



Technical Note

Determining Amorphous Content with the Internal Standard Method

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Introduction

Amorphous content presents a challenge when interpreting powder x-ray diffraction results. The relative amounts produced by Rietveld semi-quantitative analysis won't reconcile easily with elemental assays if even a small amount of amorphous content is present. Determining the amount of amorphous content not only gives you that added information about your sample, it also lets you treat the amounts of the crystalline phases as a "floor" value when trying to reconcile elemental results.

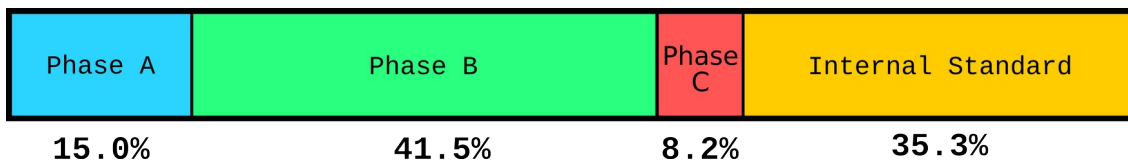
The Problem

X-ray diffraction (XRD), broadly speaking, cannot characterize amorphous materials directly. This limitation is especially true with unknown amorphous materials, where there is no compositional information or a pure reference sample available. Unfortunately, most mixed mineral powder samples contain some amorphous content, and the amorphous material typically has an unknown composition. So how do we go about measuring unknown amorphous material in mixed samples using XRD, given that it cannot directly characterize amorphous material? We indirectly quantify it instead, using the absolute amounts of everything crystalline.

The Internal Standard Method

Rietveld semi-quantitative phase analysis only yields the *relative* amounts of the various crystalline phases in a sample. The solution that we use is to not measure the amorphous material, but to measure the crystalline content absolutely and accurately. We then assume that the remaining unaccounted-for content is amorphous.

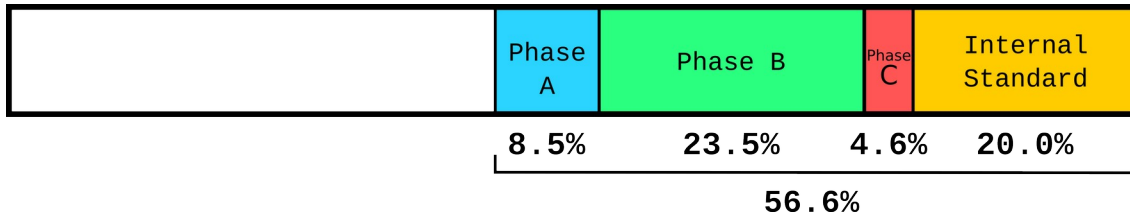
The internal standard method (ISA) extends Rietveld analysis by using a known addition ("spike") of highly crystalline phase pure material which is added to the unknown mixture. Suppose we add an amount of spike so that we know it now comprises 20% of the mass of the sample. The combined sample is then scanned in an x-ray diffractometer, and we analyze the sample using Rietveld analysis. Here's a bar graph that represents that result:



Since we know the amount of crystalline internal standard material that we added, we can scale the value obtained from Rietveld analysis to the known value, and scale all of the other phases identified by the same factor. In this case, the known amount of internal standard was 20.0%. So, for each phase we apply the following equation:

$$\text{Corrected (Weight)} = \text{Weight} \frac{\text{Standard}_{\text{Known Amount}}}{\text{Standard}_{\text{Measured Amount}}}$$

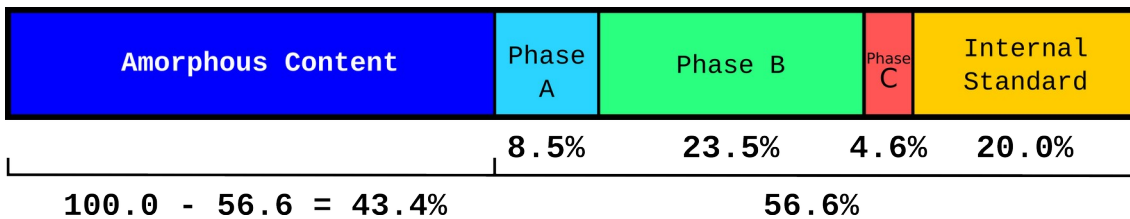
This means that in this case, we multiply the Rietveld result for each phase by (20.0/35.3), or **0.57**. Now instead of *relative* amounts, we have the following estimated *absolute* amounts of material:



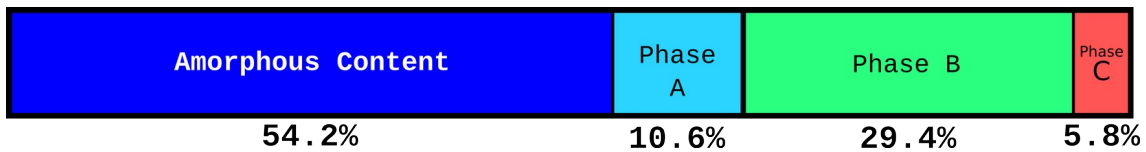
You can see that the result no longer adds up to 100%. It's now easy to calculate the amount of material we didn't explicitly quantify using the following equation:

$$Weight_{Amorphous} = 1 - \sum_{n=1}^{Number\ of\ Phases} Corrected(Weight_n)$$

This calculation results in the following composition:



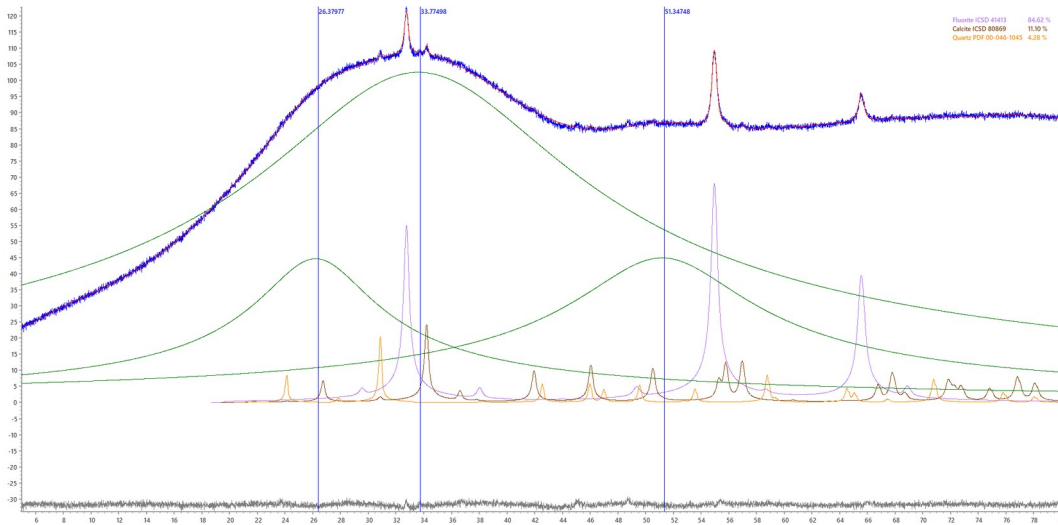
We now have a result for the amorphous content, which is the remainder after scaling the crystalline content. To make the data more presentable, we can remove the internal standard from the results:



We're left with the phase composition of the original sample and the amount of amorphous content.

Real World Example

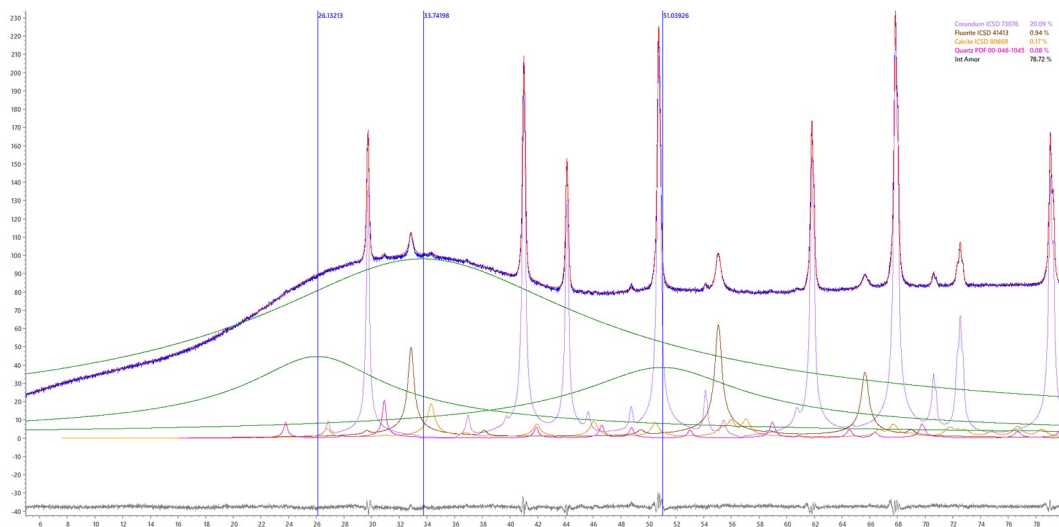
Here's a pattern of a sample dominated by amorphous content:



It's easy to see that there's amorphous material here from the broad peaks, but how much? We can fit the peaks (in green), but without other information, we can't make a reasonable determination. Here's the amounts from Rietveld:

Phase	Amount
Fluorite	84.6%
Calcite	11.1%
Quartz	4.3%

This sample is a great example because we can clearly see the massive amount of amorphous material. It's the broad hump in the diffraction signal. Usually, it can be difficult to spot under the many phases in a geological sample. Here's the plot with the corundum internal standard added:



You can see the new peaks from the standard. This analysis immediately gives us a sense of scale for the true amount of amorphous material we're dealing with in this sample, and the relatively small amount of crystalline material:

Phase	Amount
Fluorite	1.2%
Calcite	0.2%
Quartz	0.1%
Amorphous	98.5%

The crystalline components are absolutely swamped by the amorphous content.

Advantages

The internal standard method is an indirect method of measuring amorphous content so you don't need to know much about the composition of the amorphous material in a sample to measure it. That's a convenient feature for unknown field samples. Most laboratories can provide it, and the additional equipment is a normal analytical balance.

Disadvantages

For really accurate results, the internal standard should be selected to match the mass absorption of the sample, but the choices aren't infinite. The common choices are lithium fluoride, corundum ($\alpha\text{-Al}_2\text{O}_3$), calcium fluoride, and zinc oxide. Some of these choices degrade under atmospheric conditions, or aren't available with well-controlled crystallinity. Calcium fluoride should probably be annealed under vacuum regularly if used. Lithium fluoride will take up water from the air, especially if finely divided in a powder. Even the stable materials need specialty sourcing. Most sources of corundum won't be phase pure or won't have an appropriate particle or crystallite size distribution.

Alternatives

The next best choice for amorphous content measurement is the external standard. The external standard method uses a standard sample that is run before the unknown sample to determine a calibration constant, which allows for the measurements of the crystalline components of the sample to be put on an absolute basis. The amorphous content is again determined indirectly by using the sum of the crystalline components. Unfortunately, the external standard method requires you to determine the sample's mass absorption coefficient, so you need elemental assay results for all the major elements.

Another alternative is the Partial Or No Known Crystal Structure (PONKCS) method, which uses a calibrated empirical model of an amorphous or disordered component to fit an amorphous or disordered component. This method is handy for well characterized amorphous or disordered components like clays. The advantage is that you can fit more than one of these components, such as

multiple clay species. The disadvantage is that you need a relatively pure sample of the disordered or amorphous material to make a model of it to start with.

Another option is the degree of crystallinity method. In this case, you fit peaks to the amorphous material in the scan. You assume that the chemistry of the amorphous material is identical to the average chemistry of the crystalline material. The calculation for the amorphous material is then determined from the area of the amorphous versus the crystalline. This is a poor method for a few reasons. First, the chemistry is very unlikely to match. In our example above, the amorphous material is likely silica glass, but the calcium fluoride dominates the crystalline results. Also, fluorescence signal is not accounted for. A small amount of manganese or chromium in the sample would massively skew the results. Lastly, single peak fits tend to conflict with background functions, so the background must be controlled very carefully to avoid fitting beam spill on sample holders. Use with caution.