Quantitative determination of mineral content of geological samples by X-ray diffraction: Reply

GAYLE A. PAWLOSKI

Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550, U.S.A.

Briant L. Davis has commented that the theory of the external-standard–intensity-ratio quantification method described in Pawloski (1985) is sound, but that the experimental procedure contains serious flaws (Davis, 1987). These flaws exist because the procedure was compromised to maintain the geologic integrity of the samples. I needed to establish an X-ray diffraction (XRD) method that was "rapid and routine" and would quantify 5 to 10 minerals in one sample. I was willing to accept a larger error in this quantification than some people who may not be able to do so. I feel confident that this method can easily be refined to serve their needs.

Size-fraction tests showed that 35 to 45 μm was the best particle-size range to work with using multicomponent samples of compositions similar to Nevada Test Site (NTS) samples. Many authors have shown that it is easy and desirable to control particle size when systems are composed of a single component or a small number of components. However, it is important to note that NTS samples may contain up to 10 different minerals of many crystal classes. In determining which particle size range to work with, I tested six different size fractions (60 to <20 μm) of known compositions to find which fraction (1) best represented the original composition, (2) required the least amount of sample preparation, and (3) presented sufficient XRD intensity to guarantee acceptable statistical data. Reason (1) was by far the most important consideration. The test samples contained quartz, montmorillonite, clinoptilolite, feldspar, and calcite. Large particles (>100 μm) of each component were mixed together in known compositions, and were then ground, sieved, and X-rayed. The XRD data showed that increasing particle size lowered intensities, as expected (Klug and Alexander, 1954), but that statistically acceptable intensities were obtained even at 45 μm. Long grinding and sieving periods (~45 min) were necessary to obtain sufficient material for a sample of small size fraction (<20 μm). The deciding factor in this matter was in determining how representative each size fraction was of its original composition. For size fractions larger than 45 μm, quartz and calcite became predominant components upon sieving, even for short durations. Quartz and calcite were in error up to 16 wt% from the known compositions. In smaller size fractions— <35 μm—clays and zeolite predominated. They were present in errors up to 20 wt% of the known compositions. Physical properties and crystal habit affect both sieving and grinding (Tatlock, 1966) and rendered these size fractions unrepresentative of their original

compositions. The size fraction between 35 to 45 μm exhibited a 6 wt% error from the known compositions. It required short sample preparation time (15 min for grinding and sieving), and the XRD data were statistically acceptable. Because of these reasons, I chose to work with the size fraction between 35 to 45 μm. Using particles of this size has been a compromise; XRD data may be less intense and probably are affected by microabsorption as a result of the larger particle size. However, I decided that maintaining sample representation was by far a more important factor.

Well mounts were chosen because they are easy to use with powdered samples. Our use of particles in the 35 to 45-μm range eliminated the use of aerosol suspension on filter substrates (Davis and Johnson, 1982) and spray drying to form spherical agglomeration (Calvert et al., 1983), methods that require a particle size <10 μm. Substances deposited on filter substrates require transparency corrections and measurements of mass-absorption coefficients for amorphous components, which are additional measurements I tried to avoid making. It has been shown that aerosol suspension and spray drying reduce and eliminate preferred orientation, while well mounts do not address this topic. Smith et al. (1979) obtained accurate quantitative results using spray drying of natural geologic samples after sieving through <325 mesh sieves (particle size <45 μm). Snyder (1982) indicated that as long as agglomerates are kept below 100 μm in size, reliable, reproducible orientation-free intensity measurements can be made, although he stated that the particle size should be under 10 μm. It is possible that the spray-drying method would reduce preferred orientation while maintaining the integrity of the sample for the suite of minerals used in this study.

Comparison of quartz-based K constants converted to Al_2O_3-based reference-intensity ratios (RIR) based on calculated X-ray powder patterns does show variation (Davis, 1987, Table 1). This may indeed be the result of particle size and preferred orientation, as suggested by Davis. Certainly chemical variation in samples will also affect these numbers, although I don't believe this can account for large discrepancies. I would like to point out though that feldspar RIR values are documented to range between 0.28 to 1.71 (Davis and Walawender, 1982) as opposed to 0.5 to 0.7 as presented in Davis's Table 1. The converted RIR values from my data are still above this range.

Errors shown in Table 2 of my original report are actual

TABLE 1. Calculated and expected mineral contents for each test sample

Sample	Q	MO	IL	CC	CR	FS	CA	DO	GL	HO	KA	MU	BO
						Mineral content (wt%)							
1 calculated	29	23	—	—	—	26	22	—	—	—	—	—	—
expected	25	25	—	—	—	25	25	—	—	—	—	—	—
2 calculated	19	32	—	—	—	41	9	—	—	—	—	—	—
expected	15	30	—	—	—	40	10	—	—	—	—	—	—
3 calculated	12	12	9	18	—	15	8	13	—	—	14	—	—
expected	10	15	10	25	—	10	5	10	—	—*	15	—	—
4 calculated	14	3	—	14	—	42	—	5	—	4	—	18	—
expected	10	5	—	15	—	40	—	5	—	5	—	20	—
5 calculated	9	6	22	7	—	22	—	5	—	3	8	12	6
expected	5	10	15	10	—	20	—	5	—	5	10	10	10
6 calculated	24	7	5	5	—	8	—	26	—	8	17	—	—
expected	20	10	5	5	—	5	—	25	—	10	20	—	—
7 calculated	21	—	—	28	—	—	—	—	—	19	26	6	—
expected	15	—	—	35	—	—	—	—	—	20	25	5	—
8 calculated	16	—	21	—	—	26	12	10	—	—	5	11	—
expected	9	—	23	—	—	23	14	14	—	—	5	14	—
9 calculated	9	5	—	6	—	39	6	5	—	13	5	—	12
expected	10	5	—	5	—	35	5	5	—	15	5	—	15
10 calculated	11	43	25	—	—	8	—	—	—	—	—	—	—
expected	5	50	30	—	—	5	—	—	—	—	—	—	—
11 calculated	20	—	—	—	—	44	—	—	36	—	—	—	—
expected	20	—	—	—	—	40	—	—	40	—	—	—	—
12 calculated	12	19	—	—	—	19	—	—	49	—	—	—	—
expected	10	20	—	—	—	20	—	—	50	—	—	—	—
13 calculated	15	—	—	14	—	24	—	—	48	—	—	—	—
expected	15	—	—	15	—	20	—	—	50	—	—	—	—
14 calculated	15	13	—	18	7	48	—	—	—	—	—	—	—
expected	15	10	—	20	5	50	—	—	—	—	—	—	—
15 calculated	33	—	17	—	8	10	5	5	—	9	13	—	—
expected	30	—	20	—	10	10	5	5	—	10	10	—	—
16 calculated	22	—	—	—	20	8	—	—	49	—	—	—	—
expected	20	—	—	—	20	10	—	—	50	—	—	—	—

Note: Mineral symbols are as follows: Q = quartz; MO = montmorillonite; IL = illite; CC = clinoptilolite; CR = cristobalite; FS = feldspars; CA = calcite; DO = dolomite; GL = glass; HO = hornblende; KA = kaolinite; MU = muscovite; BO = biotite.

weight percent error in quantifying each mineral in 16 samples using the external-standard–intensity-ratio technique. The samples were composed of 3 to 11 components and made to be representative of the geologic environment at NTS. (Table 2 in my original report contains an error. Sample 12 should have shown these values: Q +2, MO −1, FS −1, and GL −1.) Table 1 herein shows calculated and expected values for each mineral in these 16 samples. Calculated values were determined using the equation

$$\sum_{k=1}^{n} x_k = 1.0,$$

where n = number of components in sample and x_k = weight fraction of mineral k. Input values were obtained by averaging ratios from six repeat XRD scans on the same sample. The sample was repacked and replaced in the diffractometer each time. Because of summation in the quantification, variation or error in one value forces variation in another. The error in the quantification is the maximum weight percent error in quantifying any mineral in the sample.

The minimum amount of each mineral detectable in a multicomponent sample is important because it places a lower limit on the quantification procedure. This is simply the smallest amount of a mineral that produces XRD data that can be distinguished from background, i.e., the analyst can identify that the mineral is present. For example, if the computer program calculates 4.0 wt% illite, users should recognize that there is at least 7.0 wt% illite present. Similar to the discussion by Davis, my experience also shows that error in quantification increases as quantities decrease—error is larger with smaller quantities.

Determining the content of glass proved to be the most difficult feature of the quantification procedure because of the amorphous character of glass. It is true that other methods could identify and more accurately quantify amorphous compositions, but they would require additional measurements. My intent was to formulate a method for rapid routine quantification. Some accuracy is sacrificed for this reason.

In summary, the external-standard–intensity method provides rapid routine quantification of geologic samples by XRD. It does have some features that fall outside normal procedure. Further work may need to be done to reduce the effects of preferred orientation. For our work with NTS samples, this quantification works well. Others may need to refine the procedure for their work.

REFERENCES

Calvert, L.D., Sirianni, A.F., and Gainsford, G.J. (1983) A comparison of methods for reducing preferred orientation. Advances in X-ray Analysis, 26, 105–110.

Davis, B.L. (1987) Quantitative determination of mineral content of geological samples by X-ray diffraction: Discussion. American Mineralogist, 72, 438–440.

Davis, B.L., and Johnson, L.R. (1982) On the use of various filter substrates for quantitative particulate analysis by X-ray diffraction. Atmospheric Environment, 16, 273–282.

Davis, B.L., and Walawender, M.J. (1982) Quantitative mineralogical analysis of granitoid rocks: A comparison of X-ray and optical techniques. American Mineralogist, 67, 1135–1143.

Klug, H.P., and Alexander, L. (1974) X-ray diffraction procedures, second edition. Wiley, New York, 966 p.

Pawloski, G.A. (1985) Quantitative determination of mineral content of geological samples by X-ray diffraction. American Mineralogist, 70, 663–667.

Smith, S.T., Snyder, R.L., and Brownell, W.E. (1979) Quantitative phase analysis of Devonian shales by computer controlled X-ray diffraction of spray dried samples. Advances in X-ray Analysis, 22, 181–192.

Snyder, R.L. (1982) Accuracy in angle and intensity measurements in X-ray powder diffraction. Advances in X-ray Analysis, 26, 1–10.

Tatlock, D.B. (1966) Rapid modal analysis of some felsic rocks from calibrated X-ray diffraction patterns. U.S. Geological Survey Bulletin 1209.