ, the variable of the second set of observations, the distance of the point from the nearest degree tick (not the half-degree tick) registered by the degree marking pen was measured by ruler. This is the standard operating procedure of the second named author.

In the first set of observations only glass smear mounts were used. The second set utilized both these and a mount of the type described by Adams and Rowe (1954). The surface of the Adams mount was ground and polished to make it as nearly flat as possible. The smear mounts were made on ordinary microscope slides with a mixture of clear lacquer and acetone; the smear was barely translucent.

Error of a Distance Between Two Peaks ($\Delta 2\theta$)

The data are measurements, made mostly on the same instrument over a period of more than a year, of distances between the same two peaks on 30 specimens of synthetic albite selected at random from over 300 similar records. Instrumental settings were: scale factor 1, multiplier 1, time constant 16. The appropriate interval was scanned at $\frac{1}{4}$° per minute and the chart speed was adjusted so that 1° 2θ is represented by 1 inch. By means of an automatic oscillator six records of each specimen were made with a single insertion of the mount; alternate comparisons are thus scanned in the same direction, each chart providing three scannings from high angle to low and three from low to high. Information is

TABLE 1. VALUES OF $\Delta 2\theta = 2\theta_{131} - 2\theta_{1\bar{3}1}$ FOR SYNTHETIC ALBITES

Sample No.	Decreasing	Increasing	Decreasing	Increasing	Decreasing	Increasing
53	1.880	1.880	1.880	1.905	1.895	1.885
65	1.795	1.785	1.790	1.795	1.785	1.785
89	1.930	1.940	1.930	1.930	1.920	1.940
95	1.750	1.760	1.765	1.760	1.745	1.750
102	1.905	1.935	1.900	1.900	1.910	1.900
116	1.960	1.945	1.940	1.950	1.940	1.945
127	1.955	1.955	1.960	1.945	1.940	1.960
135	1.950	1.970	1.950	1.960	1.965	1.950
141	1.920	1.945	1.925	1.945	1.945	1.955
169	1.945	1.940	1.935	1.950	1.945	1.945
172	1.920	1.910	1.925	1.910	1.910	1.905
175	2.005	1.985	1.980	1.995	1.970	1.980
176	1.815	1.815	1.815	1.805	1.810	1.810
181	1.915	1.935	1.915	1.935	1.905	1.930
183	1.885	1.905	1.890	1.900	1.910	1.915
192	1.875	1.890	1.885	1.880	1.895	1.895
200	1.815	1.820	1.820	1.830	1.810	1.820
221	1.745	1.760	1.745	1.745	1.745	1.770
223	1.875	1.885	1.875	1.895	1.895	1.885
232	1.860	1.845	1.870	1.865	1.840	1.870
249	1.915	1.935	1.915	1.940	1.945	1.920
267	1.800	1.800	1.815	1.820	1.820	1.820
270	1.865	1.870	1.855	1.880	1.855	1.870
277	1.930	1.945	1.920	1.940	1.940	1.925
284	1.865	1.860	1.875	1.860	1.870	1.865
293	1.710	1.740	1.730	1.735	1.725	1.740
301	1.980	2.005	2.000	2.000	1.965	1.980
307	2.005	2.015	2.000	2.020	2.015	2.015
315	1.755	1.790	1.765	1.780	1.765	1.780
327	2.000	1.985	2.020	2.000	1.985	2.005

desired on the error attached to individual distances ($\Delta 2\theta$) and to the mean of a set of six such distances. It is also necessary to reach some decision about the significance of a small but common discrepancy between the mean values for the two directions of scanning.

The data, shown in Table 1, were collected primarily for the purpose of comparing the specimens with each other, deciding whether the patterns were the same or different, and attempting to measure the differences where these appeared significant. If we define

(1) an *observation* as the average of the two distances generated in a single complete oscillation, and

(2) a *specimen value* as the mean of three observations made in continuous operation of the instrument,

the variance analysis calculated from Table 1 is:

Source	*Degrees of freedom*	*Mean square*
Between specimens	29	1,643,778.24
Error	60	4,319.45

For convenience in calculation the data were coded by

$$Y_i = (X_i - 1.7)(10^4)$$

so the error of a single observation, as a standard deviation, is

$$s = (4{,}319.45)^{1/2}(10^{-4}) = 0.0066°$$

and the error attached to the mean of three observations made with a single setting and insertion is $0.0066/\sqrt{3} = 0.004$.

By using the mean of a full oscillation as a "single" observation, we have avoided discussion of the small but persistent difference between distances scanned in opposite directions. In 24 of the 30 specimens listed in Table 1, the average distance is larger for the subset scanned in the direction of increasing 2θ, and the over-all average value for the difference is 0.006°.

Table 2 shows a partition of variance in which the items of the sample are individual distances (e.g., each oscillation provides two distances and a specimen estimate is the mean of six). With this arrangement it is possible to isolate a separate mean square for scanning direction, and this mean square turns out to be highly significant.

TABLE 2. VARIANCE ANALYSIS OF TABLE 1 SHOWING EFFECT OF SCANNING DIRECTION

Source	Degrees of freedom	Mean square
Specimens	29	32,867.45**
Scanning direction	1	1,742.23**
Interaction	29	96.53
Error	120	91.18

The error of a single peak interval is estimated by $(91.18)^{1/2}(10^{-3}) = 0.0095°$. The error of the mean of six is estimated by $0.0095/\sqrt{6} = 0.004°$, as before.

It is to be stressed that for the stated purpose of the work the scanning direction bias does not affect the random error as long as even numbers of consecutive peak intervals are averaged. Nothing at all is gained by letting the machine run $(n-1)$ times in the "wrong" direction in order to obtain n runs in the "right" direction. The net result of this stratagem is the loss of $100(n-1)/(2n-1)$ per cent of machine time and recording paper.

The question of what to do about the scanning direction bias becomes much more complex if the results are to be used as estimates of a "true" value defined as something more than the average of an indefinitely large number of replications of this particular procedure. From parameters determined by some other type of experimentation, for instance, we can calculate an "expected" value for $\Delta 2\theta$, and may wish to determine whether the observed values are in satisfactory agreement. One can get nowhere with this matter unless one is willing to make some reasonable assumption about the nature and location of the bias. The simplest would appear to be that one of the two scanning directions provides an unbiased estimate, the bias being entirely situated in the other. In this circumstance the practice of using only alternate readings would be appropriate, but one would have to know which set to use.

Further, it is not unreasonable to suppose that *both* scanning directions lead to biased results, and the justification for supposing that the bias is constant, an assumption basic to the argument, is purely practical. The possible complications are virtually infinite in number; which, if any, of them may be usefully explored is determined, ultimately, by the random error of the procedure by which the exploration is to be conducted.

Random Error of 2θ Values for Quartz on Glass Smear Mounts

The main object of the work described in this and succeeding sections was to estimate the random error attached to routine measurements of 2θ for each of several peaks in the specimen, a sample of Lake Toxaway quartz widely used in this laboratory, in conjunction with the table of 2θ values given by Parrish (1953), as an internal standard. We desired information on the size and nature of differences between our measured values and those calculated by Parrish, on whether alteration of the scale factor influenced these differences, and on whether results obtained from smear mounts differed significantly from those given by the Adams mount.

All runs were made on the Norelco wide-angle x-ray diffractometer which provided most of the data for the preceding section, with the following settings: scanning speed 0.5° per minute, chart scale 1° = 1 inch, scale factor 2 or 4,* multiplier 1, time constant 8. The scanning proceeded

* To keep certain peaks on scale it was sometimes necessary to insert additional Al filters.

from 54° to 20°. All determinations were made on two glass smear mounts and one of the Adams type.

Each mount was scanned twice at each of the scale factors, the scannings were carried through in a predetermined random order, and the operation of "scanning" in each case included insertion of the slide. Each chart was measured once in the fashion already described; the charts were measured in a random order different from that in which the scannings were made, but as a matter of convenience all peaks on a single chart were measured consecutively. The data are shown in Table 3.

Considering only the glass smear mounts, the arrangement conforms to the so-called 2^2 factorial type, and the variance calculations, though somewhat tedious, are simple and straightforward. (A sample calculation is given in Appendix A-2; for details see the excellent outline in Cochran and Cox, 1950, pp. 122–129.) If the data are coded by subtracting off the smallest observed value for each peak and eliminating decimals, the following average mean squares may be formed from the results for each peak:

Source	*Average mean square*
Scale factor	64.106
Mounts	133.036
Interaction (M×S)	140.179
Error	233.821

The tabulation affords a convenient résumé of our major findings; if the results are examined peak by peak, as is done for the (112) reflection in Appendix A-2, it will be found that in no case does either scale factor or mounts (or interaction) generate a mean square significantly larger than that for error. The experimental error is of about the anticipated size but is not to be attributed to either of the assigned "causes."

Many of the systematic errors studied by Parrish and Wilson appear to decrease with increase in 2θ. A closer examination of our results indicates, however, that in the range investigated the *random* error probably *increases* with increase in 2θ. Table 4 shows average values for 2θ and standard deviations for error calculated from Table 3. Each estimate is based on only 4 degrees of freedom, of course, and variance estimates based on small samples are notoriously unreliable. Indeed, it cannot even be shown from the data that the sub-group variance is inhomogeneous. A persistent trend of this sort is nevertheless quite unlikely unless there is in fact some tendency for direct variation of random error with 2θ.

TABLE 3. MEASUREMENTS OF POSITIONS OF X-RAY REFLECTIONS OF VEIN QUARTZ FROM LAKE TOXAWAY IN 2θ (CuKα)

Reflection	Adams mount				Smear mount 1				Smear mount 2			
	Scale factor 2		Scale factor 4		Scale factor 2		Scale factor 4		Scale factor 2		Scale factor 4	
	A	B	A	B	A	B	A	B	A	B	A	B
(112)	50.000	50.055	50.020	50.070	50.100	50.115	50.100	50.100	50.110	50.105	50.140	50.095
(201)	45.705	45.690	45.705	45.705	45.755	45.760	45.750	45.760	45.735	45.750	45.785	45.740
(200)	42.340	42.340	42.335	42.340	42.400	42.425	42.400	42.420	42.410	42.420	42.430	42.400
(111)	40.190	40.215	40.220	40.205	40.260	40.265	40.260	40.265	40.230	40.260	40.270	40.235
(102)	39.375	39.375	39.370	39.375	39.420	39.440	39.435	39.440	39.445	39.450	39.455	39.420
(110)	36.455	36.460	36.470	36.465	36.500	36.510	36.510	36.515	36.505	36.495	36.520	36.485
(100)	20.870	20.820	20.835	20.830	20.800	20.815	20.800	20.810	20.790	20.810	20.835	20.815

TABLE 4. AVERAGE 2θ AND RANDOM ERROR BY PEAKS, CALCULATED FROM TABLE 3

(*hkl*)	Average 2θ	Random error as a standard deviation in degrees
(112)	50.108	0.0169
(201)	45.754	0.0172
(200)	42.413	0.0159
(111)	40.256	0.0165
(102)	39.438	0.0145
(110)	36.505	0.0135
(100)	20.809	0.0118

Comparison of Adams and Smear Mount 2θ Values

The standard deviations listed in Table 4 estimate the random error of a single determination of $2\theta_{hkl}$. Differences between mounts and scale factors having proved negligible, the average $2\theta_{hkl}$ for the smear mounts is based on eight such determinations. Its error is accordingly $1/\sqrt{8}$ that of an individual determination. As shown in Table 5, the difference between the mean value for the smear mounts and that for the Adams mount is never less than seven and may be as much as twelve times this error.

There seems to be no reasonable doubt that this particular Adams mount gives results quite different from those found for the smear mounts. We have no explanation either for the gross effect or for the peculiar circumstance that for six of the peaks the observed 2θ is smaller on the Adams mount while for the seventh it is larger. This whole matter requires careful and more detailed investigation.

Table 5. Comparison of Adams Mount and Smear Mount (Data of Table 3)

(hkl)	Smear mount average −Adams mount	Error of smear mount average
(112)	0.072	0.006
(201)	0.054	0.006
(200)	0.074	0.006
(111)	0.047	0.006
(102)	0.064	0.005
(110)	0.043	0.005
(100)	−0.030	0.004

Comparison of Observed 2θ Values with the Parrish Standard Quartz Spacing

The Parrish values are now often used as a kind of correction or calibration of quartz serving as an internal standard. It is sometimes difficult to decide whether a particular reflection is best compared with the Parrish value calculated for α_1 or α. In the present instance, however, we can avoid the difficulty by adopting the procedure of J. V. Smith (1956), who in a recent paper on plagioclase lattice parameters uses α_1 for reflections with 2θ greater than 31°. Table 6 compares Parrish α_1 values with averages calculated from Table 3 for the six reflections satisfying this condition.

As the Parrish values are always larger and the Adams values smaller than the smear mount results, we need consider only one set of differ-

TABLE 6. AVERAGE 2θ VALUES FROM TABLE 3 COMPARED WITH PARRISH α_1 VALUES

Index	2θ			
	Parrish α_1	Smear mount (S_1)	Smear mount (S_2)	Adams mount
(112)	50.142	50.104	50.112	50.036
(201)	45.796	45.756	45.752	45.700
(200)	42.454	42.411	42.415	42.339
(111)	40.292	40.262	40.249	40.209
(102)	39.468	39.434	39.442	39.374
(110)	36.546	36.509	36.502	36.462

ences, those between the Parrish and smear mount values. This comparison is shown in Table 7. The difference is always more than five times as large as the estimated random error of the smear mount average. There is again no reasonable doubt of the significance of the difference, which is so nearly constant as to suggest systematic, probably instrumental, origin. It is to be remembered, however, that the data include only a small part of the spectrum.

A number of prepublication readers have taken serious exception to Tables 6 and 7 and the accompanying discussion, all of which appear to imply that smear mounts are superior to Adams mounts. Extended discussion of this matter revealed considerable confusion concerning the nature and relevance of the Parrish 2θ table for quartz, as well as a strong feeling that because of the differing "geometries" of the two mount types no direct comparison of the results was legitimate.

Despite Parrish's clear description (1953) of the construction of his table, many users of it remain unaware that it is calculated directly from a and c estimates published by Lipson and Wilson in 1941. The Parrish table is thus quite independent of design and adjustment characteristics

TABLE 7. DIFFERENCES BETWEEN PARRISH α_1 VALUES AND SMEAR MOUNT AVERAGES

(hkl)	Parrish value − smear mount average	Error of smear mount average
(112)	0.034	0.006
(201)	0.042	0.006
(200)	0.041	0.006
(111)	0.036	0.006
(102)	0.030	0.005
(110)	0.041	0.005

of any modern recording diffractometer. From this point of view it is quite legitimate to compare either the smear mount or the Adams mount results with the relevant Parrish values, and there would accordingly appear to be no justification for refusing to compare them with each other.

The Lipson-Wilson measurements were made on photographic powder patterns of a crystal of unknown source. Parrish mentions that "some care" should be exercised in the selection of quartz for use as a standard and concludes that at present it "should not be used as a primary standard for measurements requiring the highest precision." On this account, however, our comparison is neither more nor less suspect than innumerable other similar uses to which the table has been put and for which it was presumably designed. Every one of the critics who raised this objection had himself many times used the Parrish table for standardization or cross-calibration. Indeed, it would be difficult to find mineralogical users of the diffractometer who have not done so.

It was also argued that since no instrumental adjustments were made during the test, mounts of different "geometry" *ought* to yield different results, the implication being that an instrument adequately aligned and calibrated for one type of mount would not be so for the other. It is obvious that in the Adams mount the target is at or below the theoretical target plane, while in the smear mount the upper surface of the target must be somewhat above the theoretical target plane. Whether the difference of elevation exerts a measurable effect on the results is a matter for experimental determination. From a priori considerations of mount geometry the Adams mount would appear to be preferable, but the smear mounts gave considerably better agreement with the Parrish values. Whatever the meaning of this result, criticism of it on the basis suggested above is quite irrelevant. In the recommended procedure (Parrish, Hamacher, and Lowitzsch, 1954), alignment of the instrument and adjustment of the zero point are accomplished without benefit of a mount of *any* type. The alignment and adjustment may be tested by a pressed silicon standard; if further refinement is required, however, it is carried through without direct reference to the standard. We did not vary the adjustment to "fit" the mount type for the reason that under the recommended standard operating conditions—the only kind we were concerned with—no adjustment of this type is possible.

Comparison of the Error Estimates

The error of a single (131–$1\bar{3}1$) interval in the feldspar data was estimated as 0.0095°. If the peak locations from which the difference is formed are subject to equal random error, this error may in turn be estimated as $0.0095/\sqrt{2}=0.0067$, a figure considerably smaller than any of the quartz errors shown in Table 4. This may be inherent in the materials involved, but examination of the charts offers no support for such an explanation. It seems much more reasonable to attribute the difference to the structure of the experiments rather than of the materials on which they were performed.

The feldspar error pertains to repeated scannings made with the instrument in continuous operation, all based on a single insertion of the mount into the specimen holder. In the quartz work, on the other hand, only one scanning (per peak) is made on each chart; the error accordingly includes variation introduced by inserting the mount into the specimen holder and setting the instrument in motion. This suggests a further subdivision of error variance. The total analytical error contributes to the quartz estimates, while only a "within-chart" component is reflected by the feldspar estimates. The uncertainty contributed by operations essential to starting the machine, possibly largely by insertion of the mount, is readily estimated as the square root of the difference between the squares of the quartz and feldspar errors. At $2\theta=20°$, for instance, we have

Source	*Mean square*	*Standard deviation*
Between charts	0.000094	0.0097°
Within charts (feldspar)	0.000045	0.0066°
Total (quartz)	0.000139	0.0118°

At $2\theta=50°$ the same calculation yields a "between chart" standard deviation of 0.0156°. If this explanation is correct, the bulk of the random error is occasioned by the various manipulations incident upon setting up the specimen and getting the instrument in motion. This is one of the strongest arguments in favor of the use of internal standards wherever close decisions are to be made.

Possible Rounding Errors

The ruler used for measurement of our charts, one of two specially made here, is equipped with a vernier reading to 0.005 inch, in our case 0.005°. The work reported above persuades us that even further refinement would be desirable whenever close decisions are to be made about the distances between well-defined peaks. A unit of measurement of 0.005° is wastefully coarse for procedures whose random errors fall in the range 0.007–0.017, about that encountered in the present study. Indeed, it is impossible to take full advantage of such procedures unless the unit of measurement is considerably less than 0.005.° Whenever internal standards can be used or a distance between two peaks is at issue, a ruler with a vernier reading to 0.001° could be used to good advantage. This is especially so when, as in our work, estimates of error are desired.

Coarse grouping often yields distorted error estimates; commonly a class interval broad in relation to the parent error leads to overestimation of error variance, but this is not necessarily the case, particularly in small samples such as most of us use. The worker who imagines that excessive rounding necessarily provides protection against overstating precision is often living in the kind of paradise not inhabited by wise men.

Appendix A-1

Since most readers will not be particularly concerned with arithmetic details we have relied rather heavily on a few simple statistics together with close inspection of tables of averages, differences, etc. The data were obtained in a pattern which permits more elegant procedures, and all of our conclusions are based on the results of standard statistical calculations. The most troublesome finding is probably the conclusion that the differences between the Adams and smear mount values are significant, for there is a clear implication that the two types of mount do not in fact estimate the same parameters. Here, as elsewhere, the inspection procedure relied on in the text leads to a conclusion easily substantiated by more formal calculation.

If we designate the Adams mount by A, and the smear mounts by S_1 and S_2, we have for each peak a difference $\Delta_1=(S_1-S_2)$ reflecting the failure of the smear mount averages to agree exactly, and a difference

$$\Delta_2 = \left(\frac{S_1 + S_2}{2} - A\right)$$

reflecting the failure of the average for the Adams mount to agree exactly with the grand mean for the smear mounts.

The mean square of the differences between means is an estimate of

$$s^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

where s^2 is the pooled error mean square per unit, and r_1 and r_2 are the numbers of replicates upon which the two means are based (Cochran and Cox, p. 91). Summing and solving for the pooled error sums of squares (SS), we have

$$SS\Delta_1 = \frac{1}{2}\sum\Delta_1^2$$

for the differences between the smear mount averages, and

$$SS\Delta_2 = \frac{2}{3}\sum\Delta_2^2$$

for the differences between the Adams mount and the smear mounts. On the null hypothesis these are estimates of the same quantity. Actually, they compare as follows:

Source of variation	*SS*	*Degrees of freedom*	*Mean square*
Between Adams and smear mounts (Δ_2)	0.015145	7	0.002163
Between smear mounts (Δ_1)	0.000207	7	0.00002957

The mean square for Δ_2 is very much larger than for Δ_1—the ratio, $F = MS\Delta_2/MS\Delta_1 = 73.1$ is so large that a test would be trivial. The Adams and smear mounts evidently do not estimate the same angle for a given (hkl).

Incidentally, the mean square 0.00002957 is for an average of eight determinations. For a single determination this would lead to an estimate of 0.0002366, without direct reference to the individual measurements. The average mean square calculated from the individual measurements, which may be reclaimed by squaring the entries in the right column of Table 4, summing, and dividing by 7, is 0.0002340. The square root of either value is an estimate of the standard deviation of a single observation; they are obviously in good agreement.

Appendix A-2

Some readers may be interested in the factorial design and accompanying calculations. The reference cited in the text covers this material admirably, and should certainly be consulted by anyone planning to use the procedure in his own work. The following résumé is intended as an introduction for such readers, but may also provide useful orientation for those whose interest is less immediate.

The smear mount data for the (112) reflection, given in the first line of Table 3, are

Mount	Scale Factor	
	2	4
1	50.100; 50.115	50.100; 50.100
2	50.110; 50.105	50.140; 50.095

Subtracting off the smallest of these and eliminating decimals; a useful step in any calculation of variance, we have:

Mount	Scale Factor		$\sum_{(M)}$
	2	4	
1	5, 20	5, 5	35
2	15, 10	45, 0	70
$\sum_{(SF)}$	50	55	

At this point we could calculate and partition the sum of squares in the usual way, but the factorial procedure, which uses only the marginal totals, is much simpler.

For the main effects and interaction we have the following sums of squares:

Differences between mounts $(35-70)^2/8 = 153.125$
Differences between scale factors $(50-55)^2/8 = 3.125$
Interaction $[(45+0+5+20)-(15+10+5+5)]^2/8 = 153.125$

If there were only one measurement per mount-scale combination, this would exhaust the data, and we would have the analysis:

Source of variation	*Degrees of freedom*	*Mean square*
Mounts	1	153.125
Scale factors	1	3.125
Error (interaction)	1	153.125

showing that neither main source of variation is significant. Actually there are two observations in each cell, so that we have a means of estimating directly the reproducibility of results on the same mount at the same scale. In the ordinary variance analysis procedure this would be found by subtracting the sum of squares for subclasses (mount-scale combinations) from the total sum of squares calculated from individual observations. But there is actually no need to calculate either of these sums of squares. From the argument of the first part of the appendix, the sum of squares for reproducibility is simply

$$\tfrac{1}{2}[(5-20)^2+(5-5)^2+(15-10)^2+(45-0)^2]=1137.5$$

and one degree of freedom attaches to each difference. The full analysis for the (112) reflection is then:

Source of variation	*Sum of squares*	*Degrees of freedom*	*Mean square*
Mounts	153.125	1	153.125
Scale factors	3.125	1	3.125
Interaction	153.125	1	153.125
Reproducibility error	1137.5	4	284.325

There is no evidence that the use of different mounts and scale factors has contributed appreciably to the observed variation; comparable dispersion would be expected if a similar number of charts were made on the same mount at the same scale setting, providing the mount were removed from the specimen holder at the conclusion of each scanning. Although the numerical values of the mean squares of course vary from peak to peak, similar calculation leads to the same general conclusion for all the smear mount data of Table 3.

References

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