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” (GIIF) 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, $T(0)$, 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 $A_f \varphi$ of the effective cross sectional area ($A_f$) of the incident (and outgoing) beam and the effective incident beam intensity ($\varphi$), 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 standardless) 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...