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

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The reference-intensity-ratio method of quantitative X-ray diffraction is rapidly coming to the forefront of quantitative X-ray powder diffraction analysis. Pawloski (1985) has completed quantitative analysis of prepared mixtures of fine-grained geologic materials by this procedure. Pawloski is to be commended for using this approach and for her method of obtaining reference-intensity constants from calibration curves by the intensity ratio/weight ratio slope method. Nevertheless, I believe that several experimental and interpretive difficulties arise in this paper and bring into question the application to Pawloski's samples, which I feel warrants some discussion here.

As a point of clarification, it should be noted that Pawloski's constant K is the reciprocal of the well-established reference intensity constant, k_i (Chung, 1974), also known as the reference intensity ratio RIR (Hubbard et al., 1976; Cline and Snyder, 1983), but with quartz as the reference material. The theoretical basis for Pawloski's approach is sound, in my opinion, but I have some concern over several other aspects of the presentation, briefly listed as follows: (1) the large size (between 35- and 45-μm diameter) of the sample particles, (2) the "backpacking" procedure of sample mounting, (3) the manner in which the errors are presented, and (4) the use of diffused diffraction intensities for glass quantification.

The effects of large particle size on X-ray diffraction are well known. The extreme variability of intensities from a layer of particles this coarse grained has been well documented by Wolff et al. (1965) and Klug and Alexander (1974). Since the number of particles (spheres) of a material found within a given volume varies as the diameter cubed, it is easy to show, for example, that there will be 125 times more 5-μm particles than 25-μm particles in a given component volume. Thus, the probability that a particle will have the proper orientation for constructive beam interference is increased by a like factor. Compared to a scan taken from the large particles, a set of intensities from a sample of the smaller particles would not show the large variation in intensities on sample rotation as was observed for 20–30-μm particles by Wolff et al. (1965). Other effects were demonstrated by Cline and Snyder (1983), whose data showed a change in the reference-intensity-ratio values determined with Al_2O_3 as a standard as the particle size of the material being analyzed increased. This is also a common observation in our laboratory; that is, the reference-intensity ratio will increase markedly with decreasing particle size of the material being analyzed as a result of the reduction in microabsorption and primary extinction with decreasing particle size.

With regard to the second point, there are at least two techniques now available for the preparation of samples without introducing significant preferred orientation (Davis and Cho, 1977; Davis and Johnson, 1982a, 1982b; Calvert et al., 1983; Cline and Snyder, 1983; Davis, 1984). One method used in our laboratory (Davis, 1984) consists of aerosol suspension in a 4- or 8-L aspirator jar and collection on glass fiber filters with corresponding application of corrections for transparency and matrix effects. The sample particles are reduced to an average of under 10-μm diameter by mixer-mill pulverization for such samples. Actual sample loading takes from 1–5 min. Since a large proportion of Pawloski's samples contains phyllosilicates and carbonates, it would appear that any sample preparation without due concern for preferred orientation would yield highly suspect results.

I believe that the particle size and preferred orientation aspects just discussed will create reference-constant values such as presented in Pawloski's Table 1 that cannot be used for accurate quantitative analytical work. I have converted most of these K constant values into Al_2O_3-based reference-intensity ratios as formally defined using the calculated quartz k_i as the common basis of conversion. Table 1 lists values given by Pawloski, values used in our laboratory's aerosol suspension inventory, and cal-

Table 1. Reference-intensity constants of selected minerals according to various authors (Al_2O_3 basis)

Mineral	Reference-intensity ratio (I/I_c)			
	Pawloski	Davis	Borg and Smith†	Jahanbagloo and Zoltai‡
Quartz	3.8	2.8	3.8	4.3
Montmorillonite	0.17	0.5	—	—
Illite	0.13	0.60	—	—
Kaolinite	0.4	0.8	0.2	—
Cristobalite	2.9	2.9	4.4	—
Feldspars	3.0	0.5–0.7	0.3–0.6	—
Calcite	5.8	2.0	—	3.3
Dolomite	10.8	1.4	—	2.7
Hornblende	1.4	0.7	0.6	—
Muscovite	2.0	0.3	0.3–0.5	—
Biotite	8.8	2.4	3.7*	—

* Ferriannite.

† Borg and Smith (1969).

‡ C. Jahanbagloo and T. Zoltai (1966, unpub. data).

culated values from Borg and Smith (1969) and Jahanbagloo and Zoltai (1966). As can be seen, very large disparities exist with some materials, notably phyllosilicates and carbonates. Experimental values of k_i should not be as high as the calculated values, and certainly the experimental values should not be significantly larger than the calculated ones as we see for the feldspars, carbonates, and micas in Pawloski's data. Pawloski's k_i values for calcite, dolomite, muscovite, and biotite are a factor of two or more greater than either our experimental values or the calculated values; they are highly suspect as being amplified by the effects of preferred orientation. The three species not fitting this pattern are montmorillonite, illite, and kaolinite; Pawloski's values appear anomalously low to us, but little calculated data are available for a "neutral-ground" comparison here.

It might be argued that preferred orientation in both the material being analyzed and the reference standard will result in a cancelling of the intensity anomalies in the final data processing. This may be true in the case of Pawloski's data in question here, and one might justify a general approach based on this assertion. However, I would strongly argue against such a philosophy on the basis that one simply cannot reproduce a certain degree of preferred orientation in any manual sample preparation scheme.

As an alternative, I can only recommend the aerosol suspension–filter collection technique that has worked so well for us. It gives reproducible results, and the high degree of randomness of particle orientation has been demonstrated and reported on several occasions at X-ray conferences and in the literature (e.g., Davis and Cho, 1977; Davis, 1984; Davis, 1986). The laboratory equipment is inexpensive and the required intensity and matrix-absorption corrections are simple to apply (Davis and Johnson, 1982a). The reference-intensity constants are determined by this same procedure and therefore become truly "universal" constants, applicable to data obtained on any diffractometer kept in good alignment.

On the third matter under discussion, I am disappointed that the author would not present at least some of the actual component weight data for the prepared samples (Table 2 in Pawloski, 1985). The errors presented are of little value unless the absolute weight percent of each component is also given. It is our experience that even under the most ideal conditions of quantitative X-ray analysis, minor components whose weight fractions fall below 5% may well have associated uncertainties of 50 or 100% of the stated value. It is not clear here whether the percentages given in Pawloski's Table 2 are actual weight percent errors or percent of the analyzed quantity (relative error). Under the latter interpretation, the maximum error of ±7% would be a very high level of accuracy for any component falling below the 5% weight percent level of analysis. It also appears that Pawloski's uncertainties given for the CO_2 reduction from the carbonates suggest that the actual relative errors are much higher, since for the observed variation in CO_2 (from carbonate minerals), she gives an uncertainty of 147% of the stated amount [100 × (1.26/0.86)]. In work recently published in our laboratory on the southern California batholith (Davis and Walawender, 1982), minor components (below 5%) demonstrated errors of up to 100% of the stated amount, although in general, our agreement with polarizing optical modal analysis was very good.

With regard to the fourth point, although it is conceivable that some rough analysis of amorphous materials can be completed by measuring the area under the broad diffused diffraction band, this exercise is really not justified in view of the much more accurate procedure available by mass-absorption balance methods (Davis, 1981; Davis and Johnson, 1982b). In this regard, how can one report uncertainties in glass composition of 1–4% (Table 2 of Pawloski, 1985) when the limit of detection (Table 3 of Pawloski, 1985) of glass is 40%?

In summary, I believe that the paper under discussion contains serious flaws in experimental procedure such as to render the analysis rather suspect, and although the procedure used by Pawloski appears to be appropriate, the reference-constant values resulting from the analysis are of questionable value. Furthermore, one cannot make a definitive judgment on the errors expected for the results of the sample analyses since the error definition is unclear and none of the fundamental analytical data were published in this paper.

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