Absolute quantification by powder X-ray diffraction of complex mixtures of crystalline and amorphous phases for applications in the Earth sciences

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ABSTRACT

Many natural surface-environment samples, such as soils and marine and lacustrine sediments, are complex mixtures involving several mineral phases (both petrogenic and authigenic), several amorphous and nanoparticulate inorganic phases (usually authigenic or pedogenic), and a heterogeneous amorphous component of “organic matter” (OM). The main inorganic amorphous and crystalline components are often operationally separated and quantified by various selective or sequential chemical extraction methods that are subject to various artifacts and that can be significantly affected by the presence of OM. Here we develop a general method of absolute quantification based on powder X-ray diffraction (pXRD) measurements that are obtained using standard 0-0 or 0-20 type diffractometers. The method does not require calibration or the use of standards and does not require instrument parameter determinations but relies instead on exact normalization conditions that we prove. In particular, we develop a “general integrated intensity formula” (GHIF) for X-ray diffraction. All relevant sample-radiation interaction phenomena are considered, including polarization, mass absorption, Compton scattering, and resonance absorption re-emission. We show that the mole fraction of any given phase (crystalline, amorphous, quasicrystalline, or nanophase) is exactly given by the collection sphere integrated intensity of the resolved phase-specific contribution to the Compton corrected and electron unit normalized diffraction pattern, T(θ), divided by the wavevector (q) integrated average squared atomic form factor of the phase. Electron unit calibration is achieved by a global normalization that directly gives the product A_l(θ) of the effective cross sectional area (A_l) of the incident (and outgoing) beam and the effective incident beam intensity (l_0), including counter efficiency, beam path losses, etc. The problem of incomplete collection sphere integration (including the q = 0 region) is resolved by showing that all the results hold for a given Bragg angle range of measurement for a sufficiently large range. We evaluate the accuracy of the method by application to synthetic binary amorphous-crystalline mixtures of (1) a rock standard, that provides an assembly of crystalline phases, (2) a certified OM standard, and (3) a synthetic inorganic amorphous phase (silica gel). We expect that the method will be particularly useful in surface sediment and environmental geochemistry applications.

INTRODUCTION

Despite an obvious need, in the study of clays, sediments, and soils in particular, there does not presently exist a straightforward (and calibrationless and standarless) physical method to accurately and non-destructively quantify all the resolvable crystalline and non-crystalline (i.e., organic or inorganic amorphous and nanophase) components of a given sample. Natural surface-environment samples generally contain a broad array of phases and the key reactive ones are often amorphous or nanophase. Diffraction is generally regarded as the most promising approach for such problems, compared to microscopy where image analysis and statistical methods are required and spectroscopy that is resonance based and therefore not equally sensitive to all solid phases. X-ray diffraction is equally sensitive to all materials on an electron density basis. Powder X-ray diffraction (pXRD) has the added advantage that any type of material that is already powdered or can be powdered can be used, without particle size or shape limitations other than certain manageable complexities related to homogeneity and micro-absorption. The potential of pXRD in treating complex solid mixtures, environmental samples in particular, has not been fully developed (McCarty 2002), although the practical difficulties have been reviewed (e.g., Bish and Chipera 1988).

Absolute quantification in X-ray diffraction is, in practice, rarely performed, for three main reasons: (1) the significant effort required, during laboratory calibration, in controlling, measuring, and monitoring all the needed instrumental parameters, such as incident beam intensity, counter efficiency, beam-path attenuation and scattering, effective beam widths as determined by various slits, degree of incident beam polarization, etc.; (2) the effort in securing appropriate standard or certified reference samples for use either in establishing the calibration or for use as internal standards; and (3) the diffraction-theory difficulties in dealing with coexisting phases, such as crystalline, amorphous, and nanoparticulate forms, that produce intrinsically different diffraction patterns. Indeed, the crystalline (i.e., mineral), amorphous (i.e., glassy), and nanoparticulate (or nanophase) classes have produced three different mathematical formalisms for treating their diffraction patterns. These three approaches are the Bragg theory of classic crystallography, the radial distribution function (RDF) approach for glasses (e.g., Toby and Egami 1992; Wright 1998), and the Debye sum method for molecules and
nanoparticulates (Debye 1915; Vogel et al. 1998), respectively.

Whereas the Bragg theory has been developed to give quantitative relative amounts of coexisting crystalline phases via the reference intensity ratio (RIR) (Chung 1974; Hubbard et al. 1976; Smith et al. 1987; Hubbard and Snyder 1988; Li and O’Connor 1998; O’Connor and Li 2002) or Rietveld full-profile fitting (Rietveld 1969; Hill and Howard 1987; Bish and Howard 1988; Hill 1992; Young 1995; Bergmann and Kleeberg 1998; O’Connor and Li 2000) methods, for example, no practical standardless and calibrationless method presently exists for absolute quantification of coexisting crystalline, amorphous, and nanophase materials in bulk samples. Standardless whole-pattern deconvolution methods have been used but only for crystalline phases (e.g., Schofield et al. 2002). Rietveld methods can be used to extract total amorphous contents but only by using an internal standard (e.g., Bish and Howard 1988; Gualtieri 2000) and with the limitation that the structures of the crystalline phases must be determined (or reliable RIRs obtained).

Other whole-pattern methods have been developed that use a semi-constrained Rietveld-like approach (e.g., Toraya 1987), or measured reference sample patterns (e.g., Cressey and Schofield 1996; Batchelder and Cressey 1998), or a combination of measured reference sample and Rietveld patterns with an internal standard (Chipera and Bish 2002). Whereas these methods are helpful in solving the problem of separating the solid-phase-specific components of a pXRD pattern, they are not rigorous and complete quantification methods. They are also not standardless or calibrationless. For example, all the reference samples must be measured under conditions identical to those used for the sample of interest and internal standards are typically used for each reference sample and the sample of interest. Whereas RIR and Rietveld methods are in principle exact (for crystalline phases), these new whole-pattern methods have not been put on a firm theoretical basis such as the one we develop here. For example, the FULLPAT method (Chipera and Bish 2002) incorrectly treats absorption in such a way that it will give approximate results for phases with similar absorption coefficients but systematically incorrect results for mixtures of phases with very different absorption coefficients, such as with mineral and organic matter (OM) mixtures. Another significant limitation of all these whole-pattern methods is that one must be able to obtain reference patterns of the phases to be quantified, whereas the method presented here allows one to quantify a single or multi-phase component of unknown structure without having a corresponding reference sample or pattern, as long as its elemental composition can be reasonably estimated.

Without even a theoretical basis for pXRD quantification of multi-phase samples containing both crystalline and non-crystalline phases and given the complexity of the mostly approximate methods developed to date, pXRD has not been widely adopted for modal analysis of natural surface-environment samples. Instead, various physical (e.g., Pilkington and Warren 1979; Reynolds et al. 2001) and chemical separation methods have been developed. Selective and sequential chemical methods are widely used (Piper 1950; Mehr and Jackson 1959; Anderson 1961; Fey and LeRoux 1976; Malo 1977; Tessier et al. 1980) and suffer from various documented artifacts and difficulties (McKeague 1967; Agemian and Chau 1976; Guy et al. 1978; Rendell et al. 1980). None of these methods, for example, produce a clean separation between total crystalline and total non-crystalline phases, without some ancillary attack of the assumed refractory phase(s) or without the possibility of residual phase transformation and new phase formation. The potential advantages of a physical method such as diffraction that is sensitive to all phases that contain electrons and that can both resolve patterns arising from different phases and in principle allow accurate quantification of the resolved phases, cannot be overstated.

Here we develop such a method from first principles, that is, starting with the basic physical theory of X-ray diffraction, that underlies the theoretical developments in dealing with the three classes of materials described above. We have been able to put all three types of diffracting materials on the same common basis, to allow an exact analysis of samples that contain mixtures of these material types. We are not providing an improved method to resolve or separate the solid-phase-specific components in the measured (or corrected) powder diffraction pattern. Rather, we are providing the first derivation and proof of the exact general relation between any resolved diffractogram component, obtained by any of the various profile analysis methods that have been developed (Rietveld, full-pattern extraction, peak removal, etc.), and the mole fraction of the solid phase corresponding to this component, irrespective of the nature of the solid material. We also develop this relation into a practical and robust absolute quantification method. We evaluate the accuracy of this method and illustrate its application with a study of known mixtures of reference samples.

We were motivated by our work in characterizing sediments from 100 boreal forest lakes that contain highly variable and often comparable amounts of mineral, inorganic amorphous, inorganic nanophase, and organic amorphous phases (George et al. 2004; Rancourt et al. 2004a). The developments presented here are new in the area of diffraction theory and should also find broad applications in materials science, as they extend the power of X-ray diffraction methods. Our Lake Sediment Structure and Evolution (LSSE) project has a mandate to develop new physical methods for environmental geochemistry and this has also been done in the areas of Mössbauer spectroscopy (Lagarec and Rancourt 1997; Rancourt 1989, 1994a, 1994b, 1998; Rancourt and Ping 1991; Rancourt et al. 1993, 1994) and mineral magnetometry (Rancourt et al. 2004b).

**NECESSARY BASIC CONCEPTS AND NOMENCLATURE**

Many of our results apply to X-ray diffraction in general, without reference to sample type, instrument geometry, or reciprocal space exploration method, but, in the end, one must specify how one’s particular measurements were performed and adapt the method accordingly. In the last sections, we tailored our method to the most common pXRD configuration, standard θ-θ or θ-2θ automatic diffractometer geometry with constant divergent slit, and for a flat surfaced sample of semi-infinite depth. These settings correspond to a constant irradiation volume geometry and allow straightforward absorption corrections (when sample preparation problems of micro-absorption are avoided). Because so many different instrumental and sample configurations are possible, we have chosen to carefully spell out how our method was derived, and show all the underlying steps, to ensure that it can be adapted to any situation by the interested user. This is also neces-
sary so that the expert reader can follow (and be convinced by) our proofs of the few key and new theoretical results that the method is based on. This section, therefore, establishes the needed concepts and definitions. Readers that will not supervise the measurements themselves or be responsible for implementing the method in their laboratory can skip to the last main section of the paper.

**Basic scattering and absorption processes**

The incident X-ray beam interacts with the material sample via various routes (each mechanism has more than one common name) (Kirz 2001): (1) elastic or unmodified or Rayleigh or coherent radiation scattering, in which the atom or ion remains in its ground state after interaction with the photon, which includes Bragg scattering from crystals, thermal diffuse scattering from crystals, and scattering from amorphous and nanophase materials; (2) inelastic or modified radiation scattering, the main non-resonant type of which is Compton scattering; and (3) fluorescence or resonant absorption followed by re-emission and the atomic photo-effect (electron ejection) followed by re-emission. At higher incident photon energies (>10^8 eV) other processes also occur that include pair production and photonuclear absorption. Both the incoming radiation and the radiation scattered by the above parallel processes are affected by ordinary mass absorption (which includes resonance absorption components), which is treated by simply removing intensity away from the respective beams. In the kinematic approximation, used here throughout, the elastic scattering is not considered as causing removal of intensity from either the primary or any of the secondary beams (i.e., second or multiple elastic scattering is ignored), as the net elastic cross section is taken to be sufficiently small to validate this simplification (Chap.14, Warren 1990).

**Classical scattering from a single free electron**

Although it may seem like a purely academic exercise, X-ray diffraction theory makes use of the central result for the classical scattering from a single free electron. The reason is that the correct quantum calculations for scattering from atoms or molecules or entire solids give results that always contain the classic free electron expression as a multiplicative factor (e.g., Warren 1990). This allows one, therefore, to define the scattered intensity in “electron units”. That is, in units of what one would obtain for classical electromagnetic wave scattering from a single free electron.

The scattered intensity (in J/m^2) for classical electromagnetic wave scattering from a single free electron is (Warren 1990)

\[ I_{cl}(\theta) = I_e \left[ e^{i(l/c \cdot \hat{R} \cdot \hat{r})} \right] P(\theta) \]

with

\[ P(\theta) = \frac{1 + \cos^2(2\theta)}{2} \]

where \( I_e \) is the incident intensity, \( e \) is the electron charge, \( m_e \) is the electron mass, \( c \) is the speed of light, \( R \) is the distance between the electron position and the detector that measures the scattered intensity \( I_{cl} \), and \( \theta \) is the Bragg angle or half the scattering angle \( \phi \approx 2\theta \). Note that \( e/(m_e c^2) = 7.94 \times 10^{-6} \text{ m}^2 \). Note also that the result (Eq. 1) is valid for forward scattering \( \theta = 0 \), in which case the original incident beam is understood to be ideally separated from the measurement and to not contribute to the scattered forward intensity.

The term \( P(\theta) = \frac{1 + \cos^2(2\theta)}{2} \) (Eq. 2) is called the polarization factor for an unpolarized primary beam. Note that the characteristic (e.g., Kα or) radiation from a conventional X-ray tube is perfectly unpolarized, within measurement error. A different polarization factor results from a partially polarized primary beam, such as would be generated by using a primary beam single-crystal monochromator, for example. Using a secondary beam monochromator will also modulate the resulting outgoing intensity according to a different effective polarization factor than that given in Equation 2. For example, in θ-θ reflection geometry and using a secondary beam single-crystal monochromator having Bragg angle \( \psi \) for the reflection and wavelength \( \lambda \) of interest, one has (e.g., Eq. 2 of Magini and Cabrini 1972)

\[ P(\theta) = \frac{1 + \cos^2(2\psi)\cos^2(2\theta)}{1 + \cos^2(2\psi)}. \]  (3)

Here, one recovers the result of Equation 2 when \( \psi = 0 \), as one should.

**Quantum scattering from a single electron**

In a full quantum mechanical calculation, one obtains (Warren 1990)

\[ I_{QM}(q) = I_{cl}(\theta) |f(q)|^2 \]

where

\[ f(q) = \int dV \rho(r) \exp(iq \cdot r) \]

is called the form factor of the electron and the scattering vector \( q \) is defined as

\[ q = (2\pi/\lambda)(s - s_e) \]

such that its magnitude is given by

\[ q = (4\pi/\lambda) \sin(\theta). \]

Here, \( \rho(r) \) is the electron number probability density at \( r \) and \( s_e \) and \( s \) are unit vectors along the incident and scattered beams, respectively. This general result applies to any electron, in any type of local potential, such as that caused by its host atom or ion or solid.

**Atomic form factor**

The full quantum mechanical calculation for scattering from an entire atom (or ion) gives the same result as Equation 4 except that \( f(a) \) is replaced by the atomic (or ionic) form factor,

\[ f_{\text{a}}(q) = \int dV \rho_{\text{a}}(r) \exp(iq \cdot r), \]

where, as before, the volume integral is over all space, and \( \rho_{\text{a}}(r) \) is the electron number probability density for the whole atom (or ion), normalized as

\[ \int dV \rho_{\text{a}}(r) = Z. \]
In other words, \( f_\theta(q) \) is the scattering intensity from the atom, in units of the classical scattering intensity for a single electron, under the same experimental conditions.

If the atomic (or ionic) electron density distribution has spherical symmetry, then

\[
F(q) = \int dV \rho(r) \exp(iqr) 
\]

where \( q \) is given by Equation 7 and the integral is over all radii, from 0 to \( \infty \). Equation 9 becomes simply

\[
\int 4\pi r^2 \rho(r) = Z \tag{11}
\]

such that \( f_\theta \rightarrow Z \) as \( q (\text{and} \ \theta) \rightarrow 0 \). This all assumes that the wavelength used is such that we are far from any atomic resonances. Otherwise, we must use appropriate resonance corrections, with real and imaginary parts:

\[
f_\theta = f_\theta + f_\theta^* \tag{12}
\]

The required terms are tabulated, as functions of \( \theta \) and for different wavelengths.

### Form factor for molecule or sample and the Debye sum for a powder

One can generalize the above results as follows. In the absence of resonance and ordinary mass absorption, the elastic (i.e., unmodified radiation) scattering from a molecule or sample is given by Equation 4 except that \( f_\theta(q) \) is replaced by the form factor of the molecule or sample:

\[
F(q) = \int dV \rho(r) \exp(iqr) \tag{13}
\]

where \( \rho(r) \) is now the electron number density of the entire molecule or sample and it is not spherically symmetric, as it involves several separate atoms. The integral is over all space and is therefore effectively an integral over the sample volume. This shows the central place of the scattering amplitude, \( F(q) \), in the theory of diffraction. The general expression that is Equation 13 applies to any type of sample: crystalline, amorphous, polycrystalline, quasicrystalline, liquid, multi-phase, single-phase, etc. For the case where \( \rho(r) \) has the symmetry of a Bravais lattice (i.e., for a crystal), Equation 13 directly leads to sharp (Bragg) diffraction peaks at values of \( q \) equal to reciprocal lattice vectors (see below).

To the extent that the sample electron density can be written as a sum of spherically symmetric atomic electron densities centered at \( r_i \) (that may or may not overlap),

\[
\rho(r) = \sum_i \rho_i(r) \tag{14}
\]

where the sum is over all atoms “i” in the sample and \( r = r_i + u \), (whatever \( u \)), one has

\[
\left| F(q) \right|^2 = \sum_i \sum_j f_i(\theta) f_j(\theta) \exp[iq(r_i - r_j)] \tag{15}
\]

where the double sum includes the \( i = j \) terms. Without making any assumptions about the crystal symmetries of the sample components (or even that the sample is made up of crystalline phases), we can next assume that we have a perfect random orientation powder sample. This leads to the well known Debye sum result (Debye 1915; Warren 1990)

\[
\left| F(q) \right|^2 = \sum \sum_i f_i(\theta) f_i(\theta) \sin(qr_i)/qr_i \tag{16}
\]

where \( q \) is defined by Equation 7 and \( r_i = |r_i - r_j| \) is the distance between atom-i and atom-j. The angular brackets, \( \langle \rangle \), here mean “the powder average of”. Clearly, as usual, the Debye sum (Eq. 16) gives the elastic scattering intensity of a powder sample, in units of the classical scattering intensity of a single electron, that is, in electron units. One must therefore add the corresponding polarization factor, etc., to obtain the measured intensity.

The Debye sum formula, although it is not as well known as the approaches of classical crystallography, is the best-adapted diffraction theory calculation method for molecules, clusters, and nanoparticles, and it has been widely applied in the study of metallic clusters (e.g., Vogel et al. 1998). Since it is quite general (and valid for extended crystals and amorphous or polycrystalline materials), its simplicity can allow certain mathematical derivations that would otherwise be more difficult. We exploit this below.

### The Patterson function and electron density correlation

Starting again from Equation 13, in general we have

\[
\left| F(q) \right|^2 = V \int \rho(r) \exp(i\mathbf{q} \cdot \mathbf{r}) \tag{17}
\]

where \( V \) is the sample volume and \( P(r) \) is the Patterson or electron density correlation function,

\[
P(r) = (1/V) \int \rho(r') \rho(r' + \mathbf{r}). \tag{18}
\]

It follows that the most information one can obtain from a diffraction experiment is the electron correlation function of the material.

In performing a powder average of Equation 17, that is, acting on both sides of the equation with \( (1/4\pi) d\Omega_q \), where \( d\Omega_q = \sin(\theta) d\theta d\phi \), one obtains

\[
\langle |F(q)|^2 \rangle = V \int \rho(r) \sin(qr)/qr. \tag{19}
\]

Next, using \( dV = d'r = r'^2 \sin(\theta)d\theta d\phi = r'^2 d\Omega_q = dr dA \),

\[
\langle |F(q)|^2 \rangle = \int d'r D(r) \sin(qr)/qr \tag{20}
\]

where the integral is over radii from 0 to \( \infty \) and the pair distribution function (PDF), \( D(r) \), is defined as

\[
D(r) = V \int dA \rho(r') = \int dA \int dV' \rho(r') \rho(r' + r). \tag{21}
\]

This is a general result valid for all types of samples and it is also the central quantity in diffraction studies of amorphous systems, where \( D(r) \) is obtained by inverse Fourier transformation from the diffraction pattern (in absolute electron units) via Equation 20 and represents the most structural information that can be obtained from the amorphous material. The constants required to put the measured diffraction data in electron units are normally painstakingly obtained by calibration measurements.
(e.g., Magini and Cabrini 1972; Egami and Billinge 2003) but the calibration could alternatively and more easily be obtained by the method described in this paper (below).

Sample form factor vs. unit-cell form factor and Lorentz factor

The reader should note that the sample form factor (Eqs. 13, 15, 17) relates to the actual sample, without making any assumptions about crystallinity or single-phase character. The sample form factor is different from the usual form factor of a crystalline phase, that is a sum on a single unit cell, over average unit-cell atomic positions, and is usually defined only at q equal to a reciprocal lattice vector G of the crystal structure. The sample form factor arises from an integral over the sample volume, is a continuous function of q, and contains all of the sample features, including strain, lattice defects, thermal (vibrational) displacements, shape and size effects, compositional non-uniformity, etc.

In the usual (but less general) pXRD treatment of a powdered crystalline sample (e.g., Warren 1990; Langford and Louër 1996), one writes the integrated intensity of a given (hkl) reflection in terms of the unit-cell form factor squared |F(hkli)|². In the latter treatment one has two factors, the reflection multiplicity m(hkl) and the Lorentz factor L(θ) = 1/|sin(θ)sin(2θ)|, that do not arise and are not needed in our more general treatment using the sample form factor |F(q)|². By design, our method does not and must not use the usual Lorentz-polarization factor but must only use the bare polarization factor (Eqs. 2–3), even when treating crystalline components in the pXRD pattern. The extra factor arises because one is defining the integrated intensity for a given reflection and because one is not performing full collection sphere integration over all Bragg reflections (Warren 1990).

In our method, we use the more general sample form factor and perform full collection sphere integration, using corrected and renormalized data.

Q-SPACE NORMALIZATION CONDITIONS FOR DIFFERENT SAMPLE TYPES

Having introduced the necessary concepts and definitions, we next review and extend a key result that relates the entire q-space sum or integral of scattered intensities at q to a simple physical property of the sample, a volume integral of its squared electron number density. Since this result is exact for crystals or samples containing only crystalline phases (as shown below), it represents a promising starting point for developing an exact normalization and calibration method based on actual experimental scattered radiation total collection sphere integration (next section). The present section, therefore, is included to establish the theoretical prerequisites for our absolute quantification method (next two sections) and can be skipped by those readers willing to accept our main results without proof.

Form factor for a single-crystal sample and q-space normalization condition

When the ρ(r) in Equation 13 has the symmetry of a crystal, this leads to the usual reciprocal space results of crystallography (e.g., Kittel 1986). In particular, there are sharp Bragg peaks only at reciprocal lattice vectors, G, with peak intensities, F_G, that are proportional to squares of structural form factors, F_c, defined as

\[ F_G = \sum_n f_n(G) \exp(iG \cdot r_n) \]  

(22)

where the sum is on the n-atoms (basis atoms) in the primitive unit cell and \[G = [na^* + kb^* + lc^*] = (4\pi^2/\lambda^2)\sin(\theta_{m0})\]. These form factors are the Fourier components of the electron density at a point in the unit cell, as

\[ \rho(r) = (1/\nu) \sum_n F_n \exp(iG \cdot r) \]  

(23)

where \(\nu\) is the volume of the primitive unit cell. Equation 23 follows directly from the Fourier series of a periodic function [here \(\rho(r)\), in 3D] and the definition of \(F_c\), (Eq. 22) in terms of \(\rho(r)\). By squaring Equation 23 and integrating over the volume of the unit cell, one obtains the exact normalization condition described by Kartha (1953), that is in fact the well known Bessel-Parseval equality of Fourier analysis (in 3D):

\[ \nu \int dV |\rho(r)|^2 = \sum_n |F_n|^2 \]  

(24)

Note that, for a monoatomic structure with one atom per primitive unit cell, Equation 24 reduces to

\[ \nu \int dV |\rho(r)|^2 = \sum_n |f(G)|^2 \]  

(25)

where \(f(G)\) is the atomic form factor (Eq. 8) evaluated at \(G\).

This important and little result (Eq. 24) can be used to relate on an absolute scale the sum over all the scattered Bragg peaks (peak intensities in electron units) from a large crystalline sample (including the \(G = 0\) peak that cannot easily be measured), in the limit \(\lambda \rightarrow 0\) such as not to exclude any \(G\) vectors, to an integral over a specified volume of the square of the sample’s electronic density. However, past attempts (Yü and Wilson 1942; Kartha 1953; Krogh-Moe 1956) to apply or extend this idea have been limited to specific material types (crystalline or amorphous), have not dealt correctly with the missing q values arising from a non-zero wavelength, have needed to assume non-overlapping atomic electronic distributions, and have not correctly extended the results to incomplete collection sphere integration. We have solved these problems (next section).

In pursuing Equation 24 further, care must be taken to note that the above squared form factor per primitive basis, |\(F_G|^2\), is not simply proportional to the actual squared form factor, |\(F(G)|^2\), of the sample (i.e., using Eq. 13 evaluated at \(G\)). Indeed, they are related as

\[ |F(G)|^2 = N^2 |F_G|^2 \]  

(26)

where \(N\) here is the number of primitive unit cells in the sample. This is important because it is the squared form factor of the sample that is equal to the diffracted intensity in electron units, when we ignore absorption effects or include them into the “electron units”, along with the polarization factor, as is usually done. For example, the relation analogous to Equation 24 using the form factor of the sample is

\[ \sum_n |F(G)|^2 = N^2 \nu \int dV |\rho(r)|^2 = \nu \int dV |\rho(r)|^2 \]  

(27)
where \( N_v = V \), the volume of the irradiated sample. Furthermore, it is easy to demonstrate that

\[
v \int dV \rho(r)^2 = \tau (\sum Z_i r)^2
\]  
(28)

where the sum is on atoms in the unit cell and

\[
V \int dV \rho(r)^2 = \tau (\sum Z_i r)^2
\]  
(29)

where the sum is on all atoms in the volume \( V \) (of the irradiated sample or of the diffraction unit). \( Z_i \) is the number of electrons on atom-\( i \) (or ion-\( i \)). Here, \( \tau = 1 \) in the limit that the electronic charge is uniformly distributed over the volume (\( V \) or \( V \)), respectively and is greater than and of the order of 1 (\( \tau \approx 1 \)) for more realistic intra-material electronic distributions, depending on the structure and composition of the material.

This would mean that the q-space integrated intensity would be proportional to the square of the number of atoms in the sample, a result that is inconsistent with physical measurements and that illustrates the extent to which one does not approach a full q-space integration on collecting all the diffracted intensity for a given wavelength (see below). For a given non-zero \( \lambda \), the maximum accessible reciprocal space vector is

\[
q_{\text{max}} = G_{\text{max}} = (4\pi/\lambda) \sin(\pi/2) = 4\pi/\lambda.
\]  
(30)

This cutoff does not, as claimed (Kartha 1953), result in good approximations to the full reciprocal space totals, with usual wavelengths and atomic form factors.

Nonetheless, one is tempted to propose that similar normalization conditions as those given by Equations 24 and 27 might hold for any type of sample including non-crystalline and nanophase samples, where one replaces the discrete sums over delta-function Bragg peaks by corresponding reciprocal space volume integrals that allow broadened Bragg peaks and even continuous diffraction profiles such as those arising from amorphous materials, and that these normalization conditions might be modified for the limited q-spaces of the experiments in such a way as to give a useful and correct calibration method.

In relating the discrete sums in q-space to their corresponding integrals in the continuum limit, one finds

\[
[V(2\pi)^3] \int d^4q |F(q)|^2 = \sum_{ij} |F(q)|^2
\]  
(31)

and

\[
[V(2\pi)^3] \int d^4q |F(q)|^2 = \sum_{ij} |F(q)|^2
\]  
(32)

where \( d^4q \) is the volume element in q-space. Indeed, for a crystalline structure at \( T = 0 \) K, it is easy to start from the definitions of the form factors in terms of electron densities, in the left hand sides of Equations 31 and 32, to obtain the volume integrals of Equations 24 and 27, respectively. We are therefore led to advance that, in general and for any type of structure, that may or may not be describable using a unit cell, we have:

\[
[V(2\pi)^3] \int d^4q |F(q)|^2 = V \int dV \rho(r)^2.
\]  
(33)

To our knowledge, the latter relation, applying to any type of material (including non-crystalline), has not been previously proposed or proved, nor has it been applied as a starting point for a method of quantification. Following the arguments underlying Equation 29, a good approximation for the right hand side of Equation 33 should be

\[
V \int dV \rho(r)^2 \cong N^2Z^2
\]  
(34)

where \( N \) is the number of atoms in the sample and \( Z \) is the (average) number of electrons per atom. Therefore, the integral in Equation 33 would simply be given by the square of the total number of electrons in the sample, irrespective of the structure of the sample or of the material phase being considered. Next, we perform a calculation that establishes that, if it is not exact in general, Equation 33 must at least be a very good approximation, irrespective of the material structure. We also prove that, with Gaussian atomic electron number density distributions, Equation 33 is exact in the continuum approximation of the pair distribution function.

**General form factor for a material phase and corresponding q-space normalization condition**

Equation 15 is a quite general expression for the square of the total form factor of a given (single-phase or multi-phase, crystalline or non-crystalline) sample and can be written as

\[
|F(q)|^2 = \sum_i f_i(q) f_i(q) \exp(iq \cdot r_i)
\]  
(35)

where the sums are on all atoms or ions in the sample. Here, the vector \( r_i \) is defined as \( r_i = r_i - r \), for convenience. We now evaluate the q-space integral represented by the left hand side of Equation 33, using the general expression for \( |F(q)|^2 \) given by Equation 35. For mathematical convenience and presentation clarity we assume that the atomic or ionic electron number distributions are Gaussian and each normalized to the atomic or ionic electron number \( Z_i \) (for atom-i):

\[
\rho_i(r) = Z_i \left\{ \frac{1}{(2\pi\sigma^2)^{3/2}} \exp\left(-r^2/2\sigma^2\right) \right\}
\]  
(36)

where \( \sigma_i \) is the radial Gaussian standard deviation width (\( \sigma \)) of the electron number distribution for atom-i. Such a distribution is, from a mathematical perspective in terms of the development that follows, quite general because a given real (spherically symmetric) electron number distribution on site-i can be well approximated by a sum of such Gaussian components, all centered on \( r \) = 0, having different \( Z_i \) and \( \sigma_i \) and collectively normalized to \( Z_i \).

The corresponding atomic form factor (using Eq. 8) is:

\[
f_i(q) = Z_i \left\{ \frac{1}{(2\pi\sigma^2)^{3/2}} \exp\left(-q^2/2\sigma^2\right) \right\}
\]  
(37)

This form factor is again quite general, in that real atomic form factors (leaving out the resonance terms) can be well approximated by sums of such Gaussian components (e.g., Waasmaier and Kirfel 1995). One obtains

\[
[V(2\pi)^3] \int d^4q |F(q)|^2 = \left[ \frac{V(8\pi)^3}{8\pi^3} \right] \sum_i \left\{ \frac{Z_i}{(\alpha_i^2 + \alpha^2)^{3/2}} \exp\left(-q^2/\left(4(\alpha_i^2 + \alpha^2)\right)\right) \right\}
\]  
(38)
where the identity of the atom or ion must be taken correctly in each term of each sum over all atoms. Here we see that, because of the sums on all atoms in the sample and because there are no interference terms (only additive positive contributions), the end result, for a given sample composition and a given set of inter-atomic (nearest neighbor) bond lengths, will be closely independent of the structure (i.e., of the atomic positions).

We next evaluate the double sum of Equation 38. Consider that an “average” Z’ and an “average a” can be defined (see below) that will produce the same result in evaluating the double sum or, equivalently and for simplicity, consider the case of a monoatomic material. Equation 38 then reduces to

\[ \frac{V}{2(2\pi)^3} \int d^3q \left| F(q) \right|^2 = \frac{V}{8\pi^2} \left[ Z^2/a^3 \right] \sum_i \exp(-r^2/4a^2). \]  

(39)

The sum over j can be evaluated first by simply taking the continuum (pair distribution function) approach as

\[ \sum_i \exp(-r^2/4a^2) \approx 4\pi(N/V) \int dr r^2 \exp(-r^2/4a^2) \]  

(40)

where the integral over radial distance from site-i can be extended to \( \infty \) because of the rapid decay of the Gaussian term. \( N \) is the number of (“average”) atoms in the sample and \( V \) is the sample volume. Equation 40 follows directly from the integral approximation to a discrete sum in calculus and does not involve any other approximations. The second sum then simply gives \( N \). Alternatively, one could evaluate the discrete double sum itself but since one thus runs over all atomic pairs in the sample, one would not obtain a result that is very different from that resulting from the above approximations (of an average atom and the integral approximation). The final result is

\[ \frac{V}{2(2\pi)^3} \int d^3q \left| F(q) \right|^2 = N Z^2 \]  

(41)

which is exactly the approximate value for \( VdV \rho(r)^2 \) given by Equation 34. This constitutes a rigorous demonstration that Equation 33, that was tentatively proposed above, must hold in general (i.e., irrespective of the structure of the material or of the sample) to a very close approximation. The reader should be warned however that this result (Equation 41) and consequently the general validity of Equation 33 depend on the particular typical values of \( a \), that are comparable to both \( \lambda \) and typical bond lengths. Neither the large or small \( a \) limits produce this result, in general. Only the case of the crystal produces an exact identity (Eqs. 24–27 and 31–33).

**Absolute quantification based on total collection sphere intensity integration**

Based on the q-space integration results of the previous section as a starting point, we next establish our key result, an essentially exact relation between the entire collection sphere sum or integral of scattered intensities at scattered angle \( (2\theta, \phi) \) to another simple physical property of the sample, a collection sphere integral (transformed to a q-magnitude integral) of the sample average squared atomic form factor. Here, \( 2\theta \) is the scattering angle (i.e., \( \theta \) is the Bragg angle) and \( \phi \) is the azimuthal angle about the incident beam axis. We then detail how this result can be applied in powerful new absolute quantification strategies (last section).

**From impossible q-space integral to measurable collection sphere integral**

To the extent that atomic form factors fall off quickly with diffraction angle and to the extent that \( \lambda \) is small enough that not many \( q \) vectors that contribute significant intensities are excluded (Eq. 30), one can argue that the left hand side of Equation 33 should be closely approximated by an \( dA_q \) integral, \( I_q \), over the area of the entire diffracted intensity collection sphere of radius \( R \) as

\[ \frac{V}{2(2\pi)^3} \int d^3q \left| F(q) \right|^2 \equiv I_q = \frac{1}{4\pi R^2} dA_q \left| F(q) \right|^2 \]  

(42)

where \( dA_q = R^2 \sin(\theta) d\theta d\phi \). That is, one imagines collection of all the diffracted (unmodified) radiation intensity (in electron units and for the entire irradiated sample) emanating from the irradiated volume and one hopes to be effectively in the limit \( \lambda \to 0 \) such as not to exclude too many \( q \) contributions. In fact, this is not correct. The wavelength is not effectively zero and far too many \( q \) contributions are missed in a collection sphere integral.

Nonetheless, we established (below) a valid general expression for the sum on the collection sphere (i.e., the right hand side of Eq. 42), that correctly takes into account the \( q_{\max} \) (Eq. 30) limitation. In doing this, our hope was that \( I_q \) would be independent of the structure, as is \( \frac{V}{2(2\pi)^3} \int d^3q \left| F(q) \right|^2 \), and that it would depend, via a definite and convenient mathematical expression that can be deduced, only on \( q_{\max} \), the sample composition, the atomic form factors, and the size of the sample (\( N \) or \( V \)) to the power 1. The latter condition is a requirement for quantitative analyses of complex samples containing several solid phases. A dependence on \( N^2 \) (Eqs. 33–34) leads to physical inconsistencies and does not permit quantitative analysis. One also needs to account for the experimental difficulty of collecting the \( q = 0 \) intensity.

The calculations of \( I_q \) are generally complicated. A simple useful form that we have found is the one that results from using the Debye sum expression for \( |F(q)|^2 \) (Eq. 16), which would apply for finely dispersed, uniform, and non-textured powder samples – our main samples of interest when developing a quantification method for powder X-ray diffraction. Using \( \sin(2\theta)d2\theta = 4q dq/q_{\max}^2 \), one obtains

\[ I_q = \frac{2}{q_{\max}^2} \int dq \sum_i f_i(q) f_i(q) (1/r_{ij}) \sin(q r_{ij}) \]  

(43)

where the integral on \( q \) is from 0 to \( q_{\max} \). Next the double sum (each sum running from 1 to \( N \)) can be written (exactly) as

\[ \sum_i \sum_j f_i(q) f_j(q) (1/r_{ij}) \sin(q r_{ij}) = N q \left( |f(q)|^2 \right) + 2 \sum_{qij} f_i(q)f_j(q) (1/r_{ij}) \sin(q r_{ij}) \]  

(44)

where \( \{ \} \) in the first term on the right hand side means the average on the sample as

\[ \left( |f(q)|^2 \right) = \frac{1}{N} \sum_i |f_i(q)|^2 \]  

(45)

with the sum running over all ionic or atomic species in the sample.
and $N_e$ is the number of ions or atoms of species-k in the sample. The sum $\Sigma_{ij}$ in the last term of Equation 44 is a sum on all $N(N - 1)/2$ atom-atom $(ij, i \neq j)$ pairs in the sample. Inserting Equation 44 into Equation 43 and applying the integrations, one obtains

$$I_h = N (2/q_{\text{max}}^2) \int dq \, q \, |f(q)|^2 + (4/q_{\text{max}}^2) \int dq \, \Sigma_{ij} f_i(q) f_j(q) (1/r_{ij}) \sin(q r_{ij}). \quad (46)$$

The last term involves a sum on pairs that is analogous to the Madelung constant sum of ionic crystal theory in that the terms go as $1/r$, as does the electrostatic potential, and the term $\sin(q r_{ij})$ causes periodic sign changes. It therefore has all of the well known inherent difficulties of a Madelung sum, with intrinsic convergence problems and potentially strong dependencies on sample size and shape. The sum can be positive or negative and is also very sensitive to $q$, which sets the period of sign changes. Given the sign changes induced by the $\sin(q r_{ij})$ term and after integration over the broad and continuous range of $q$ (from 0 to $q_{\text{max}}$), the last term in Equation 46 should be zero for sufficiently large and regular shaped samples (not constituent grains or crystallites but actual irradiated whole samples). We therefore take the last term in Equation 46 to be exactly zero. This solves all the problems related to dependencies on sample shape, scale and degree of uniformity in inter-solid-phase dispersion, and dependencies of $I_h$ that are not exactly as $N^2$. Our final result, therefore, is

$$I_h = N (2/q_{\text{max}}^2) \int dq \, q \, |f(q)|^2 \quad (47)$$

which has all the desired characteristics described above.

Starting from the general expression for $|F(q)|^2$ (Eq. 15) rather than the Debye sum expression (Eq. 16), one obtains exactly the same result. The only difference, in the main intermediate step, is that the last term in Equations 46 is replaced by

$$(4/q_{\text{max}}^2) \int dq \, q \, \Sigma_{ij} f_i(q) f_j(q) \exp[i \cdot \cdot \cdot (1 - 2(q/q_{\text{max}})^2)] \quad (48)$$

which, by the same arguments as used above, is taken to be exactly zero. Indeed, if it were not zero, one would have the added complication that it is not necessarily real, as required.

For the sake of illustration, we assume $|f(q)|^2$ to be Gaussian and define an average $\langle Z \rangle$ and average $\langle a \rangle$ as

$$\langle |f(q)|^2 \rangle = \langle Z \rangle^2 \exp(-q^2 \langle a \rangle^2). \quad (49)$$

To the extent that $\langle a \rangle$ is large enough for the upper integration limit of the resulting integral on $q$ (in Eq. 47) to be extended from $q_{\text{max}}$ to $\infty$, this then leads to

$$I_h = N \langle Z \rangle^2 (1/4q_{\text{max}}^2 \langle a \rangle^2). \quad (50)$$

Clearly, the integral over the entire intensity collection sphere (Eq. 47) is not equal to the integral over all of $q$-space (Eq. 33). That is, Equation 42 does not hold for typical measurement conditions. Nonetheless, $I_h$ is evaluated (Eq. 47) and is independent of structure.

Equation 47 is a central result and an alternative and rigorous proof for it is given in the next sub-section. It applies in any X-ray measurement geometry where one sums the elastically scattered intensity (in electron units) over the entire collection sphere and for any type of sample. It applies to the whole sample, where $N$ is the total number of atoms in the sample. It also applies to each material phase in the sample, where $N$ is the number of atoms in the phase and $\langle |f(q)|^2 \rangle$ is the phase-specific average, to the extent that the parts of the measured intensity profile can be attributed to different material phases in practice (see below). That is, to the extent that the different solid phase contributions to the measured diffractogram can be resolved—which is a practical limit rather than a theoretical one. For example, when the scattered radiations from the different material phases interfere coherently, resolving the material phase contributions in the measured intensity profile can be impossible in practice.

Equation 47 should also approximately apply to any measurement condition, such as in powder X-ray diffraction where one measures up to some maximum Bragg angle $\theta_{\text{max}}$ that is not necessarily $\pi/2$, in which the intensity collection is effectively done up to some $q_{\text{max}}$ (i.e., without missing any $q < q_{\text{max}} = (4\pi/\lambda)\sin\theta_{\text{max}}$, as long as the range of $q$ is large enough to ensure that the sum on pairs term (Eqs. 46 and 48) is zero. In this case, the only modification to Equation 47 is to change the upper integration limit from $q_{\text{max}}$ to $q_{\text{end}}$ (i.e., from $4\pi/\lambda$ to $(4\pi/\lambda)\sin\theta_{\text{max}}$), while keeping the original $q_{\text{max}}$ value as the $1/2q_{\text{max}}^2$ prefactor to the integral since it arises from the change of integration variable. This application of incomplete sphere integration, Equation 47, with the required change in upper limit of integration, is not exact (see below) but it should be a good approximation for any sufficiently large range of $q$ (i.e., changing upper and lower integration limits but with an integration range that remains large) and it must become a better and better approximation as the width of the range in $q$ approaches $q_{\text{max}}$.

Alternative derivation and proof of the general collection sphere integrated intensity formula

Our Equation 47, where $I_h$ is defined in the right hand side term of Equation 42, can be referred to as the general integrated intensity formula (GIIF). In this section, rather than give mathematical arguments such as those given above in relation to Equations 46 and 48, we provide an alternative derivation of the GIIF, that is a rigorous proof based on a physical argument. We start from Equation 13, which is the basis of kinematic X-ray diffraction theory. To the extent that Equation 13 holds, our proof is rigorous.

Although Equation 13 follows from non-relativistic time-dependent perturbation quantum scattering theory (Chap. 8, Cohen-Tanoudji et al. 1973), where $\rho(r) = |\psi(r)|^2$ is the square of the electronic wavefunction of the sample evaluated at $r$, it nonetheless has exactly the same mathematical form as the classical expression for the total scattered classical wave amplitude (at $q$) arising from spherical wave point sources distributed in the sample volume according to a number density $\rho(r)$. Since energy is conserved, the total scattered intensity, integrated on the entire collection sphere (or any closed surface containing the sample) must be independent of the particular spatial distribution $\rho(r)$ for a given total number of point scatterers (i.e., of electrons) in the sample. This implies that, for integration over the entire enclosing surface, the total scattered power (i.e., $I_h$) cannot depend on
the structure of the sample, irrespective of whether the sample is constituted of one or many solid phases. It also tells us that the same is true of each part or material phase in the sample, to the extent that the individual number densities \( \rho(r) \) of each part or material phase can be specified.

In particular, if we take the sample to be composed of separate atoms or ions, each having its own \( \rho(r) \) (Eq. 14), then to the extent that this is valid (e.g., that we can neglect the shared bonding electrons that are not included in simplified formulations of \( \rho(r) \)), Equation 47 (the GIIF) follows immediately, using \( \sin(2\theta)d\theta = (\lambda/2\pi)^2 q \, dq = 4 \, q \, dq/q_{\text{max}}^2 \). This does not depend on an approximation that the different atomic electronic distributions do not overlap and it is as exact as we care to make our description of \( \rho(r) \) exact, for example, by dividing all shared or bonding electrons between specific atoms in our definition of \( \rho(r) \).

The same holds for any combination of atoms taken to represent separate material phases in the sample and the only practical limitation is in separating the intensities arising from the different material phases in the measured diffraction pattern. The latter difficulty is largely solved with crystalline phases because their sharp peaks can often be separated and groups of peaks can be analyzed together with full-profile methods such as Rietveld analysis. It is also easy to resolve sharp Bragg peaks from the broad profiles arising from amorphous and nanophase materials.

Within the context of the kinematic theory of X-ray diffraction, the only other difficulties are: (1) correcting for modified radiation contributions to the background, (2) taking into account ordinary mass absorption effects, on both the incoming and outgoing radiation, (3) converting the intensities into electron units; (4) taking into account the diffuse “thermal” scattering from the crystalline phases. The latter represents unmodified radiation that is taken out of the sharp Bragg peaks to be added to the diffuse background. Such a correction need not be applied to the patterns from amorphous and nanophase materials because it is only relevant to Bragg peak intensities. We will not consider dynamic (i.e., non-kinematic) scattering corrections, although they could also be applied (e.g., Egami and Billinge 2003).

**EXPERIMENTAL FACTORS AND RESULTING QUANTIFICATION EQUATIONS**

**Unmodified scattered intensity and Compton scattering background**

The unmodified radiation scattering intensity (in \( J/m^2s \)) at Bragg angle \( \theta \), in powder X-ray diffraction say, is given by

\[
I_0(\theta) = I_0(\theta) \, |F(\theta)|^2 \, A(\theta)
\]

where \( I_0(\theta) \) is given by Equation 1, \( |F(\theta)|^2 \) is given by the square magnitude of the sample’s form factor (Eq. 13) or by Equation 17 or 35 or by the powder average expression (Eq. 16) for powder diffraction, and \( A(\theta) \) is an angle-dependent mass absorption correction factor (see below). In the same experiment on the same sample, the total intensity (in \( J/m^2s \)) of Compton scattering at Bragg angle \( \theta \) is given by

\[
I_{\text{cp}}(\theta) = I_0(\theta) \, [\Sigma, C_i(\theta)] \, A(\theta)
\]

where the sum is over all atoms in the sample and \( C_i(\theta) \) is the atomic Compton scattering factor for atom-i. The sum can be replaced by a sum over atomic (or ionic) species in the sample as

\[
\Sigma_i C_i(\theta) = \Sigma_i N_i C_i(\theta) = \Sigma_i (\{C(\theta)\})
\]

where the right hand sum is over all atomic species, \( N_i \) is the number of atoms of species-k in the sample, and \( \{C(\theta)\} \) is the sample average Compton factor at \( \theta \). The atom-specific Compton factors are known, tabulated, and include the Breit Dirac factor correction (e.g., Warren 1990; Egami and Billinge 2003).

**Mass absorption factor**

The ordinary wavelength dependent atomic mass absorption coefficients \( \mu_i(\lambda) \) for atomic species-k, in \( \text{cm}^2/\text{g} \) or \( \text{m}^2/\text{kg} \) are known and tabulated (International Tables of Crystallography). The linear absorption coefficient of the sample, in \( \text{cm}^{-1} \) or \( \text{m}^{-1} \), is given by

\[
\mu_i(\lambda) = \{\rho\} \, \{\mu(\lambda)\}
\]

where \( \{\rho\} \) is the assumed uniform mass density of the actual sample being irradiated, including air filled voids between grains, etc., and \( \{\mu(\lambda)\} \) is the sample average (by weight) absorption coefficient defined as

\[
\{\mu(\lambda)\} = (1/m) \Sigma_i m_i \mu_i(\lambda)
\]

where the sum is over all atom species in the actual irradiated sample, again including air filled voids between grains, etc., \( m \) is the total sample weight, and \( m_i \) is the weight of element-k in the sample. Note that \( \mu_i(\lambda) \) is (arbitrarily) defined on the basis of unit mass of the element-k, rather than on a per atom or per mole basis. For a powder sample and assuming that the mass density of the sample grains is much larger than the mass density of the ambient gas or vacuum, \( \{\rho\} \) is closely given by \( \{\rho\} = f_v \rho_v \), where \( f_v \) is the volume fraction of the sample that is occupied by material grains and \( \rho_v \) is the average density of the material grains (i.e., the “grain mass density”). On the other hand, \( \{\mu(\lambda)\} \) is closely given by an average analogous to that of Equation 55 where one sums only on the grains and excludes the inter-grain voids. Consequently, \( \mu_i(\lambda) \) is sensitive to the degree of powder sample packing or actual irradiated sample density and is not simply a function of the grain mass density and grain composition alone. Fortunately, as shown below, density related factors cancel out in the final expression for \( A(\theta) \) and sample density evaluations are not required. By comparison, quantification methods based on direct measurements of sample absorption coefficients are experimentally complicated and prone to systematic errors (e.g., Lennox 1957).

Next, in taking mass absorption into account in the actual diffraction experiment, we consider that the radiation is transformed in successive steps as: (1) incident beam intensity, \( I_0 \), (2) surviving incident intensity at depth \( d \) within the sample, after mass absorption removal, (3) scattering (both modified and unmodified) of the latter local incident radiation by the material at depth \( d \), per elementary volume of material at depth \( d \), and (4)
surviving outgoing scattered radiation, after an additional mass absorption on exit from depth \( d \) within the sample.

For powder diffraction measurements from flat uniform samples of semi-infinite depth (i.e., filled trough depths sufficient to stop all X-rays of the relevant wavelength), in 0-0 or 0-20 geometries where sample penetration and exit lengths for a given depth are equal, and in the case of a constant divergent slit (i.e., a constant, angle-independent, incident beam cross sectional area), one finds that Equations 51 and 52 are obtained with

\[
A(\theta) = A_\perp / [2N \Sigma (N_i/N) (M_i/N_A) \mu_i(\lambda)] = A_{\alpha}(\theta) / N \tag{56}
\]

where \( A_\perp \) is the effective cross sectional area of the incident (and outgoing) beam, the sum is over all atomic or ionic species in the sample, \( M_i \) is the mass of one mole of atom-\( k \), \( N_A \) is Avogadro’s number, and \( N \) is the effective number of atoms in the irradiated sample. Equation 56 also defines \( A(\theta) \) as \( A(\theta) \) times \( N \) and divided by \( A_\perp \), for convenience (see below). A similar derivation of \( A(\theta) \) and other derivations relevant to several other instrumental and sample geometries are given, for example, by Egami and Billinge (2003).

Consequently, in this (Eq. 56) most common geometry for quantitative analysis, \( A(\theta) \) is not angle dependent. Automatic divergent slits and other geometries will of course give angle dependencies. Note that, the derivation for the effect of absorption on the Compton scattered radiation (Eq. 52), that leads to Equation 56, relies on the fact that the phenomenon of Compton scattering does not affect the wavelength enough to require using atomic absorption coefficients evaluated at wavelengths different from the incident wavelength of interest. Indeed, the increase in wavelength is approximately given by (Kirz 2001)

\[
\lambda_{\text{sc}} - \lambda = (h/m_ec) [1 - \cos(2\theta)] \tag{57}
\]

where \( h \) is Planck’s constant, \( m_e \) is the electron mass, \( c \) is the speed of light, and \( h/m_ec = 0.02426 \) Å. Note also that, the final result (Eq. 56) is not dependent on actual sample density ((\( p \))) or compactness. This is important, given the experimental difficulty of controlling and measuring \( (p) \), even when uniform density powder absorbers can be made.

**Absolute quantification and material phase analysis**

Absolute quantification, where one evaluates the needed incident beam intensity and its spatial distribution, the true irradiated sample surface area, X-ray counter efficiency, absorption and scattering along the X-ray beam paths to and from the sample, etc., is difficult, tedious, and prone to measurement errors. On the other hand, obtaining a total chemical analysis of the sample (including all major light and heavy elements) is relatively simple and in any case is needed in absolute quantification to calculate Compton corrections, etc. Therefore, it is a great advantage when one can devise a robust quantification scheme that uses only chemical analysis data and some fundamental normalization condition, without requiring a direct absolute intensity measurement. We present the practical version of our method in this sub-section, based on the above relations regarding experimental factors. We leave out considerations of resonance fluorescence contributions to the background because this radiation can be effectively removed by an energy selective detector or by using a secondary beam single crystal monochromator or resonance filters or by selecting wavelengths that avoid such resonances. With samples rich in fluorescing elements at the wavelength being used, one can calculate the fluorescence contributions using tabulated fluorescence emission factors and subtract this contribution. We also leave out considerations of contributions to the background from ancillary scattering from the diffractometer instrument itself and its components because these can be easily monitored and are often negligible in X-ray diffraction using standard instruments.

From the above (Eqs. 1, 51, and 52), clearly one has

\[
(\langle f(\theta) \rangle^2 / N) + \langle C(\theta) \rangle = I_{\text{meas}}(\theta) / I_{\text{meas}}(\theta) A_\perp(\theta) \tag{58}
\]

where \( I_{\text{meas}}(\theta) \) is the actual measured intensity at Bragg angle \( \theta \) and \( a(\theta) \) is defined in Equation 56. For an unpolarized source and in the absence of a secondary beam monochromating crystal, Equation 2 is the correct expression to be included in Equation 1. On multiplying both sides of Equation 58 by the incident intensity \( I_\perp \) [because \( I_\perp \) in the expression for \( I_\perp(\theta) \) is not known] and by \( A_\perp \) and using the G/H/F (Eq. 47), one readily obtains an absolute evaluation of the product \( A_\perp \) where \( A_\perp \) is the effective cross sectional area of the incident (and outgoing) beam as:

\[
A_\perp I_\perp = ([1/4\pi]\Sigma d\Omega d\Omega_{\text{meas}}(\theta) / I_{\text{meas}}(\theta) a(\theta)) / [((2/q_{\text{max}}^2)) d\theta d\Omega_{\text{meas}}(\theta)] + [(1/4\pi)d\Omega_{\text{meas}}(\theta)] \tag{59}
\]

where the integrals are either over the entire angular space of the collection sphere or over the corresponding entire range (0 to \( q_{\text{max}} \)) of \( q \). From the definition in Equation 56, \( a(\theta) \) is given by

\[
a(\theta) = 1 / [2 \Sigma (N_i/N) (M_i/N_A) \mu_i(\lambda)] \tag{60}
\]

One therefore obtains an absolute evaluation of the product \( A_\perp I_\perp \) where only the sample composition is required, to evaluate the sample averages ((\( f(\theta) \)) (Eq. 45) and \( \langle C(\theta) \rangle \) (Eq. 53). Interestingly, if one has measured the diffraction pattern only over some incomplete range, say from \( \theta_{\text{meas}} \) (not including zero) to \( \theta_{\text{meas}} \) (smaller than \( \pi/2 \), one need only evaluate the integrals in Equation 59 over the corresponding range (the \( \phi \) part of \( d\Omega_{\text{meas}} \) gives \( 2\pi \) in powder diffraction geometry) to obtain a very close approximation to \( A_\perp I_\perp \) to the extent that the range is sufficiently broad.

Next, one can now define and calculate the Compton and absorption corrected diffraction pattern (in electron units multiplied by \( A_\perp I_\perp \) and on a per atom basis), \( T(\theta) \), as

\[
T(\theta) = A_\perp I_\perp |\langle f(\theta) \rangle^2 / N| = [I_{\text{meas}}(\theta) / I_{\text{meas}}(\theta) a(\theta)] - [A_\perp I_\perp \langle C(\theta) \rangle] \tag{61}
\]

The latter pattern can be analyzed by various diffraction pattern deconvolution methods and can often be resolved into separate contributions arising from different material phases or sample components as

\[
T(\theta) = \Sigma T(\theta) \tag{62}
\]

where the sum is over all resolved sample components or material phases and \( T(\theta) \) is the Compton and absorption corrected diffraction pattern in electron units (multiplied by \( A_\perp I_\perp \) and on
a per atom basis) of sample component-p. For example, the crystalline and amorphous components could be resolved or two different amorphous components giving rise to features in different angular ranges might be resolved. Consequently, one directly obtains the mole fraction, $f_p$, of component-p as

$$f_p = \frac{N_p}{N} = \frac{1}{A_{I_p}} \left[ \frac{1}{(4\pi)} \int d\Omega_k t_p(\theta) / \int (2/\text{atom}) \int dq q |f(q)|^2 \right]$$  \hspace{1cm} (63)

where one needs only to have an estimate of the composition of component-p to evaluate the component average $|f(q)|^2$ as

$$|f(q)|^2_p = \frac{1}{N_p} \sum f_i(q)$$  \hspace{1cm} (64)

where $N_p$ is the number of atoms or ions of type-k in component-p and the sum is over all ionic or atomic species in component-p. Equation 63 represents a general and exact expression that relates a diffraction pattern $[\theta(q)]$ area to a molar fraction quantity. It is the practical expression of the GIIF (Eq. 47) for phase quantification. One phase of undetermined chemical composition can be independent of texture, in that it is meant to represent a full one component. This general result (Eq. 63) may also be largely integrals over the ranges corresponding to the actual range of $\theta$ used in the measurement (from $\theta_{\text{min}}$ to $\theta_{\text{max}}$), as described above for Equation 59. In this case, all the integrals in both Equations 59 and 63 are evaluated over the actual angular or q ranges of the measurement. This is the simplest way to correct for measured patterns that are never taken on the entire theoretical maximum range (of 0 to $\pi/2$) and it should represent a good approximation to the ideal case. Only unusual patterns, such as $t_p(\theta)$ curves with unusually large [i.e., far beyond the angular variations in $|f(q)|^2$] contributions at $\theta < \theta_{\text{min}}$ or at $\theta > \theta_{\text{max}}$, compared to the integrated values between $\theta_{\text{min}}$ and $\theta_{\text{max}}$, will give rise to a breakdown of these approximations.

We stress that the final quantification result (Eq. 63) is completely general, in that it applies equally and without further approximations to any solid phase in the sample, whether crystalline, amorphous, nanophas, or even quasicrystalline, and to any sample that may be a mixture of such phases. Equation 63 also applies to any grouping of solid phases, such as, for example, all or some of the crystalline phases taken together as one component. This general result (Eq. 63) may also be largely independent of texture, in that it is meant to represent a full phase-specific pattern integration. In the case where a true full collection sphere integration is performed, as opposed to only a reconstructed one from a traditional powder diffractogram and assuming an absence of texture, then Equation 63 is exact for any degree of phase-specific orientational texture provided the integral in the numerator is replaced by the actual full collection sphere integral.

**APPLICATION OF THE METHOD: PROCEDURE AND ACCURACY**

**Example of a step by step procedure**

Consider a natural sediment or soil sample, such as a freeze dried lacustrine sediment, which contains significant contributions of three types: crystalline (mineral) phases, an organic amorphous phase (organic matter, OM), and an inorganic amorphous and nanoparticulate phase. The bulk chemical composition is easily measured and is assumed to be known. The amount of OM can be quantified by loss on ignition (Dean, 1974; Heiri et al., 2001) and the composition of the OM can be obtained by gas chromatography. The sharp Bragg peaks of the crystalline phases can be used for phase identification and mineral phase relative quantification, via the RIR method (Chung 1974; Hubbard et al. 1976; Smith et al. 1987; Hubbard and Snyder 1988), for example. The latter analysis provides a measure of the composition of the crystalline phase component, within the uncertainties associated with the ranges of mineral compositions for given mineral identifications. An important application of our method would then be to quantify the inorganic amorphous phase component, a determination that is rarely attempted by a direct non-destructive physical measurement.

The steps to quantification could be as follows, having already obtained the bulk chemical composition: (1) One first obtains the relative quantifications of the detected and identified crystalline phases, by usual methods and as part of the routine analysis of powder diffraction data. This gives an approximate chemical composition for the crystalline component. (2) One performs the integrals in Equation 59 to obtain the parameter $A_{I_p}$, using the appropriate limits of integration, as explained above. Note that, for a given experimental range of Bragg angles that is commonly used, one need only evaluate the relevant integrals for the atomic form factor and the atomic Compton factor once, for each atomic or ionic species, and then simply apply the compositions of the various samples studied without recalculating these integrals. (3) Using this value of $A_{I_p}$, one then calculates $T(\theta)$ using Equation 61. (4) One could next sum all the intensity of the sharp Bragg peaks found in $T(\theta)$ and supplement this total intensity by the crystalline thermal diffuse scattering by multiplying the integrated intensity of each peak (or unresolved group of peaks) by $\exp(+<u^2>q^2)$ where $<u^2>$ is the usual average square (thermal and or static) displacement (assumed spherically symmetric for simplicity) of atoms in the relevant crystalline phase (or phases). Note that this multiplicative factor is Bragg angle dependent via $q^2$. After accounting for collection sphere integration, the result is the correct integrated intensity, $(1/4\pi)\int d\Omega_k t_p(\theta)$, that corresponds to the crystalline phase component. One then applies Equation 63 to obtain the $f_p$ of this component, where one uses the estimated composition of the crystalline component obtained in step 1 to calculate $|f(q)|^2$ in the denominator of the right hand side. (5) Having achieved this, the molar fraction of the total amorphous component (organic and inorganic) is simply $1 - f_p$, using the $f_p$ of step 4. (6) Using the independently obtained weight fraction and composition of the OM component, one then deduces the separate molar or weight fractions of the two amorphous components. (7) By difference, one obtains the composition of the inorganic amorphous component and one can test the resulting composition (and overall self-consistency) by applying Equation 63 to the inorganic amorphous fraction. This gives a constraint that removes some of the uncertainty related to the ranges of mineral compositions consistent with the given mineral identifications.

Alternatively, if quantitative micro-analysis methods can
be used to quantify the separate chemical compositions of the components of interest that can be resolved in the \( T(\theta) \) diffraction pattern, then the corresponding uncertainty is removed. With fine sediments and soils this is not usually possible and diffraction remains the best physical method for whole sample quantifications. Our method offers the possibility of routinely quantifying the above three components in soils and sediments, with reasonable accuracy, as shown below.

**Evaluating practicality and accuracy using synthetic mixtures**

We prepared synthetic binary mixtures from three starting powders of reference materials: (1) RHY-1, an internal rock standard (rhyolite) for elemental analysis at the University of Ottawa, having major phases quartz, feldspar, chlorite, and mica; (2) BS103P, an OM certified material from the International Humic Substances Society, known as Pahokee peat soil; and (3) SiGel, a commercial silica gel (amorphous SiO\(_2\)) from VWR Canlab, 230–400 mesh (40-63 μm). The latter starting material had an 8% weight loss, assumed to be water (see below), and the following manufacturer specifications: Cl 0.02% max, Fe 0.02%, loss on drying 9% max, pH (10% suspension) 7.0(5). Some samples were mixtures of the rhyolite rock standard and the OM standard whereas the other samples were mixtures of the rhyolite rock standard and the amorphous silica. The resulting synthetic mixtures are fair representations of natural sediments containing several crystalline phases and an amorphous fraction that is predominantly either organic or inorganic, respectively.

A chemical composition of each solid phase to be resolved and quantified is required, in addition to the whole sample chemical composition, to calculate the \( \langle I(q)\rangle \) phase-specific average (Eq. 64). The major element composition of the rock standard was used as provided. Light elements (C, H, N, S) were obtained by combustion gas chromatography (e.g., Rancourt et al. 2001). Oxygen was calculated assuming the common metal oxidation states and correcting for the Fe\(^{3+}/\text{Fe}^{2+}\) ratio measured from the whole-rock standard by Mössbauer spectroscopy, assuming equal ferric and ferrous Mössbauer recoils fractions (e.g., Rancourt 1989). The OM reference composition was evaluated by combining X-ray fluorescence spectroscopy (XRF), including (predominantly OM) weight loss on ignition (LOI), with combustion gas chromatography (C, H, N, S). The ash (i.e., non-organic) residual fraction resulting from ignition was used to obtain the weights of the major element oxides of Al, Ca, Fe (assumed as Fe\(_2\)O\(_3\)), K, Mg, P, Si, and Ti. The missing weight was taken to be O in OM. The silica material was taken to have composition SiO\(_2\)\(\_n\)H\(_2\)O where \( n \) was evaluated by weight loss from furnace heating at 550 °C for 4 hours. The errors contributed by uncertainties in phase-specific chemical compositions are negligible compared to the identified main source of error (see below). Total compositions of mixtures were calculated using the end-member compositions and the known weight fractions of the mixtures.

Powder X-ray diffractograms were collected using an automated Philips X’Pert PW3710 system \( \theta-\theta \) powder diffractometer, with CuKα radiation, an automatic variable divergent slit, and a KeveX™ solid state detector with electronic energy window set on the Kα line. Ground and well-mixed powder samples were mounted in flat surface filled trough (i.e., semi-infinite) geometry and the holder rotated continuously about the axis perpendicular to its plane during data accumulation. Most diffractograms were collected in the \( 2\theta \) angular range 5–70° and select samples were also run in the two larger ranges 5–135° 20 and 1.5–135° 20. With such multi-phase samples (especially natural sediments) we find that using filled troughs (as opposed to smears) and spinning sample holders are essential to minimize sub-sampling (i.e., particle statistics) and texture problems. Spinning cannot remove most texture effects but with our mixtures (and with natural aquatic sediments) we did not find it necessary to use special texture-removing sample preparation methods (e.g., Zhang et al. 2003). Readers considering other sample preparation methods should beware of the large systematic quantification artifacts that can occur and should always test their method with the samples of interest (e.g., Gibbs 1965).

The automatic variable divergent slit procedure is intended to provide constant irradiation volumes of thin smear samples by keeping the sample irradiation area constant. It has been shown to be accurate and reliable (Kimmel 1987). With a filled trough sample, however, it does not provide a constant irradiation volume condition and this is simply corrected in the data before the constant irradiation volume expressions given above are used. The correction is the usual exact geometric factor (Kimmel 1987; Bowden and Ryan 1991). This is better than collecting the data with a constant divergent slit because the latter produces smaller sample irradiation areas at larger angles and corresponding losses in counting statistics. On the other hand, at the larger divergent slits of the larger Bragg angles one has the situation that the recommended 1° scatter slit of the Philips diffractometer system becomes the limiting collection aperture, above approximately 29° 20. A second geometric correction is therefore applied to take this into account (Bowden and Ryan 1991). Note that one must know one’s diffractometer before applying the procedures described here. There would be advantages to using variable count time strategies (e.g., Cockcroft 2002) but the user must then carefully modify our quantification equations accordingly.

Complications related to axial divergence (e.g., Cheary and Coelho 1998) and to difficulties in extracting the instrumental function in general (e.g., Ida and Toraya 2002) do not arise in our method because we are extracting full diffraction sphere integral values without concern for the exact lineshapes, except to the (minor) extent that such lineshape considerations might affect our ability to resolve the solid-phase-specific diffractogram components of interest. Problems related to intensity calibration, arising from counter saturation effects, etc., should be considered (Kern and Eysel 1994). Although we have encountered electronic counter saturation with high symmetry, pure synthetic samples (i.e., intense Bragg peaks), we did not have this problem with our test mixtures (below) or natural samples (unpublished).

The measured (raw) diffractograms of the three reference materials are shown in Figure 1. These three diffraction patterns were measured using a step size of 0.02° 20 and an accumulation time of 2s per step. Note that the diffraction patterns of the two amorphous materials are significantly different from each other. This would allow direct quantifications of amorphous phase mixtures, by the methods presented here, in cases where \( N-1 \) of the \( N \) amorphous phases in a mixture have known diffraction pattern shapes. One would simply use least squares fitting with con-
strained end-member diffraction pattern shapes in extracting the
N corresponding t,θ patterns of Equation 62. The OM standard
contains an impurity of quartz (Fig. 1a) that was neglected in all
our analyses except for the OM end-member, as it contributed
negligibly to our errors in the non-OM-end-member mixtures.
Indeed, the molar fraction of quartz from applying our XRD
analysis is only 0.9(4)%. The determination of division lines such as the latter one
(Fig. 4c), between diffraction contributions from phases that are
to be resolved and quantified, is a key challenge in applying our
method and was the largest and dominant source of error in the
final quantification. The method now reduces to separating area
contributions to T(θ) and applying Equation 63 without any fur-
ther calibrations or corrections, keeping in mind that every Bragg
peak gives a thermal diffuse contribution to the broader features

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{As measured (raw, CuKα) 5–70° 2θ range diffraction patterns of the three end-member reference materials used to make the binary (mineral and amorphous phase) mixtures: (a) the OM certified reference material (Pahokee peat soil), (b) the inorganic amorphous reference material (commercial silica gel), and (c) the rock standard material. Main Bragg peaks from the major mineral phases in the rock standard are labelled as follows: C, for chlorite; M, for mica; Q, for quartz; and A, for albite (feldspar). A small impurity of quartz is detected in the OM material.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Correction and treatment sequence applied to the 5–135° 2θ range diffraction data for the OM certified reference material (Pahokee peat soil). (a) Raw, as measured (CuKα), data and scatter slit corrected. The scatter slit correction applies only above ~29° 2θ. The upper curve is the corrected data. (b) The constant irradiation volume corrected data. (c) The final, Compton corrected and electron units normalized, absolute T(θ) diffraction data (Eq. 61).}
\end{figure}
The latter approach, as can be easily implemented in a diffraction analysis software such as Jade™. We estimated the error by eying the total "background" that would include only the bottoms and tails of all the Bragg peaks. We used the estimated by eying the total "background" that would include the amorphous phase contributions. The method is general and can be applied to the diffraction contributions from any phase, such as all the Bragg peaks from a single given mineral phase where there are several crystalline phases or separate amorphous profile contributions from distinct amorphous phases.

The division line between all Bragg peaks and the rest is best estimated by eying the total "background" that would include only the bottoms and tails of all the Bragg peaks. We used the latter approach, as can be easily implemented in a diffraction analysis software such as Jade™. We estimated the error by eying both maximum and minimum division lines that overestimate and underestimate the total Bragg area, respectively, but in ways that remain just acceptable in our best judgement, based on years of full profile fitting of diffraction patterns. The average of the minimum and maximum total Bragg areas is taken to be our measured value. Alternatively, since in these tests we know the \( T(\theta) \) profiles of the amorphous phases, one can simply scale up the amorphous profile to just touch (at the noise half-level) the bottom of the overall \( T(\theta) \) pattern. The latter method gave the same quantification results, within error.

The evaluation of the crystalline component obtained from Equation 63 as a function of the known atomic fraction of the mineral component in our synthetic mixtures. The results show general agreement with the 1:1 line. Mineral phases are the ones expected to suffer most from not using the full 20 range in the measurement and, indeed, the results are sensitive to the 20 range used in the high mineral fraction mixtures (Fig. 5). In all cases of mineral-rich mixtures, the values converged to the known values as the range was increased from 5–70° to 5–135° to 1.5–135° 20.

The OM end-member point in Figure 5 (near \( f_a = 0 \)) requires more explanation. As mentioned above, our XRD method gave 0.9(4) mol% quartz, consistent with the small Bragg peak in Figure 1a, however, the XRF analysis gave a total non-organic major element oxide weight corresponding to 3.7 mol%, that we expressed as a mineral fraction (\( f_a = 0.037 \)) only for the OM end-member point in Figure 5 for the sake of illustrating its magnitude. The latter fraction, however, probably corresponds to major non-OM elements either complexed to the OM or included in an inorganic amorphous fraction or both. In either case, it will be counted as part of the (nominally OM) amorphous component in our \( T(\theta) \) evaluations and is therefore not corrected for in determining the known \( f_a \) values of the OM-rock mixtures in Figure 5.

The final test results are shown in Figure 5 where we plot the atomic fraction of the crystalline component obtained from Equation 63 as a function of the known atomic fraction of the mineral component in our synthetic mixtures. The results show general agreement with the 1:1 line. Mineral phases are the ones expected to suffer most from not using the full 20 range in the measurement and, indeed, the results are sensitive to the 20 range used in the high mineral fraction mixtures (Fig. 5). In all cases of mineral-rich mixtures, the values converged to the known values as the range was increased from 5–70° to 5–135° to 1.5–135° 20.

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Figure 5 serves several purposes: It shows that the proposed quantification method works in practice and gives accurate results (to 1–2% atomic fraction), it shows that a 20 range of 5–70° is often adequate, and it shows that the method works just as well for organic and inorganic amorphous components. The only other experimental difficulty that we encountered (not shown) was an artifact, prob-
using the known rock composition, within error for a given $\theta$ range. This insensitivity was expected from the quantification of the mineral, OM, and inorganic amorphous components, using only physical methods (heating and pXRD). These may be the first reliable quantifications of the inorganic amorphous component in particular, including an evaluation of its composition, in complex and OM-rich samples. Different inorganic amorphous phases occur in different diagenetic and pedogenic environments. These results will be reported elsewhere.

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