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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 θ-θ or θ-2θ 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, $T(\theta)$, 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 $A_\perp I_o$ of the effective cross sectional area ($A_\perp$) of the incident (and outgoing) beam and the effective incident beam intensity (I_o), 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.