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, \( k \) (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 \( \text{Al}_2\text{O}_3 \) 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 I that cannot be used for accurate quantitative analytical work. I have converted most of these \( K \) constant values into \( \text{Al}_2\text{O}_3 \)-based reference-intensity ratios as formally defined using the calculated quartz \( k \), as the common basis of conversion. Table 1 lists values given by Pawloski, values used in our laboratory’s aerosol suspension inventory, and calculated values in this paper and bring into question the application to Pawloski’s samples, which I feel warrants some discussion here.

### Table 1. Reference-intensity constants of selected minerals according to various authors (\( \text{Al}_2\text{O}_3 \) basis)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Pawloski</th>
<th>Davis</th>
<th>Borg and Smith†</th>
<th>Jahanbagloo and Zoltai‡</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>3.8</td>
<td>2.8</td>
<td>3.8</td>
<td>4.3</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>0.17</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Illite</td>
<td>0.13</td>
<td>0.60</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.4</td>
<td>0.8</td>
<td>0.2</td>
<td>—</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>2.9</td>
<td>2.9</td>
<td>4.4</td>
<td>—</td>
</tr>
<tr>
<td>Feldspars</td>
<td>3.0</td>
<td>0.5-0.7</td>
<td>0.3-0.6</td>
<td>—</td>
</tr>
<tr>
<td>Calcite</td>
<td>5.8</td>
<td>2.0</td>
<td>—</td>
<td>3.3</td>
</tr>
<tr>
<td>Dolomite</td>
<td>10.8</td>
<td>1.4</td>
<td>2.7</td>
<td>—</td>
</tr>
<tr>
<td>Hornblende</td>
<td>1.4</td>
<td>0.7</td>
<td>0.6</td>
<td>—</td>
</tr>
<tr>
<td>Muscovite</td>
<td>2.0</td>
<td>0.3</td>
<td>0.3-0.5</td>
<td>—</td>
</tr>
<tr>
<td>Biotite</td>
<td>8.8</td>
<td>2.4</td>
<td>3.7</td>
<td>—</td>
</tr>
</tbody>
</table>

culated values from Borg and Smith (1969) and Jahan-
bagloo and Zoltai (1966). As can be seen, very large dis-
parities exist with some materials, notably phyllosilicates
and carbonates. Experimental values of $k_0$ should not be
as high as the calculated values, and certainly the experi-
mental 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 $k_0$ 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 “neu-
tral-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 prepara-
tion 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 equip-
ment is inexpensive and the required intensity and ma-
trix-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 disappoint-
et 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 max-
imum error of ±7% would be a very high level of accu-
raczy for any component falling below the 5% weight per-
cent 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 car-
bonate minerals), she gives an uncertainty of 147% of the
stated amount [100 $\times$ (1.26/0.86)]. In work recently pub-
lished in our laboratory on the southern California batho-
lith (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 conceiv-
able 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 justi-
fied in view of the much more accurate procedure avail-
able 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 re-
sults 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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