Introduction Quantitative X-Ray Diffraction Methods

(prepared by James R. Connolly, for EPS400-001, Introduction to X-Ray Powder Diffraction, Spring 2010)

Introduction

Qualitative analysis usually involves the identification of a phase or phases in a specimen by comparison with "standard" patterns (i.e., data collected or calculated by someone else), and relative estimation of proportions of different phases in multiphase specimens by comparing peak intensities attributed to the identified phases.

Quantitative analysis of diffraction data usually refers to the determination of amounts of different phases in multi-phase samples. Quantitative analysis may also be thought of in terms of the determination of particular characteristics of single phases including precise determination of crystal structure or crystallite size and shape. In quantitative analysis, an attempt is made to determine structural characteristics and phase proportions with quantifiable numerical precision *from the experimental data itself*. Though "standard" patterns and structural data are used as a starting point, the most successful quantitative analysis usually involves modeling the diffraction pattern such that the calculated pattern(s) duplicates the experimental one.

All quantitative analysis requires precise and accurate determination of the diffraction pattern for a sample both in terms of peak positions and intensities. While some kinds of analysis (i.e., particle shape and clay structure) rely on the existence of preferred orientation, most require a uniformly sized, randomly oriented fine (ideally 1-2 μm) powder specimen to produce intensities which accurately reflect the structure and composition of the phase(s) analyzed.

As will become evident, the successful application of quantitative methods requires careful sample preparation, good quality data and a very thorough understanding of the material you are working with and the possible sources of error in your experiments. Since diffraction data are generally very dependent on the systematics of your diffractometer and its data collection system, application of quantitative methods that involve ratios of peak intensities requires careful calibration with well-known standards before a quantitative analysis is attempted.

The most effective quantitative methods, particularly those involving pattern modeling, are computationally intensive can only be applied with powerful analytical software. Commercial versions of this type of software are very expensive. Fortunately there are several inexpensive (or free) versions of software to do pattern refinements and quantitative analysis. Though they are not as "user friendly" as the commercial versions, once the learning curve is climbed, they can be very effective analytical tools.

This chapter will focus on approaches to quantitative determination of the amounts of particular phases in multiphase samples. At best this chapter is a skimpy introduction to a very large field. The basic organization is modified from Chapter 13 of Jenkins and Snyder (1996). The last section, essential for anyone wanting to apply these methods to their own work, is a partial list of reference material related to quantitative methods.

The Intensity Equation

The diffraction pattern includes information about peak positions and intensity. The peak positions are indicative of the crystal structure and symmetry of the contributing phase. The

peak intensities reflect the total scattering from the each plane in the phase's crystal structure, and are directly dependent on the distribution of particular atoms in the structure. Thus intensities are ultimately related to both the structure and composition of the phase.

The diffraction intensity equation has been described previously, and is summarized below.

$$I_{(hkl)\alpha} = \frac{I_0 \lambda^3}{64\pi r} \left(\frac{e^2}{m_e c^2} \right)^2 \frac{M_{(hkl)}}{V_\alpha^2} \left| F_{(hkl)\alpha} \right|^2 \left(\frac{1 + \cos^2(2\theta) \cos^2(2\theta_m)}{\sin^2\theta \cos\theta} \right)_{hkl} \frac{v_\alpha}{\mu_s}$$

where:

- $I_{(hkl)\alpha}$ = Intensity of reflection of *hkl* in phase α.
- I_0 = incident beam intensity
- r = distance from specimen to detector
- λ = X-ray wavelength
- $(e^2/mc^2)^2$ = square of classical electron radius
- μ_s = linear absorption coefficient of the specimen
- v_α = volume fraction of phase α
- M_{hkl} = multiplicity of reflection *hkl* of phase α
- 0 = Lorentz-polarization (and monochromator) correction (next to last term to right)
- v_α = volume of the unit cell of phase α
- $2\theta_m$ = diffraction angle of the monochromator
- $F_{(hkl)\alpha}$ = structure factor for reflection hkl of phase α (i.e., the vector sum of scattering intensities of all atoms contributing to that reflection).

Recognizing that many of these terms are consistent for a particular experimental setup we can define an experimental constant, K_e. For a given phase we define another constant, $K_{(hkl)\alpha}$, that is effectively equal to the structure factor term for phase α. Substituting the weight fraction (X_α) for the volume fraction, the density of the phase (ρ_α) for the volume, and the mass absorption coefficient of the specimen ($\mu/\rho)_s$ for the linear absorption coefficient yields the following equation:

$$I_{(hkl)\alpha} = \frac{K_e K_{(hkl)\alpha} X_\alpha}{\rho_\alpha (\mu/\rho)_s}$$

This equation describes in simpler terms the intensity for peak *hkl* in phase α.

The fundamental problem (aside from the non-trivial problem of getting accurate intensity measurements from a homogeneous randomly oriented powder) lies in the mass absorption coefficient for the sample, ($\mu/\rho)_s$. If this quantity is known, the calculations are simple. ***The problem is that in most experiment ($\mu/\rho)_s$ is a function of the amounts of the constituent phases and that is the object of our experiment.*** Basically, all of the peak intensity-related methods for doing quantitative analysis discussed subsequently involve circumventing this problem to make this equation solvable.

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Sample Preparation Issues

With the possible exception of whole-pattern (Rietveld and similar) methods of quantitative analysis (in which specimen characteristics become another parameter to be modeled), successful quantitative analysis requires a specimen that presents a very large number of randomly oriented, uniformly sized crystallites to the X-ray beam. Preparation of specimens that start out as large solid objects (i.e., rocks, ores, concrete, ceramics, etc.) for quantitative analysis will usually involve a multi-phase process involving a variety of equipment. Most of the equipment currently available in the Department of Earth and Planetary Sciences are listed in the chapter on "Errors and Sample Preparation" (p. 12-13).

The statistics of particle size and consequent statistical errors in intensities determined by a diffractometer have been discussed previously in the chapter on "Errors and Sample Preparation" (p. 8-10). The point of this discussion is that to achieve peak intensity errors of less than ±1% for a single phase (100% of specimen) requires particles between 0.5 and 1.0 µm in size. This particle size range, in practice is extremely difficult to obtain. The best methods generally result in a 1-5 µm size range, and the statistics are further degraded by the fact that every phase in a multi-phase sample will be less than 100% of the whole. All of this means that a statistical error of ±5% for major phases in an intensity-related quantitative analysis should be considered reasonable. Be suspicious of analyses that report lower errors.

All of the errors related to sample preparation discussed in the previous chapter may be a factor in quantitative analysis. Clearly the most successful quantitative analyses will be with materials in which particle size is uniform, small and well known; engineered materials frequently fall into this category.

Particular caution must be exercised in situations where crystallite sizes vary widely within a particular sample; many rocks and most soils fall into this category. The author worked for many years with extrusive volcanic rocks from southern Nevada. These pyroclastic rocks included non-welded vitric and zeolitized fall and flow deposits and very densely welded devitrified ash-flow tuffs. A goal of the analyses was to produce repeatable quantitative determinations of the amounts of different phases in the specimens. Although techniques were developed using an internal standard that could produce repeatable results (± 5%) in known binary mixtures, the method could not be successfully applied to the actual rocks and results varied by up to 30% from independent determinations with petrographic microscope, electron microprobe and chemical techniques. The most likely root of this failure was the inability to produce homogeneous crystallite sizes in source materials containing a wide range of constituents (from <<1 µm devitrification products to 50+ µm pore filling crystallization products to 1-2 mm phenocrysts of quartz and feldspar).

An excellent and concise reference summarizing most of what you need to know about sample preparation for all purposes in XRD (including quantitative analysis) is the article by Bish and Reynolds in Bish and Post (1989).

Measurement of Line Intensities

All of the methods of quantitative analysis (even whole-pattern methods) require accurate intensity measurements. The table below (from Jenkins and Snyder, p. 356) summarizes the various factors which control absolute and relative intensities in a powder pattern.

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Structure Sensitive Factors: These factors are mostly included in the $K_{(hkl)\alpha}$ term in the intensity equation. Most of these factors are intrinsic properties of the phase producing the reflection, but their intensity can be modified both temperature and the wavelength of the incident radiation.

Factor	Parameter
1. Structure-sensitive	Atomic scattering factor
	Structure factor
	Polarization
	Multiplicity
	Temperature
2. Instrument-sensitive (a) Absolute intensities	Source Intensity
	Diffractometer efficiency
	Voltage drift
	Takeoff angle of tube
	Receiving slit width
	Axial divergence allowed
(b) Relative intensities	Divergence slit aperture
	Detector dead time
3. Sample-sensitive	Microabsorption
	Crystallite size
	Degree of crystallinity
	Residual stress
	Degree of particle overlap
	Particle orientation
4. Measurement-sensitive	Method of peak area measurement
	Degree of peak overlap
	Method of background subtraction
	$K\alpha_2$ stripping or not
	Degree of data smoothing employed

Instrument-sensitive Parameters: Variation in power supplied to the X-ray tube can cause notable variation in incident beam intensity over time. Fortunately most modern digital power supplies (including our Spellman DF3 unit) include very sophisticated circuitry to virtually eliminate voltage drift. All X-ray tubes will decrease in intensity as they age, however, and it is important to monitor this over time.

Detector dead time can cause very intense peaks to be measured with lower intensity; the proper dead time correction should be applied to correct your data for this.

Sample-sensitive Parameters: These are by far the most important class of factors affecting quantitative work. All of these factors have the capability of severely compromising the usefulness of your diffraction data. ***Bottom line:*** keep your crystallite size at 1 μm for all

phases and eliminate preferred orientation in your specimen and you've got a chance of getting usable data.

Measurement-sensitive Parameters: The selection of the 2θ points at which background will be measured is critical to determination of accurate integrated peak intensities. The choice of where the peak starts and ends relative to backgro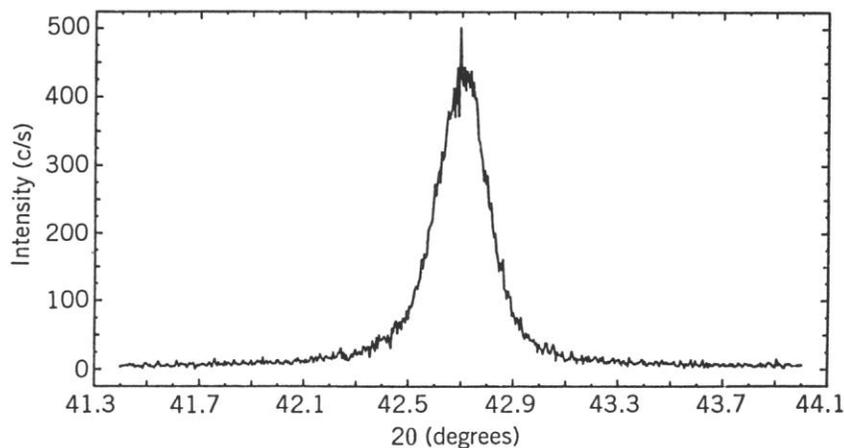und will have a significant effect on integrated intensity as illustrated in the figures (from Jenkins and Snyder, 1996) below.

Figure 13.3 shows an experimental trace of the (111) peak of Si using Cr radiation. Note that the peak has a notable "tail" and the start of the peak could be picked at some point between 41.5° and 42.2° 2θ.
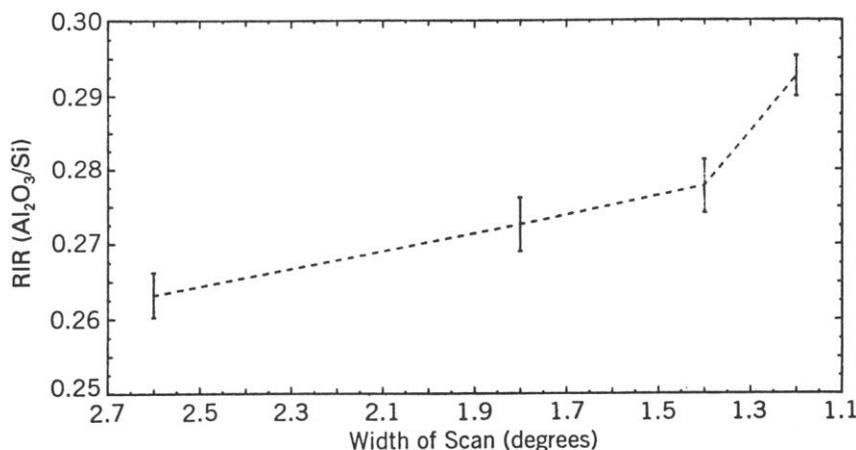
Figure 13.3. Trace of the Si (111) peak using Cr radiation.

The RIR is the ratio between the integrated intensities of the peak of interest and that of a known standard (Corundum in this case). Figure 13.4 shows how the RIR varies as a function of where the background is picked (holding the Al_2O_3 line constant). Clearly, where the background is picked will have a significant effect on peak ratios, and thus the amount of the unknown determined.

Figure 13.4. The variation of the RIR as a function of scan width of the peak shown in Figure 13.3.

It must be noted that peak areas for well-defined peaks will be proportional to peak heights, but that this relationship breaks down in peaks which show significant broadening. As discussed previously in the material on diffraction intensities (Diffraction Basics Part 2 – Week 6), peak broadening, either by strain or particle size, results in integrated peak intensities (generally larger) which are not representative of the amounts present, thus some sort of correction for this broadening is desirable for quantitative analysis. This effect is shown in the left-most two peaks in (Fig.13.5a and 13.5b below).

Another significant problem in the use of integrated intensities is in overlapping peaks of interest and the difficulty of calculating integrated intensities. This requires one of two approaches: selection of peaks which do not overlap or decomposition of overlapping peaks into their components prior to calculating integrated intensities. The peak overlap situation is shown in Figure 13.5c below. Sophisticated digital tools for processing diffraction data make peak deconstruction or "deconvolution" possible.
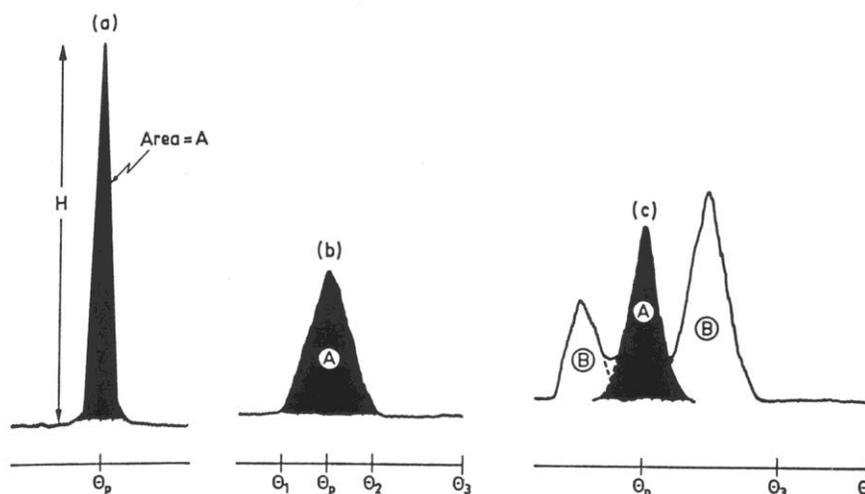

Figure 13.5. Types of line measured in quantitative analysis. From R. Jenkins and J. L. de Vries, *An Introduction to Powder Diffractometry*, p. 35, Fig. 46. Copyright © 1977, N. V. Philips, Eindhoven, The Netherlands.

Useful tools in Jade to assist in processing Intensity Measurements

The routine peak identification routine in Jade is useful for quick location of prominent peaks in a pattern, however the peak intensity determinations done by this routine are generally inadequate to intensity calculation required for quantitative analysis. Jade includes a number of processing tools which can assist in processing XRD patterns to obtain good reduced intensity data for software has several tools that are very effective in processing diffraction data to obtain background-corrected peak intensities for overlapping peaks. It should be noted that Jade does not alter the original data file when refining your data, but creates separate overlays that modify the data as used and displayed. Some of the useful intensity-related tools are:

- *Background and Kα2 Removal* (Flexible tool for removing background)

- *Profile Fitting and Peak Decomposition* (Interactive tool for differentiating and separating overlapping peaks)

- *Crystallite Size and Strain Analysis from Peak Broadening* (Tool used with standard materials – NIST 640b Si or LaB_6 – to establish instrumental broadening parameters and evaluate peak broadening from strain and crystallite size)

Quantitative Methods based on Intensity Ratios

Numerous methods have been developed to use peak intensities for quantitative analysis of diffraction data. Many of them are specialized in nature (i.e., require binary mixtures or

involve polymorphs having the same mass absorption coefficients). Jenkins and Snyder (1996) introduce most of these methods, some of which are included here. By far the methods in most general use involve addition of a known amount of an internal standard and calculating ratios of the areas of the standard peaks to those of the phases being determined.

The Absorption-Diffraction Method

The absorption-diffraction method involves writing the diffraction equation twice – once for the phase in the sample and once for the pure phase, and then dividing the equations to yield:

$$\frac{I_{(hkl)\alpha}}{I^0_{(hkl)\alpha}} = \frac{(\mu/\rho)_\alpha}{(\mu/\rho)_s} X_\alpha$$

where I^0 is the intensity of the peak in the pure phase. For most materials, the mass absorption coefficient of the mixture remains the undeterminable unknown. In the specialized case where $(\mu/\rho)_s$ is the same as the phase being determined (as in isochemical polymorphs) this equation reduces to the simple case:

$$\frac{I_{(hkl)\alpha}}{I^0_{(hkl)\alpha}} = X_\alpha$$

A special case of this method for binary mixtures in where (μ/ρ) for each pure phase is known allows calculation of the amounts of both phases without requiring $(\mu/\rho)_s$ using the following equation:

$$X_\alpha = \frac{(I_{(hkl)\alpha}/I^0_{(hkl)\alpha})(\mu/\alpha)_\alpha}{(\mu/\alpha)_\alpha - (I_{(hkl)\alpha}/I^0_{(hkl)\alpha})[(\mu/\alpha)_\alpha - (\mu/\alpha)_\beta]}$$

This equation is known as the Klug equation after H.P. Klug who first formulated it. As a check on accuracy, it is possible to make the calculation for each phase independently and compare results.

The general case of the absorption-diffraction method requires that the mass absorption coefficient of the sample be known. This quantity can be experimentally determined by a variety of methods and used in the calculations. While theoretically possible, in general errors involved in this measurement are too large to be practically useful for quantitative XRD.

Since mass absorption is largely a function of atomic scattering, $(\mu/\rho)_s$ may be estimated from atomic scattering factors if the bulk chemistry of a sample is known. Tables of elemental mass attenuation coefficients are published in the *International Tables for X-Ray Crystallography* (and reproduced in most XRD texts) can be used to estimate the bulk coefficient with reasonable accuracy. This then allows the generalized absorption-diffraction equation to be used directly.

Method of Standard Additions

This method requires a variety of diffraction patterns run on prepared samples in which varied amounts of a well-known standard, β, are added to the unknown mixture containing phase α, the each mixture is analyzed . This method was developed and still widely used for

elemental analysis by X-ray Fluorescence. Because of tedious sample preparation and data errors encountered at low concentrations of both phases, this is seldom applied in X-ray diffraction.

Internal Standard Method

The internal standard method, or modifications of it, is most widely applied technique for quantitative XRD. This method gets around the $(\mu/\rho)_s$ problem by dividing two intensity equations to yield:

$$\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} = k\frac{X_\alpha}{X_\beta}$$

where α is the phase to be determined, β is the standard phase and k is the calibration constant derived from a plot of $I_{(hkl)\alpha} / I_{(hkl)'\beta}$ vs. X_α / X_β. Direct application of this method requires careful preparation of standards to determine the calibration curves, but can produce quantitative determinations of identified phases that are substantially independent of other phases in the specimen.

Care must be taken when choosing standards to select materials with reasonably simple patterns and well-defined peaks that do not overlap peaks in phases of interest. It is also very important that the crystallite size of the specimen and standard be the same, ideally about 1 μm.

Reference Intensity Ratio Methods

I/I$_{corundum}$: It is clear from the internal standard equation above that a plot of

$$X_\beta\left(\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}}\right) \quad \text{vs.} \quad X_\alpha$$

will be a straight line with slope *k*. Those *k* values using ***corundum*** as the β phase in a 50:50 mixture with the α phase are now published for many phases in the ICDD Powder Diffraction file, where $I_{(hkl)}$ is defined as the 100% line for both phases. In the PDF "card" this is defined as *I/I$_c$*, the reference intensity ratio for a 50:50 mixture of phase α and corundum. Ideally this provides a quick resource for quantitative determinations. In actuality, use of published *I/I$_c$* values for quantitative analysis usually falls short because of problems with preferred orientation, inhomogeneity of mixing and variable crystallinity. Using multiple lines from corundum (with RIRs calculated from relative intensities) can circumvent some of these problems by pointing out inconsistencies related to preferred orientation and other specimen irregularities. Use of experimentally determined RIR values rather than "published" values can greatly improve the accuracy of the results. For lab users wanting to use corundum as an internal standard, we have a significant quantity of 1 μm Corundum from the Linde Division of Union Carbide available for use.

Generalized RIR Method: In actual practice, reference intensity ratios (RIRs) can be defined for any reference phase using any diffraction line. I/Ic is actually just a specialized RIR where *hkl* (and *hkl'*) are defined as the 100% line for the phase of interest and corundum. The most general definition of the RIR for phase α to reference phase β is:

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$$RIR_{\alpha,\beta} = \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} \right) \left(\frac{I^{rel}_{(hkl)'\beta}}{I^{rel}_{(hkl)\alpha}} \right) \left(\frac{X_{\beta}}{X_{\alpha}} \right)$$

The I^{rel} term ratios the relative intensities of the peaks used; if the 100% peaks of both phases are used, the value of this term is 1. RIRs may be experimentally determined for any phase using any material as a standard. Al_2O_3 (corundum) and SiO_2 (quartz) are commonly used as internal standards. ZnO is a popular internal standard with very good peaks. Multiple RIRs may be calculated for different peaks in the same phases to provide a method for redundant determinations as a check on accuracy.

RIRs may be determined for a variety of materials using different standards. RIRs carefully determined in the same laboratory under the same conditions as diffraction experiments can be used to produce good, repeatable analyses. In addition, having good RIRs "in the can" permits the choice of the best standard (with minimal peak overlaps) for your specimen.

Quantitative Analysis with RIRs: Rearranging the equation above yields the following:

$$X_{\alpha} = \left(\frac{I_{(hkl)\alpha}}{I_{(hkl)'\beta}} \right) \left(\frac{I^{rel}_{(hkl)'\beta}}{I^{rel}_{(hkl)\alpha}} \right) \left(\frac{X_{\beta}}{RIR_{\alpha,\beta}} \right)$$

The RIR value may be obtained through careful calibration, determination of the slope of the internal standard plot or from other RIR values by:

$$RIR_{\alpha,\beta} = \frac{RIR_{\alpha,\gamma}}{RIR_{\beta,\gamma}}$$

Note that this equation allows any determined RIR (including I / I_c) to be used as long as it has been determined for both phases. Best results will be obtained if as many as possible of the variables (the RIRs and the I^{rel} values) are experimentally determined. The more published values that are used, the more the results must be considered semi-quantitative because of likelihood of significant errors.

Note that because each phase determination is independent of the whole, this method will work for complex mixtures including unidentified or amorphous phases.

Normalized RIR Method: Chung (1974) recognized that if all phases in a mixture are known and if RIRs are known for all of those phases, then the sum of all of the fractions of all the phases must equal 1. This allows the writing of a system of n equations to solve for the n weight fractions using the following summation equation:

$$X_{\alpha} = \frac{I_{(hkl)\alpha}}{RIR_{\alpha} I^{rel}_{(hkl)\alpha}} \left[\frac{1}{\Sigma^{\#phases}_{j=1} (I_{(hkl)'j} / RIR_j I^{rel}_{(hkl)'j})} \right]$$

Chung referred to this method as the matrix flushing or adiabatic principle, but it is now almost universally referred to as the normalized RIR method, and allows "quantitative" calculations without the presence of an internal standard. ***It should be noted that the presence of any unidentified or amorphous phases invalidates the use of this method. It should be further noted that in virtually all rocks, there will be phases in the sample that are undetectable and thus the method will never rigorously work.***

Constrained XRD Phase Analysis: If independent chemical or other information about the constituents in a sample is available, this information may be quantified and added to quantitative experimental data to constrain the results. The article by Snyder and Bish (in Bish and Post, 1989) discusses the general rationale for how to approach analysis with this type of complimentary data.

Full-Pattern Analysis – the Rietveld Method

Advances in computer technology have placed the computing power of the large mainframe systems of 30 years ago on virtually everyone's desktop. The availability of this computing power (and the diligence of a lot of dedicated computer programmers) has enabled diffractionists to work with the whole XRD pattern instead of just the relative intensities of a few identified peaks. Whole-pattern analyses are predicated on the fact that the diffraction pattern is the sum total of all of the effects, both instrumental and specimen-related, that we have discussed earlier in our sections on "Diffraction Basics." The basic approach is get the best data you can (with or without an internal standard), identify all the phases present and input basic structural data for all phases, then let the computer model your data until the best fit to the experimental pattern is obtained.

The Rietveld method was originally conceived as a method of refining crystal structures using neutron powder diffraction data. The method requires knowledge of the approximate crystal structure of all phases of interest in the pattern. The quantity minimized in Rietveld refinements is the conventional least squares residual:

$$R = \sum_j w_j \left| I_{j(o)} - I_{j(c)} \right|^2$$

where $I_{j(o)}$ and $I_{j(c)}$ are the intensity observed and calculated, respectively, at the jth step in the data, and w_j is the weight. Detailed discussion of the Rietveld method is way beyond the scope of this brief introduction, but ***it is important to understand that this method, because of the whole-pattern fitting approach, is capable of much greater accuracy and precision in quantitative analysis than any peak-intensity based method.***

In Rietveld analysis, if an internal standard is used it is utilized to calibrate the scale factors used by the program to match the model and experimental data, not to compare with the phases being analyzed. A "normalized" fit can be performed without an internal standard, but as with Chung's normalized RIR method, the refinement will not usually succeed if something is missing.

Since the refinement "fits" itself to the data by modifying structure and instrument parameters iteratively, the Rietveld method holds several advantages over other peak intensity-based methods:

- Differences between the experimental standard and the phase in the unknown are minimized. Compositionally variable phases are varied and fit by the software.

- Pure-phase standards are not required for the analysis.

- Overlapped lines and patterns may be used successfully.

- Lattice parameters for each phase are automatically produced, allowing for the evaluation of solid solution effects in the phase.

- The use of the whole pattern rather than a few select lines produces accuracy and precision much better than traditional methods.

- Preferred orientation effects are averaged over all of the crystallographic directions, and may be modeled during the refinement.

The reader is referred to the referenced literature at the end of this chapter to dig deeper into the Rietveld method. There is also information in this section about GSAS and RockJock, two free software systems capable of doing whole-pattern refinements for quantitative analysis.

The Variables of a Rietveld Refinement: I will conclude here with a very qualitative outline of the factors which are entered by the analyst and varied by the analytical software to attempt a least squares fit to the experimental pattern.

Refer to any of the references at the end of this chapter for a mathematical treatment; Snyder and Bish (1989) are particularly concise. Dr. Rietveld's 1969 paper (available online at http://crystal.tau.ac.il/xtal/paper2/paper2.html) provides as good an introduction as you will find to the procedure.

- Peak shape function describes the shape of the diffraction peaks. It starts from a pure Gaussian shape and allows variations due to Lorentz effects, absorption, detector geometry, step size, etc.

- Peak width function starts with optimal FWHM values and

- Preferred orientation function defines an intensity correction factor based on deviation from randomness

- The structure factor is calculated from the crystal structure data and includes site occupancy information, cell dimensions, interatomic distances, temperature and magnetic factors. Crystal structure data is usually obtained from the ICDD database or other source (see references at end of chapter). As with all parameters in a Rietveld refinement, this data is a starting point and may be varied to account for solid solution, variations in site occupancy, etc.

- The scale factor relates the intensity of the experimental data with that of the model data.

The least squares parameters are those varied in the model to achieve the best fit to the experimental data and include two groups:

- The profile parameters include: half-width parameters, counter zero point, cell parameters, asymmetry parameter and preferred orientation parameter.

- The structure parameters include: overall scale factor, overall isotropic temperature parameter, coordinates of all atomic units, atomic isotropic temperature parameter, occupation number and magnetic vectors of all atomic units, and symmetry operators.

All parameters require initial values be entered. This requires some thought on the part of the analyst to choose starting values that are reasonable for the phases analyzed. The refinement program then varies the parameters in an attempt to minimize the difference between the experimental and calculated patterns using standard least-squares methods.

Should the values chosen be very far off, it is not unusual for the refinement to blow up and not converge on a solution. Fortunately, thanks to the speed of today's computers, this will usually result in the loss of several minutes of work rather than a few days or weeks, and parameters may be revised and rerun relatively quickly.

Detection Limit Issues

An important consideration in any analysis of multiphase samples is the question of the lower limit of detection: What is the smallest amount of a given phase that can be identified in a given X-ray tracing? The equation below defines the net counting error $\sigma(n)$:

$$\sigma(n) = \frac{100[(N_p + N_b)^{1/2}]}{N_p - N_b}$$

where N_p is the integrated intensity of the peak and background, and N_b is the background intensity. As is obvious from this equation, as $N_p - N_b$ approaches zero, counting error becomes infinite. The equation describing the error in N is:

$$\sigma(N) = \sqrt{N} = \sqrt{(Rt)}$$

With R the count rate (c/s) and t the count time. Thus detection limits will clearly depend on the square root of the count time.
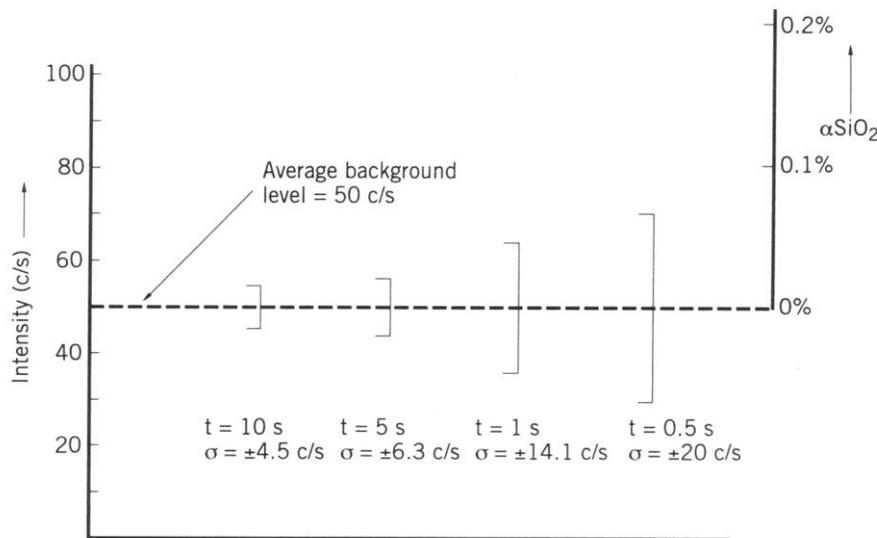

Figure 13.11. Statistical factors in the measurement of signal above background.

In the example shown above, the average background is 50 c/s and the 2σ (95% probability) errors are shown for t = 10, 5, 1, and 0.5 s. Thus, with an integration time of 5 s, any count datum greater than 55.3 c/s (6.3 c/s above background) would be statistically significant. The significance of this detection limit is dependent on the counts produced by a phase of interest at a particular concentration. In this example, if determining α-SiO$_2$ in an airborne dust sample, and a 5% standard gave 1,550 counts at the position of the (101) line with a 50

c/s background, then 1% α-SiO_2 would produce 300 c/s (1500 – 50 / 5). Thus the lower detection limit (2σ) will be 0.015% for 10s, 0.021% for 5s, 0.047% for 1s and 0.067% for 0.5s.

This exercise shows that given a known background level and counts produce by a known concentration of a phase, it is relatively easy to calculate the lower limit of detection for that phase.

Selected Resources for Quantitative Analysis

Bish, D.L, and Howard, S.A., 1988, Quantitative phase analysis using the Rietveld method. J. Appl. Crystallography, v. 21, p. 86-91.

Bish, D.L., and Chipera, S. J, 1988, Problems and solutions in quantitative analysis of complex mixtures by X-ray powder diffraction, Advances in X-ray Analysis v. 31, (Barrett, C., et al., eds.), Plenum Pub. Co., p. 295-308.

Bish, D.L., and Chipera, S.J., 1995, Accuracy in quantitative x-ray powder diffraction analyses, Advances in X-ray Analysis v. 38, (Predecki, P., et al., eds.), Plenum Pub. Co., p. 47-57

Chipera, S.J, and Bish, D.L, 1995, Multireflection RIR and intensity normalizations for quantitative analyses: Applications to feldspars and zeolites. Powder Diffraction, v. 10, p. 47-55.

Chung, F.H., 1974, Quantitative interpretation of X-ray diffraction patterns. I. Matrix-flushing method of quantitative multicomponent analysis. Jour. of Applied Crystallography, v. 7, p. 519-525.

Downs, R.T., and Hall-Wallace, M., 2003, The *American Mineralogist* crystal structure database. American Mineralogist, v. 88, p. 247-250.
Comment: If you want structural data for minerals for your Rietveld refinements, this free online source has structural data for every experimentally determined structure published in the Journal (2,627 of them). This article explains the structure of the database, how to access it, and software available to help you make use of it. It is all online at: http://www.minsocam.org/MSA/Crystal_Database.html.

Snyder, R.L. and Bish, D.L., 1989, Quantitative Analysis, in Bish, D.L. and Post, J.E., eds., Modern Powder Diffraction, Mineralogical Society of America Reviews in Mineralogy, V. 20, p. 101-144.
Comment: A very concise and comprehensive introduction in an excellent volume, includes discussion of Internal Standard RIR methods and Rietveld methods. The chapter by Bish and Reynolds on Sample Preparation is also excellent.

Young, R.A., 1993, The Rietveld Method, Intl. Union of Crystallographers Monograph on Crystallography V. 5, Oxford University Press, 298 p.
Comment: Comprehensive Monograph on all aspects of Rietveld refinements. Very valuable for anyone planning apply seriously apply the technique.

Chapter 13 in Jenkins and Snyder (1996) is also recommended as good introductory reading on quantitative methods.

Free Software for Quantitative Analysis:

GSAS – General Structural Analysis System is a very mature Rietveld program, and comes in versions to run on Windows/DOS PCs and Linux systems. It has been developed as free open-source software and is maintained and distributed by Allen C. Larson & Robert B. Von Dreele of Los Alamos National Laboratory. It comes with a 231 page manual which contains surprisingly little about Rietveld refinements and is chiefly concerned with how to interact with the 37 different program modules. Written originally for UNIX, the "port" to the Windows platform makes extensive use of Command (i.e., DOS) Windows and behaves much like a bunch of Terminal windows. Initial impressions are quite intimidating, but the software gets great reviews from those who learn to put it through its paces. All versions are available via FTP from ftp://ftp.lanl.gov/public/gsas.   We have a recent version available on our FTP site at ftp://eps.unm.edu/pub/xrd/index.htm.

FullProf – Another widely used Rietveld system produced by Juan Rodríguez-Carvajal at the Laboratoire Léon Brillouin (CEA-CNRS) in France. Though it has a somewhat friendlier GUI interface than GSAS but is still a complicated analytical tool requiring good data input by a user who understands diffraction data, and crystal structure analysis, and is willing to master fairly complicated input data file structures. The 139-page FullProf 2000 manual (in Acrobat PDF format) includes a good discussion of the Rietveld procedure and suggests the best sequence of steps to follow to produce a good refinement. We have a recent version of FullProf on our ftp site at at ftp://eps.unm.edu/pub/xrd/index.htm. The CCP14 source page for FullProf with tutorial information and links is at http://www.ccp14.ac.uk/tutorial/fullprof/index.html.

FULLPAT – Dave Bish and Steve Chipera's Excel-spreadsheet-based whole pattern fitting system uses the Excel solver functions to do a least squares refinement to fit whole-pattern data to standard pattern data to produce quantitative analyses. The program archive consists of two files -- the actual Excel spreadsheet used to do the calculations and a well written 23 page manual that explains the use of the program in sufficient detail to make it usable. It does require rather extensive development of in-house standard XRD patterns prepared using a suitable corundum standard as a "spike". This system was used routinely in Bish and Chipera's well respected LANL XRD lab. Available from CCP14 (http://www.ccp14.ac.uk/ccp/web-mirrors/fullpat/) or on our FTP site at ftp://eps.unm.edu/pub/xrd/index.htm.

RockJock – Uses Microsoft Excel Macros and the Solver function to perform a whole-pattern modified Rietveld-type refinement to perform quantitative analysis. Written by Dennis D. Eberl, the software was published in 2003 as U.S.G.S. Open-File Report 03-78, "Determining Quantitative Mineralogy from Powder X-ray Diffration Data". RockJock requires careful sample preparation, good machine characterization and the use of a ZnO internal standard for best results. It is widely used in clay analyses. Available via FTP from ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/RockJock.