



Standard Guide for Forensic Analysis of Geological Materials by Powder X-Ray Diffraction¹

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1. Scope

1.1 This guide covers techniques and procedures for the use of powder X-ray diffraction (XRD) in the forensic analysis of geological materials (to include soils, rocks, sediments, and materials derived from them such as concrete), to enable non-consumptive identification of solid crystalline materials present as single components or multi-component mixtures.

1.2 This guide makes recommendations for the preparation of geological materials for powder XRD analysis with adaptations for samples of limited quantity, instrumental configuration to generate high-quality XRD data, identification of crystalline materials by comparison to published diffraction data, and forensic comparison of XRD patterns from two or more samples of geological materials to support criminal investigations.

1.3 *Units*—The values stated in SI units are to be regarded as standard. Other units are avoided, in general, but there is a long-standing tradition of expressing X-ray wavelengths and lattice spacing in units of Ångströms (Å). One Ångström = 10^{-10} meter (m) = 0.1 nanometer (nm).

1.4 This standard is intended for use by competent forensic science practitioners with the requisite formal education, discipline-specific training (see Practice E2917), and demonstrated proficiency to perform forensic casework.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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2. Referenced Documents

2.1 ASTM Standards:²

C1365 Test Method for Determination of the Proportion of Phases in Portland Cement and Portland-Cement Clinker Using X-Ray Powder Diffraction Analysis

D934 Practices for Identification of Crystalline Compounds in Water-Formed Deposits By X-Ray Diffraction (Withdrawn 2022)³

E620 Practice for Reporting Opinions of Scientific or Technical Experts

E1492 Practice for Receiving, Documenting, Storing, and Retrieving Evidence in a Forensic Science Laboratory

E2917 Practice for Forensic Science Practitioner Training, Continuing Education, and Professional Development Programs

E3272 Guide for Collection of Soils and Other Geological Evidence for Criminal Forensic Applications

2.2 ISO Standard:⁴

ISO/IEC 17025:2017 General Requirements for the Competence of Testing and Calibration Laboratories

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *Bragg equation* or *Bragg's law*, n —describes the physical phenomenon of X-ray scattering from a crystallographic three-dimensional lattice plane as $n\lambda=2d\sin\theta$, in which n is any integer, λ is the wavelength of the X-ray, d is the crystal plane separation, also known as d -spacing, and θ is the angle between the crystal plane and the diffracted beam, also known as the *Bragg Angle*.

3.1.2 *crystal*, n —a homogeneous, solid body of a chemical element or compound, having a regularly repeating atomic

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from International Organization for Standardization (ISO), ISO Central Secretariat, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, https://www.iso.org.

arrangement that can be outwardly expressed by plane faces (adapted from Ref (1)).⁵

3.1.3 *crystal lattice, n*—the three-dimensional regularly repeating set of points that represent the translational periodicity of a crystal structure.

3.1.3.1 *Discussion*—Each lattice point has identical surroundings. Lattice is the abstract pattern used to describe the internal geometric structure of crystals. Lattice and structure are not synonymous, as structure refers to the real mineral material (adapted from Ref (1)).

3.1.4 *crystalline, adj*—having a crystal structure or a regular arrangement of atoms in a crystal lattice.

3.1.5 *d-spacing, n*—in diffraction of X-rays by a crystal, the distance or separation between successive and identical parallel planes in the crystal lattice; *d*-spacing is expressed as *d* in the Bragg equation (adapted from Ref (1)).

3.1.6 *diffractometer, n*—an instrument that records either powder or single-crystal X-ray diffraction patterns.

3.1.7 *known sample, n*—known samples of geological material are intentionally collected, typically from crime scene or alternate locations, for comparison to a questioned sample.

3.1.7.1 *Discussion*—Geological materials are typically more heterogeneous than manufactured materials, so a greater number of known samples of geological material are needed to represent the range of variation (see Guide E3272). *Reference sample* and *control sample* are synonyms of *known sample*.

3.1.8 *mineral, n*—a naturally occurring inorganic element or compound having an orderly internal structure and characteristic chemical composition, crystal form(s), and physical properties, or an element or chemical compound that is crystalline and that has formed as a result of geological or pedogenic (soil-formed) processes (adapted from Ref (1)).

3.1.8.1 *Discussion*—Artificial and biogenic crystalline materials are not minerals but can occur in geological materials (for example, cement powder, lime, lye, biogenic calcite, biogenic hydroxyapatite, bricks) and can be detected by XRD.

3.1.9 *phase, n*—a part of a chemical system that is homogeneous, physically distinct and at least hypothetically separable, and which has single or continuously variable chemical and mechanical properties (adapted from Ref (1)).

3.1.10 *provenance, n*—a place of origin; specifically, the area from which the constituent materials of a sedimentary rock or facies are derived (adapted from Ref (1)).

3.1.10.1 *Discussion*—In the context of forensic provenance analysis, geological material is analyzed and interpreted to estimate or limit the geographic or environmental conditions of the source of this material to provide an investigative lead. For example, soil on a shovel can be examined to aid in the search for a clandestine grave, typically by comparison of observations to reference data. *Geographic attribution* is an alternative term for *provenance*.

3.1.11 *questioned sample, n*—geological evidence of unknown origin, or a *questioned sample*, typically consists of

debris adhering to an evidentiary object (for example, tire, wheel well, garment, shoe, digging tool); exogenous soil left at a crime scene (transferred from a shoe/tire, or adhering to a re-buried body/object); or debris recovered from within a body (nasal, stomach, or lung contents).

3.1.12 *Rietveld refinement, n*—a procedure for carrying out a crystal-structure refinement using X-ray or neutron powder diffraction data, in which an entire powder pattern is simulated for a trial structure(s) and matched against the observed powder pattern; atomic parameters and other variables are modified to achieve an acceptable fit between the calculated and observed powder patterns (adapted from Ref (1)).

3.1.13 *unit cell, n*—the smallest group of atoms of a crystal lattice that has the overall symmetry of a crystal of that substance, and from which the entire lattice can be built up by repetition in three dimensions.

3.1.14 *X-ray diffraction (XRD), n*—the diffraction of a beam of X-rays, usually by the three-dimensional periodic array of atoms in a crystal that has periodic repeat distances (lattice dimensions) of the same order of magnitude as the wavelength of the X-rays (1).

3.1.15 *X-ray diffraction pattern* or *diffractogram, n*—the characteristic interference pattern obtained when X-rays are diffracted by a crystalline substance; the geometry of the pattern is a function of the repeat distances (lattice dimensions) of the periodic array of atoms in the crystals; the intensities of the diffracted beams give information about the atomic arrangement, and unit-cell dimensions (adapted from Ref (1)).

3.1.16 *X-ray powder diffraction, n*—diffraction of a beam of X-rays by planes of atoms in a powdered crystalline sample; the powders are prepared so they ideally represent all possible crystal orientations to the X-ray beam (adapted from Ref (1)).

4. Summary of Guide

4.1 Powder X-ray diffraction produces results related to the crystal structure(s) of one or more crystalline components of the material being analyzed that can allow phase identification.

4.2 This guide recommends specific techniques and procedures for XRD analysis of geological materials in forensic casework, including XRD analysis of minimally modified materials, small quantities of material (a common limitation in forensic casework), and in situ XRD of material adhering to a substrate.

4.3 XRD patterns are compared to reference databases as means of identifying the crystalline constituents of a sample.

4.4 XRD can be used to determine the crystal structure of a material, but this is not described in this guide.

4.5 XRD patterns from various samples are compared to each other for forensic comparison and provenance purposes.

5. Significance and Use

5.1 The overarching goals of the forensic analysis of geological materials include (A) identification of an unknown material (see 11.3), (B) analysis of soils, sediments, or rocks to restrict their possible geographic origins as part of a provenance analysis (see 11.4), and (C) comparison of two or more

⁵ The boldface numbers in parentheses refer to the list of references at the end of this standard.

samples to assess if they could have originated from the same source or to exclude a common source based on observation of exclusionary differences (see 11.5). XRD is only one analytical method that can be applied to the evidentiary samples in service of these distinct goals.

5.2 Within the analytical scheme of geological materials, XRD analysis is used to: identify the crystalline components within a sample; identify the crystalline components separated from a mixture, typically clay-sized material (see 8.8), or a selected particle class for which additional analysis is needed (see 8.11); or compare two or more samples based on the identified crystalline phases or diffraction patterns (see 11.5).

5.2.1 Non-destructive XRD analysis can be performed in situ on geological material adhering to a substrate (see 8.12.3).

5.2.2 The most common forensic applications of XRD to geological materials are (A) identification or confirmation of a selected phase or fraction of a sample (see 8.12), (B) identification of minerals in the clay-sized fractions of soils (see 8.8), and (C) identification of the phases of the hydrated cement component of concrete or mortar.

5.3 This guide is intended to be used with other methods of analysis (for example, polarized light microscopy, scanning electron microscopy, palynology) within a more comprehensive analytical scheme for the forensic analysis or comparison of geological materials.

5.3.1 Comprehensive criteria for forensic comparisons of geological material integrating multiple analytical methods and provenance estimations (see 11.4) are not included and are beyond the scope of this guide.

6. Apparatus and Materials

6.1 Powder X-Ray Diffractometer:

6.1.1 Powder X-ray diffractometers are commonly configured with a 2θ or $\theta - \theta$ geometry.

6.1.2 Alternative instrumentation configurations permit simultaneous collection of diffracted beams at multiple angles (stationary position sensitive detectors), or transmission powder XRD.

6.1.3 The X-ray tubes in XRD most commonly have copper targets, generating a $K_{\alpha 1,2}$ wavelength (λ) of 0.15418 nm (1.5418 Å).

6.1.3.1 X-ray tubes with cobalt targets (Co $K_{\alpha 1,2\lambda}$ of 0.17902 nm or 1.7902 Å) reduce fluorescence in XRD of iron-bearing materials.

6.1.4 *Parallel Beam Optics*, if available, could be beneficial for: samples that are not flat (see 8.12.1); in situ analysis, (8.12.3), or micro-XRD (8.12.4), but can reduce the diffraction signal (2). Adaptations to achieve parallel beam optics include:

6.1.4.1 Göbel mirrors,

6.1.4.2 Polycapillary collimators (3),

NOTE 1—The parallel beam adaptations need to be matched to the specific applications.

6.1.5 *Spinning Sample Stage*, if available, could be beneficial for samples of limited quantity.

6.1.6 *Adjustable XYZ Tri-axial Goniometer Head*, if available, could be beneficial for samples of limited quantity.

6.2 *Sample Milling and Preparation Equipment*—The following materials can be helpful in sample preparation.

6.2.1 Mortar and pestle composed of agate, alumina, or ceramic;

6.2.2 A McCrone Micronizing Mill⁶ (5), or other mills;

6.2.3 Filtration apparatus (6).

6.3 Sample Holders:

6.3.1 Bulk sample holders can be used when sample volume is sufficient to fill them.

6.3.2 Sample holders with minimal contribution to the diffraction pattern are recommended for many applications. Two “zero background” sample holder substrates are:

6.3.2.1 A silicon crystal cut parallel to the 510 plane;

6.3.2.2 A quartz crystal cut 6° from the 0001 plane.

6.3.3 Filters or other substrates can be used, but they could contribute to the background signal. In interpretation of diffraction patterns, this background should be considered.

6.4 Reference Materials:

6.4.1 *Standard Reference Materials*—Standard reference materials, commonly silicon, corundum, or microcrystalline quartz, are available from NIST (National Institute of Standards and Technology) or some instrument manufacturers. Standard reference materials are used to document peak position, resolution/peak width, and intensity of the diffraction peaks.

6.4.2 Mineral reference materials.

6.4.3 Crystalline materials for “internal calibration” or reference material mixed into the analyte.

6.4.3.1 Common crystalline materials that can be used include zincite (zinc oxide), halite (sodium chloride), diamond, silver, corundum, or another crystalline substance that is absent from the sample and that does not, or minimally, interferes with sample diffraction peaks, as demonstrated by prior sample analysis or prior knowledge of the sample.

6.5 *Powder XRD Reference Data*—Reference diffraction data for known materials are available as: powder XRD patterns that are digital or graphical data representing the intensity of the diffracted X-ray beam versus degrees 2θ (for a specified X-ray wavelength); tables of diffraction peaks listing the degrees 2θ or the d -spacing (Å), the relative intensity of these peaks, and the crystallographic plane (defined by h , and k , and l) causing the diffraction; and modelled diffraction patterns derived from crystal structure data. Several commercial and freely available sources are listed below; however, this list is not inclusive. The source of reference data should be considered when used to identify phases within the XRD pattern of an unknown sample.

6.5.1 *Commercial Sources of Powder XRD Patterns and Structural Data:*

6.5.1.1 International Centre for Diffraction Data (ICDD, PDF or Powder Diffraction File) (7).

⁶ The McCrone Micronizing Mill (McCrone Microscopes and Accessories, 850 Pasquinelli Drive, Westmont, IL 60559) is the only suitable commercial product for the optimal particle size reduction of geological materials for quantitative powder XRD (4) known to the committee at this time. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

6.5.1.2 NIST Inorganic Crystal Structure Database (ICSD) (8).

6.5.2 *Free Sources of XRD Patterns and Structural Data of Geological Material:*

6.5.2.1 The RRUFF Project (9) integrating the American Mineralogist Crystal Structure Database.

6.5.2.2 The Crystallography Open Database or COD (10) integrating the American Mineralogist Crystal Structure Database.

6.5.3 *Sources of Powder XRD Tables of Geological and Related Materials:*

6.5.3.1 Table 5.18 of Brown and Brindley (11).

6.5.3.2 Common soil minerals in Table 4-1 of Ref (12).

6.5.3.3 Common minerals in clay-sized material (13).

6.5.3.4 Clay mineral-specific diffraction data (12, 14-17).

6.5.3.5 Cement- and concrete-specific data (Ref (18)), see Test Method C1365).

6.6 *Powder XRD Analysis Software for Phase Identification:*

6.6.1 Diffractometer manufacturers typically provide instrument-specific, high-quality peak detection and phase identification software.

6.6.2 Alternatively, there are additional commercial (for example, Jade (19)) and no cost software packages (for example, CrystalSleuth (9), ReX (20), or GSAS II (21); see review in Ref (22)).

7. Hazards

7.1 X-rays are a hazardous source of ionizing radiation and should be contained within the safety shielding of a commercial diffractometer whenever the X-ray tube is energized. The X-ray source should be registered with the appropriate jurisdictions.

7.2 The X-ray tube requires high voltages that present a risk of electrocution if instrument safety mechanisms are overridden.

8. Sample Preparation

8.1 Recommend sample preparation methods are described below for acquisition of high-quality XRD data, but useful XRD data can be produced with minimal sample modification (for example, in situ analysis (8.12.3), or from samples of limited quantity (8.12.1, 8.12.2, 8.12.4).

8.2 *Sub-sampling of Particle Assemblages*—Representative sub-sampling of particulates can be achieved with a sample splitter, or cone and quartering, both of which can be impractical for samples of limited quantity (23).

8.2.1 An alternative method of representative sub-sampling that is appropriate for small quantities of powder, is first mixing the particles, moistening to cause particle adhesion, then scooping of one or more sub-samples.

NOTE 2—Systematic sub-sampling of particulates is crucial for quantitative XRD methods (see 10.6) to minimize bias in both particle size and modal abundance of particle type.

8.3 *Sample Treatments for Comparisons*—Sample treatments should be similar when comparing diffraction patterns of

geological materials (questioned-to-known, questioned-to-questioned, or known-to-known) (see 11.5).

8.3.1 If there is a distinct particle size difference between samples, and if there is sufficient material to conduct size fractionation, the XRD patterns for comparison should be derived from the same particle size fraction.

8.3.2 Other physical or chemical treatments should be similar for direct comparison of XRD patterns (for example, drying, crystallite orientation, glycolation, selective dissolution (24), grinding, type of sample holder).

8.4 *Sample Quantity*—Diffraction data suitable for phase identification can be acquired from very thin samples (see 8.12.2), but a powder thickness of at least ~100 μm is optimal (12, 25).

8.4.1 If samples are thinner than ~100 μm and if the sample holder is not a low background material (see 6.3.2), contribution from the sample holder should be considered in the interpretation of the diffraction pattern.

8.4.2 The minimum sample required for acquisition of XRD data suitable for phase identification will vary by sample composition, but several milligrams on a zero background sample holder can be sufficient (26).

8.5 *Sample Particle Size*—An optimal sample for powder XRD data acquisition consists of fine particles, typically less than 10-20 μm diameter (4, 12, 25).

8.5.1 *Reduction of Particle Size*—Samples of limited quantity are often ground using a mortar and pestle (12, 25).

8.5.1.1 Grinding in a liquid medium such as acetone or an alcohol is recommended. Grinding in water, while possible, will destroy potentially soluble minerals (for example, salts such as halite or gypsum). Certain minerals can be altered by aggressive grinding (25, 6).

8.5.1.2 Particle reduction mills (such as a McCrone Micronizing Mill) produce an ideal narrow particle range of the right size for powder XRD (4) but are not recommended for samples of limited quantity.

NOTE 3—To preserve the grain morphology and to permit subsequent grain selection, it can be prudent NOT to grind samples of very limited quantity. See 8.12.1.

NOTE 4—Contributions from the micronizing media should be considered when interpreting powder diffraction profiles.

8.6 *Sample Placement on Sample Holder*—Powders should be placed into a clean sample holder, with the powder surface flush with the top of the sample holder to align with the focusing circle of the diffractometer.

8.6.1 Samples too small to fill a sample holder can be placed directly on a low background substrate.

8.6.2 The powder should ideally cover the entire area irradiated by the X-ray beam, which will depend on the instrument configuration and the 2θ scan range, but is not required with a zero-background sample holder.

8.7 *Random Particle Orientation*—With the exception of samples intentionally prepared with a preferred orientation (see 8.8.3), powders should be prepared to confer random orientation of crystals.

8.7.1 Avoid pressing too hard on the powder surface to maintain random orientation of the crystals.

8.7.2 Clay minerals, common in soils, are particularly susceptible to preferred orientation (5, 6, 12, 17).

8.7.3 Use of a side-loading sample holder can minimize these effects (5, 6).

8.8 *Clay Mineral Analysis Methods*—XRD analysis is one of the principal means of differentiating minerals in the clay-sized fraction (<2 μm diameter) of soils and sedimentary rocks as these particles are too small to be analyzed by optical microscopy. Clay minerals are phyllosilicates commonly found in the clay-sized particle range. Because clay minerals have significant effects on soil chemical and physical properties, specific sample preparation protocols have been developed to functionally differentiate among these minerals by XRD analysis.

8.8.1 *Dispersion of Samples*—Dispersion of minerals in an aqueous solution is useful both for separation of size fractions to segregate clay sized material for XRD (see 8.8.2), and for removal of fine materials coating sand and silt grains prior to grain mount preparation for analysis by light microscopy.

8.8.1.1 Commonly a dispersant/surfactant is added in trace amounts to aid dispersion. Sonication in an ultrasonic bath or with an ultrasonic probe aids in dispersion.

8.8.1.2 The presence of carbonates or gypsum can interfere with dispersion but standard methods to remove these minerals are not recommended for samples of limited quantity.

NOTE 5—Dispersion in water will destroy potentially soluble minerals (for example, salts such as halite).

8.8.2 *Separation of Clay-sized Fraction*—To separate the clay-sized fraction (<2 μm), the sample is typically dispersed in water (see 8.8.1) and allowed to settle a known distance for a known length of time (either under gravity or in a centrifuge) in accordance with Stokes' Settling Law (15, 17).

8.8.3 *Oriented Samples*—To analyze clay minerals by XRD, many methods are designed to intentionally create samples in which the platy clay minerals are oriented parallel to the diffraction focal plane, selecting for the 00*l* lattice spacing. This can be achieved by:

8.8.3.1 Allowing a clay mineral suspension to sediment out and dry on the sample holder,

8.8.3.2 Filtering it through a membrane filter and transferring the sediment film on the filter to the sample holder,

8.8.3.3 Generating an XRD pattern of the material in situ on the filter, or

8.8.3.4 Smearing a dense clay paste across the sample holder.

8.8.3.5 Diffraction patterns derived from oriented samples should not be compared to standard powder XRD reference data by search-match methods due to the suppression of all peaks except 00*l*.

8.8.4 *Clay Treatments*—The clay-sized fraction (<2 μm diameter) of soils or other geological material can be subjected to treatments prior to sequential XRD analysis aiding differentiation among clay mineral varieties (6, 14, 15, 17, 27; section 7A1 in Ref (16); Table 4.2 in Ref (12)). Common treatments include:

8.8.4.1 Saturation with Mg²⁺, K⁺, or Li⁺;

8.8.4.2 Solvation with glycerin, ethylene glycol, or formalin; or

8.8.4.3 Heating to specific temperatures, typically 300 °C, 400 °C, 500 °C, or 550 °C.

8.8.4.4 For samples of limited quantity, application of cation saturation or heat treatment is not recommended because these treatments can irreversibly alter the evidence, but solvation is reversible and can be informative.

8.9 *Standard Addition for Internal Calibration*—Due to the limitations often encountered with evidentiary samples, it is not always possible to achieve the ideal sample height, particularly for in situ XRD. Because sample height is critical for both phase identification and comparison (see 10.7.3), the use of an internal standard represents one way to ensure accurate knowledge of peak position (° 2θ). Alternatively, the presence of another independently established phase (such as quartz) can also be used to serve as an internal peak position calibrant.

8.10 *Standard Addition for Quantification*—For quantitative XRD analysis (see 10.6), a common approach is to add a specified weight percent (~10 to 20 weight %) of an internal standard (see 6.4.3) to the sample, usually corundum, or zincite (28).

8.10.1 Standards should be absent from the sample and should lack preferred orientation.

8.10.2 This approach is not recommended for samples of limited quantity.

8.11 *Segregation and Concentration of a Sample Component*:

8.11.1 The segregation and concentration of a component can be done using a range of methods including hand picking particles, density separation, magnetic separation, or selective dissolution (25, 24, 29).

8.11.2 Physical concentration of a component of a mixture will aid in its identification when it is otherwise present below the XRD detection limit (see 10.7.4) in a bulk sample.

8.11.3 Segregation of the hydrated cement component of concrete prior to XRD enhances the signal of the cement phases that are useful in cement comparisons

8.11.4 Hydrated cement can show zoning around aggregate grains and near the concrete surface; thus, sampling and analysis from representative zones of the evidentiary samples is recommended.

8.12 *Adaptations of XRD Methods to Evidentiary Samples of Limited Quantity*—Evidentiary geological materials are commonly limited in quantity or may be adhered to other items in which removal could lead to loss of evidence. Several optional adaptations of sample preparation and XRD methods can be applied based on the sample characteristics, and availability of equipment (8.12.1 – 8.12.4).

8.12.1 *Unground Scant Sample*—To preserve grain morphology and to permit subsequent grain selection, XRD patterns can be acquired from unground particles of geological material.

8.12.1.1 A collection of “large” unground grains (fine sand to coarse silt sized) can be placed directly on a sample holder.

8.12.1.2 A preparation of scant material consisting of large (over 25 μm), or uneven-sized particles will have an uneven surface and will likely have few diffracting crystals (25).

8.12.1.3 Longer data acquisition times and a rotating sample stage are recommended for scant samples to acquire sufficient signal for peak detection and phase identification.

8.12.1.4 The resulting diffraction peaks from unground samples could be displaced (see 10.7.3) and peaks could broaden due to the uneven sample height (5).

8.12.1.5 Use of parallel beam optics can mitigate the artifacts of an uneven sample surface (2).

8.12.2 *Ground Scant Sample*—A small subsample can be ground in a mortar in a solvent and pipetted onto the center of a zero background sample holder, minimizing the amount of morphologically modified material.

8.12.2.1 Scant samples often require increased data collection time to acquire sufficient signal for peak detection and phase identification.

8.12.2.2 The minimum sample quantity required for XRD will vary between geological materials.

8.12.3 *In Situ XRD Pattern Collection*—In certain types of evidence, geological materials are present in trace amounts, either as intact fragments or as a collection of particles, on an object such as a bullet, fabric, or shoe outsole. When removal of the geological material from its substrate could lead to loss or modification of evidence, it is beneficial to create an in situ XRD pattern by mounting the object in or near to the focal surface of the X-ray diffractometer (examples are described in 2, 29-31).

8.12.3.1 Acquiring in situ XRD patterns is non-consumptive, leaving the sample available for other analytical methods (for example, chemical analysis, DNA extractions; or minimally manipulated bullet for toolmark examination).

8.12.3.2 When a clean area of the substrate is present and compatible with the instrument geometry, collection of a background diffraction pattern from an area of the substrate without the geological material can enable identification of possible diffraction peaks originating from the interaction of the substrate with the X-ray beam. For example, kaolinite is added in the production of many rubber materials (tires, footwear), and when identified in the substrate should be considered in the in situ XRD analysis of geological material adhering to such items.

8.12.3.3 If heterogeneous sample deposition is suspected, collection of multiple diffraction patterns from the in situ sample can capture the intra-sample variability.

8.12.3.4 Diffraction peak position shifts due to the irregular height of the in situ sample should be taken into consideration (Sample displacement, see 10.7.3).

8.12.3.5 Displacement artifacts of in situ samples can be mitigated with the use of parallel beam optics (see 6.1.4).

8.12.3.6 To account for possible peak displacement with in situ XRD analyses, samples can be reanalyzed after the addition of a crystalline standard, known to be absent from the samples, to allow for a displacement correction.

NOTE 6—These standards should amount to less than ~10 weight % applied by uniformly sprinkling over the sample(s). Example standards include zincite (zinc oxide), halite (sodium chloride), diamond, corundum,

or another crystalline substance that is clearly absent in the XRD scan made prior to its addition.

8.12.4 μXRD —Standard powder XRD methods can be adapted for the analysis of small samples (micro-XRD) (see 2, 29-32)

8.12.4.1 Better results for μXRD require a focused, collimated X-ray beam (see 6.1.4).

8.12.4.2 Use of an adjustable XYZ tri-axial goniometer head (6.1.6) can assist mitigating focal plane offset, and the presence of fewer diffraction domains in samples of limited quantity.

8.12.4.3 Sample preparations for μXRD include: miniaturized sample holders, enclosure within a glass capillary, or attachment to a filament extended to the focal plane.

8.12.4.4 Use of a sample rotational mechanism, either a rotational stage or a spinning needle, will improve detection of diffraction peaks (33).

8.12.4.5 μXRD methods can be applied to individual particles or to powders.

9. XRD Data Acquisition

9.1 Range of 2θ Angles or d -Spacing:

9.1.1 *Soils, Sediments, and Rocks*—The important diffraction peaks for soil, sediment and rocks typically occur for a d -spacing range of 2.9 nm to 0.13 nm; 3° to 70° 2θ for Cu-K α X-rays, 29 Å to 1.3 Å (28).

NOTE 7—The lowest angles of 2θ (largest d -spacings) in this range are useful for the analysis of clay minerals, particularly mixed-layer clay minerals. Some diffractometers will not permit scanning below 5° 2θ .

9.1.2 *Cement*—The important diffraction peaks of cement typically occur between 0.763 nm to 0.175 nm; 11.5° to 52.2° 2θ for Cu-K α X-rays, 7.63 Å to 1.75 Å (see Test Method C1365).

9.2 *Factors Affecting Diffraction Intensity*—Several factors affect the intensity of resultant diffraction peaks, including:

9.2.1 Intensity of incident X-rays on the sample is affected by the X-ray tube's age and tuning, the type of the X-ray tube, and the focusing slits used.

NOTE 8—Use of high energy X-ray sources at synchrotron facilities allows the XRD-based detection of low abundance and poorly crystalline materials in forensic geological materials (34), but these facilities are not easily accessible to most forensic examiners.

9.2.2 Scan rate of the diffractometer (typically expressed in $^\circ$ 2θ per second, or count time per step increment).

9.2.3 Sensitivity of the X-ray detector.

9.2.4 Quantity and crystallinity of the sample.

NOTE 9—Certain minerals inherently produce strong diffraction peaks (for example, quartz). For samples with very little material, poor crystallinity, or with very small crystal sizes, use of slower scan rates could enable detection of pertinent XRD peaks.

9.3 XRD Data Quality Assurance Practices:

9.3.1 XRD methods should be validated prior to use in casework.

NOTE 10—ISO/IEC 17025-2017 provides guidance on criteria to be evaluated during method validation.

9.3.2 Periodically, an XRD pattern should be collected from a standard reference material (for example, silicon, corundum,

or microcrystalline quartz; see 6.4.1), under specified conditions; a reasonable frequency for this check is every month of use, when an instrument is serviced, and when the instrument performance is suspect.

NOTE 11—Regular analysis of a standard reference material can confirm the proper alignment of the instrument by observation of the correct diffraction peak position (typically an offset $< 0.05^\circ 2\theta$), sufficient peak intensity, and sufficient resolution of peaks. A significant decline in peak intensity could indicate aging of the X-ray source.

10. Interpretation of XRD Data for Mineral/Phase Identification

10.1 XRD patterns can be used to identify a single phase or the major crystalline materials in a poly-phase sample. Quantification of the components of a mixture, while possible, is rarely used on casework samples (see 10.6).

10.2 *Peak Detection*—Diffraction peak positions should be identified and, optionally, the background can be subtracted from the diffraction pattern.

NOTE 12—In general, the relative peak sizes should correspond to the reference diffraction data, but factors like preferred orientation (see 10.7.2) and the overlap of peaks from other crystalline components can cause the relative peak sizes in the observed pattern to deviate from the reference patterns. In addition, preferred orientation artifacts can be present in the reference patterns.

10.2.1 It is recommended that users rely on default procedures within software packages for peak detection, baseline subtraction, and peak position determination for consistency between samples.

NOTE 13—If a possible peak is near the detection threshold, the analyst can collect a new diffraction pattern with a slower scan speed/longer count time to improve the signal to noise ratio.

10.2.1.1 Peak detection thresholds should meet or exceed three times signal to noise.

10.2.2 Clay minerals typically have small crystallite (diffraction domain) sizes that result in broad XRD peaks (35); these broad XRD peaks can be undetected by default software peak detection settings and can require manual peak identification.

10.3 *Identification of Crystalline Components Without Aid of Software*—Use of XRD analysis software is preferred (see 10.4), but methods for the identification of minerals without the aid of analysis software are briefly described here.

10.3.1 *Determination of Diffraction Peak Positions and Relative Intensities:*

10.3.1.1 After conversion of peak positions from $^\circ 2\theta$ to d -spacing using Bragg's Law, the peak positions / d -spacings and relative peak intensities are compared to published reference tables (see 6.5).

10.3.1.2 Tables of diffraction peaks to aid in mineral identification are typically ordered based on the d -spacing of the most intense peak (Hanawalt Tables) or listing each entry's top four most intense peaks (Fink Tables). These two approaches are often applied together.

10.3.2 *Manual Identification of the Minerals by XRD:*

10.3.2.1 A tentative identification of the mineral causing the largest peak is assessed by consulting reference data, with

confirmation that, at minimum, all peaks with intensities greater than 30 % of the highest peak are present.

10.3.2.2 Any additional peaks caused by this mineral present in the diffraction pattern should be noted.

10.3.2.3 When considering multiple candidate minerals, take into consideration prior knowledge of the mineralogy derived from other methods if available.

10.3.2.4 The most intense peak that is not attributed to the first identified mineral is assessed with a similar approach to that used for the largest peak, but some of the peaks could be obscured by the XRD peaks of the previously identified mineral.

10.3.2.5 Attribution of all remaining diffraction peaks proceeds systematically.

10.4 *Identification of Crystalline Components Using Automated Search and Peak Match Software:*

10.4.1 The phase identification software will provide a ranked-list of the best matches to the diffraction peaks in a sample, based on their reference diffraction data.

10.4.2 These tentative identifications should be verified by a combination of visual alignment with reference diffraction patterns, prior knowledge of the sample (for example, elemental composition information, polarized light microscopy results), and include explanations for omissions or overlap of the diffraction peaks.

10.4.3 Following the tentative identification of minerals, the relative peak sizes (peak area counts, ideally) of the candidate minerals should be assessed to ensure that all major peaks (that is, $>30\%$ of the maximum peak for the mineral) are either present or obscured by the peak of another mineral.

10.4.4 Many software systems enable differential diffraction analysis, which permits subtraction of XRD peaks from provisionally identified minerals to facilitate identification of the remaining minerals generating the lower intensity peaks.

10.5 *Criteria for Phase Identification*—There are no universally accepted criteria for phase identification by powder XRD, but the following two criteria are suggested:

10.5.1 All of the peaks in the reference diffraction pattern greater than 30 % of the maximum peak size should be present.

10.5.2 At least five diffraction peaks, for phases that have at least five characteristic diffraction lines, should be observed (36) (see Test Method C1365 and Practice D934).⁷

NOTE 14—In mixtures, some phases exhibit overlapping peaks; the relative intensities of these peaks should be evaluated prior to their assignment to a specific phase. These criteria can be relaxed by augmentation from independent analytical data, for example, by microscopy, selective dissolution, or clay solvation.

10.5.3 *Provisional Phase Identification*—If fewer than five peaks (36) (see Test Method C1365 and Practice D934) are detected, without other supporting analytical data, the phase identification should be noted as *provisional*.

NOTE 15—For consistency within this guide, the term “provisional” is

⁷ Five diffraction peaks are insufficient to determine unit cell dimensions of crystals of low symmetry, like those in the triclinic crystal system (37). However, in this guide, XRD data are not being used to determine crystallographic parameters, but rather the diffraction peaks and relative intensities are being applied as characteristic markers of the crystal, irrespective of the crystal symmetry.

used to denote an uncertain phase identification, but individual laboratories may use alternative language for similar conditions (for example, uncertain, tentative, preliminary, unverified).

10.5.3.1 A provisional phase identification can be probative in many cases.

10.5.3.2 The phase identification can be confirmed by the concentration of the phase (see 8.11) and reanalysis by XRD to enable enhancement of the diffraction peaks or by the application of alternative methods like optical microscopy, energy dispersive X-ray spectrometry, or Raman spectroscopy.

10.5.3.3 Confirmation can also be made by the disappearance of a peak upon selective dissolution, for example, removal of halite with water or calcite with acids.

10.6 *Quantification of Major Crystalline Components:*

10.6.1 Quantification of minerals within geological materials by XRD is performed infrequently because (1) geological materials in casework often have the potential for particle size bias (for example, differential attachment or loss between contact materials and soil or sediment) that can change the relative proportion of minerals between the evidence and its source, (2) the limited quantity of evidentiary material can prevent the optimal sample preparation necessary for proper quantification (30) and may not be representative of the modal abundance of its source.

10.6.2 Quantitative XRD methods are often performed on powders to which an internal standard material is added to improve quantitation and verify instrument alignment and sample position (see 6.4.3).

10.6.3 When using quantitative XRD analysis for comparisons of geological materials, collection of diffraction patterns from multiple sub-samples (see 8.2) is highly recommended to better represent intra-sample variation in modal abundance, to constrain the uncertainties in the quantitative results.

10.6.4 There are three common methods for the quantitative analysis of XRD patterns (17).

10.6.4.1 The reference intensity ratio method, which compares the peak area of a reference material to those in the pattern;

10.6.4.2 The Rietveld method, which simulates diffraction patterns with crystallographic information and attempts to minimize the difference between the synthetic and real diffraction patterns; and

10.6.4.3 A pattern fitting method, in which digital patterns of reference materials are combined to simulate the observed diffraction pattern (4).

10.6.5 Examples of applications of quantitative phase analysis by XRD applied to analysis of geological materials in casework are found in (38, 39).

10.6.6 Quantification methods for cement by XRD are described in Test Method C1365.

10.7 *Limitations to Consider in the Interpretations of XRD Patterns for Mineral Identifications:*

10.7.1 *Reliability of XRD and Software for Phase Identification:*

10.7.1.1 When a single crystalline material is analyzed by powder XRD, identification is generally unproblematic when using modern search-match software (36).

NOTE 16—The results of select inter-laboratory studies on the accuracy of phase identification in multi-phase mixtures by XRD are summarized in Appendix X1.

10.7.1.2 Many mineral structures permit elemental substitutions (solid solution) that can have minimal effect on the crystal structure. Thus, an absolute mineral species identification by XRD alone for these phases could be impossible, but categorization to a class of minerals with similar structures could be appropriate. For example, with XRD data alone, the interpretation could be a trioctahedral mica, but the specific mica could be indeterminate (for example, biotite, or mineral with similar structure).

10.7.1.3 XRD can differentiate polymorphs (minerals of the same composition with distinct crystal structures, for instance, quartz and cristobalite are both silicon oxides) whereas elemental analysis techniques such as SEM-EDS cannot. Alternatively, independent observations (for example, polarized light microscopy, scanning electron microscopy-energy dispersive spectroscopy, Raman spectroscopy) can provide the needed supplemental information to definitively identify which of several minerals with similar lattice configurations (isomorphs) is present in the sample.

10.7.2 *Preferential Orientation Artifacts*—Introduction of powders containing crystals with one or more dominant crystal growth or cleavage planes into a sample holder will often lead to preferential alignment of the dominant crystal face with the XRD focal plane. The result of biased orientation is that crystallographic planes that are preferentially aligned parallel to the diffractometer focal plane have enhanced diffraction intensity relative to the XRD peaks corresponding to other crystallographic planes (5).

10.7.3 *Displacement (Parafocusing Violation)*—If the sample powder is not aligned at the proper height, the peaks in the XRD pattern will be systematically shifted to higher or lower 2θ for samples that are higher or lower than the focal surface of the instrument, but the relative peak heights and positions are largely preserved such that interpretation of mildly displaced samples is often possible (see Fig. 1).

NOTE 17—Schreiner (40) states that displacement was the largest source of both systematic and random error on diffraction peak position.

10.7.3.1 An evidentiary sample of limited quantity failing to fill the sample holder, leaving crystals below the focus plane, could show displacement artifacts.

10.7.3.2 Use of a low background sample holder is preferable if a sample is insufficient to fill its sample holder. Scant samples placed unground on a low background sample holder can extend above the instrument focal plane and show peak displacement artifacts.

10.7.3.3 Minor displacements can be documented and corrected by the offset of peaks from strong diffractors, such as quartz, that are known to be present in the sample. Alternatively, the reanalysis with the addition of an internal standard can be used (see 6.4.3 and 8.9).

10.7.3.4 Displacement artifacts should be expected for in situ XRD analyses (see 8.12.3).

10.7.3.5 Displacement artifacts can be mitigated with the use of parallel beam optics (2).

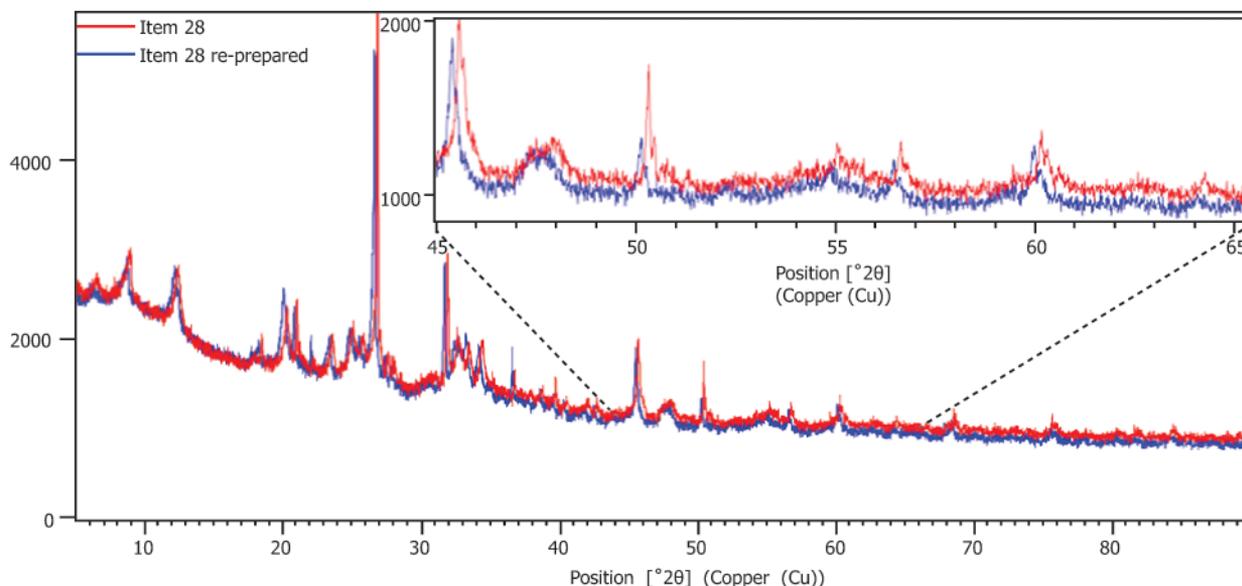


FIG. 1 Example of a Peak Shift Observed in the XRD Pattern Due to the Slightly Elevated Height of the Sample Holder for the Curve in Red. The Same Powder was Re-analyzed with the Sample at the Correct Height (Blue Curve) and Peak Positions then Aligned with the Minerals in the Sample (Figure provided by Maureen Bottrell.)

10.7.4 *Limits of Detection*—It is not possible to define universal limits-of-detection by powder XRD analysis because this will vary among samples and with instrument configuration.

10.7.4.1 Detection of low proportion crystalline components of mixtures is more likely when the mixture contains fewer components due to the presence of fewer potentially overlapping diffraction peaks (28).

10.7.4.2 Components that are poorly crystalline will be more difficult to detect.

10.7.4.3 The detection limits for a component can be constrained by collecting XRD patterns on synthetic mixtures containing sequential dilutions of that component within a matched matrix (36).

10.7.4.4 Limits of detection seldom are below 1 weight % (41), but this will vary greatly for different phases and different mixtures.

10.7.4.5 Estimates of the lowest percentage identifiable among common clay-sized minerals are listed in Table 12 of Ref (14) and range from <1 % to 10 %.

10.7.4.6 Laboratory-based XRD systems are often not sensitive enough to detect low abundance minerals that are otherwise evident in visual/microscopical analysis, but in some cases, low abundance minerals can provide probative value; detection of low abundance phases by XRD analysis can be facilitated by their concentration prior to analysis (see 8.11). High energy synchrotron X-ray sources can provide greater sensitivity and resolution than the laboratory-based XRD systems to better identify the minute amounts of poorly crystalline mineral components in the particle (Note 8).

11. Interpretation of XRD Data in Reports of Analysis of Geological Material

11.1 Reports of analysis of evidentiary geological materials typically address *identification* of material, analysis to restrict

the possible geographic source area (*provenance*), and *comparison* of two or more materials to decide if a common source is possible. Powder XRD of any portion of a sample of geological evidence can be included in a report to aid in these three goals. Several examples of identification of minerals in evidentiary soils by XRD analysis are presented in Fitzpatrick et al., 2017 (38).

11.2 Considerations Specific to the Type of Geological Material

11.2.1 *Soils*—Soil or unconsolidated sediment evidence, for example, soil recovered from a vehicle, footwear, or garment, is often subjected to biases due to selective transfer and persistence (38, 42).

11.2.1.1 Because different minerals within a soil have different size distributions, particle shape distributions, and surface chemistry, it is possible to observe variations in the relative abundance of minerals in a questioned soil compared to its putative source.

11.2.1.2 Transfer and persistence bias can be partially mitigated by comparison of similar size fractions.

11.2.1.3 The examiner should acknowledge that soil containing similar minerals to those identified by XRD can occur in alternate locations and soils with similar mineralogy can have a large spatial extent.

11.2.1.4 Soil on items of evidence can have contributions from more than one source, reflecting the presence of soil particles on vehicles, digging tools, clothing or footwear prior to the event under consideration (that is, the suspected criminal act, see Fig. 2); careful visual/microscopical analysis prior to XRD could allow segregation of the contributing components.

11.2.1.5 Minor mineral components of a soil, detectable by other analytical techniques, can go undetected by XRD unless they are physically concentrated prior to XRD analysis.

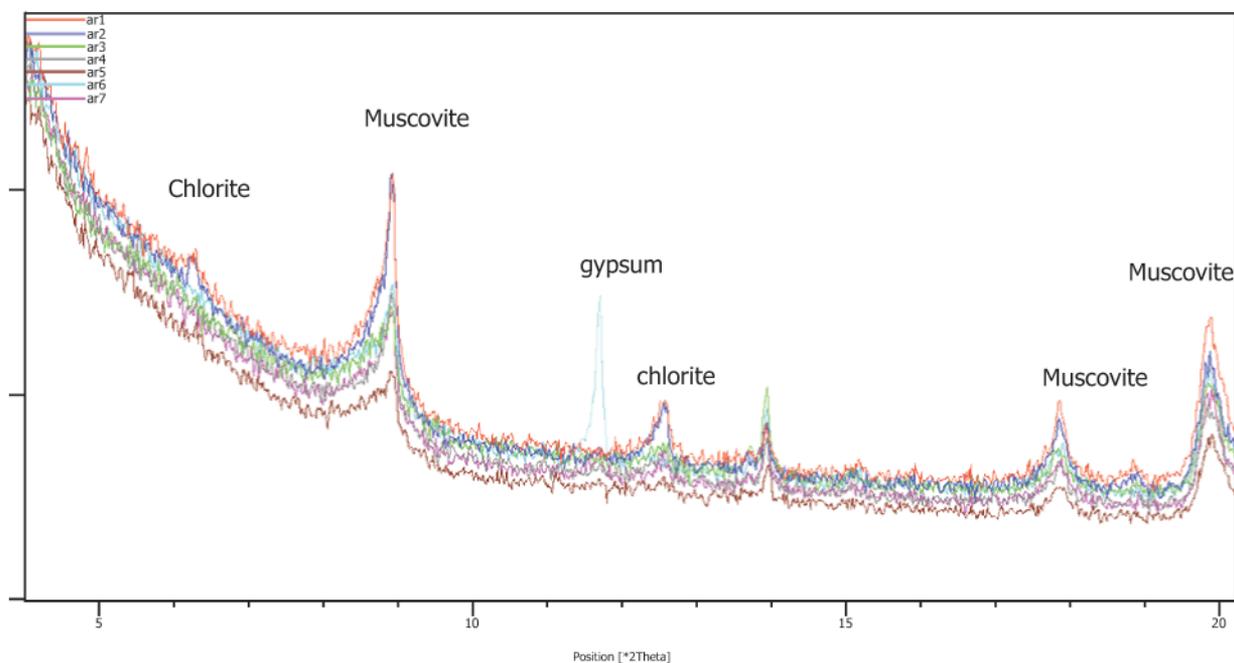


FIG. 2 An Example of an Explainable Difference Due to the Inheritance of Minerals from the Previous Environmental History of Footwear Suspected to be Associated with a Criminal Act. Samples ar1, ar2, and ar3 are from the Known Location; Samples ar4, ar5, ar6, and ar7 are from the Questioned Item of Footwear. Note the Presence of Gypsum in Sample ar6 (Light Blue) Could Suggest an Exclusionary Difference. However, the Suspect in This Case Worked as a Builder Whose Main Work Was the Installation of Plasterboard Walls Containing Gypsum. Careful Analysis of the Layering of Materials on Their Boots Showed Gypsum-rich Coatings Against the Sole of the Boots (Sample ar6), When the Soil Layers Above (the More Recent Deposits) are Without Detectable Gypsum (Figure provided by Alastair Ruffell.)

11.2.1.6 When conducting a comparison by any combination of methods, the examiner should consider how well the known exemplars represent the full range of variation within the crime scene or alternative location.

11.2.2 *Rocks*—The examiner should acknowledge that rocks containing similar minerals to those identified by XRD can occur in alternate locations and that bedrock units with similar mineralogy often have large spatial extents.

11.2.3 *Building Materials*—Building materials, like bricks or concrete blocks, are often produced in large batches that could share common characteristics.

11.2.3.1 It is not usually possible to know or predict the abundance or distribution pattern of a batch of building materials produced with the same characteristics, including characteristics observable by XRD.

11.2.3.2 In materials with greater compositional and morphological variability (for example, bricks), a lower proportion of items will be indistinguishable than materials like concrete blocks.

11.3 *Identification*—XRD analysis can be used to identify a material as a geological material or as a specific crystalline phase or combination of phases.

11.3.1 In some reports of analysis, the interpretation can consist entirely of identification of one or more phases in geological material (for example, analysis of debris on purportedly ricocheted bullets, geological debris from stomach or lung contents, or identification of lye [sodium hydroxide] used in body disposal).

11.4 *Provenance*—XRD provides a means of mineral identification that can be used, along with other observations, to aid geographic attribution of a geological material (for example, see 31, 34, 43, 44).

11.4.1 XRD-derived mineral identifications can be compared to reference data and maps in a provenance analysis.

11.4.2 XRD-derived identification of anthropogenic particles can be compared to data on relevant human activities and land use.

11.4.3 The interpretation of XRD-derived mineral identification in a provenance report is highly case-specific and beyond the scope of this guide.

11.5 *XRD in Comparisons of Evidentiary Geological Material*:

11.5.1 *Purpose of A Comparison*—The goal of comparison of geological evidence is to decide if two samples could share a common source based on having similar properties or if they have exclusionary differences, allowing for the interpretation that they were derived from different sources.

11.5.1.1 XRD is one of numerous analytical techniques applied in comparison of geological materials; analysis by orthogonal methods strengthens comparisons (for example, palynology, color, morphology, microscopy), but when XRD alone clearly demonstrates distinct component phases among the samples, these results can provide a sufficient (exclusionary) difference such that additional sample analysis methods are not required.

11.5.1.2 An exclusionary difference detectable by XRD would be the presence of a phase (whether identified or not) in high relative abundance in one sample and absent in the other, without a logical explanation of the differences (see 11.5.3.4).

11.5.1.3 The identification of rare minerals or anthropogenic particles by XRD increases the probative value of the evidence in a comparison. When available, mineral occurrence data can be used to substantiate the rarity of a mineral, in general, or specifically within an area of interest (28, 45).

11.5.2 *Comparison of Visually Similar Diffraction Patterns*—Two diffraction patterns with the same peak positions of similar relative intensities (see Fig. 3) indicate that the two samples of geological material consist of the same crystalline components in similar relative abundance above the limit of detection of the method.

11.5.2.1 Identification or provisional identification of the component phases is recommended.

11.5.2.2 These results are consistent with the possibility that the two samples could have been derived from the same source, but there can be other geological materials that share similar modal abundance of crystalline components.

11.5.2.3 There can be exclusionary differences that are not detectable by XRD (morphology, biological components, non-crystalline particles, or crystalline phases present below the XRD detection limit), therefore orthogonal methods (for example, palynology, color, morphology, microscopy, elemental analysis) should be used to detect possible exclusionary differences.

11.5.3 *Comparison of Moderately Different Diffraction Patterns*—Moderate differences can exist between the diffraction patterns of geological material that originated from the same source.

11.5.3.1 These moderate differences could include variation in the modal abundance of crystalline materials or the omission or addition of low abundance phases.

11.5.3.2 Size fractionation of the sample and re-analysis could ameliorate these moderate modal differences.

11.5.3.3 If these moderate differences cannot be explained, then these are exclusionary differences, and the soils are likely derived from different sources.

11.5.3.4 Examples of *explainable* sources of variation include bias derived in the transfer and persistence of particles

(38, 42); contamination/alteration of one of the samples (for example, by fire, stomach acid, mixing); sample size limitations; or the representativeness of the known exemplars (one example of explainable difference is shown in Fig. 2).

11.5.3.5 A justification for the observed differences should be documented if the moderate differences among diffraction patterns are not exclusionary.

11.5.3.6 Additional orthogonal methods (for example, palynology, color, morphology, microscopy) should be used to further test the possible common source of the two items.

11.5.4 *Comparison of Substantially Different Diffraction Patterns*—Diffraction patterns of geological materials that exhibit substantial differences with respect to the major phases identified, particularly the presence of crystalline components substantially above the limits of detection in only one of the comparison samples, are considered to have exclusionary differences and indicate that these geological materials were likely derived from different sources.

11.5.4.1 An example of two substantially different diffraction patterns is shown in Fig. 4.

11.5.4.2 A decision of whether differences between diffraction patterns constitute exclusionary differences is primarily a matter of expert judgment.

12. Documentation

12.1 Documentation of examination of geological materials by XRD should include:

12.1.1 Sample preparation procedures (8);

12.1.2 Instrumental conditions used (9); and

12.1.3 Information supporting the interpretations of phase identification, provisional phase identification (10), or comparisons (11) (Practice E620).

12.2 Documentation should allow a second analyst to understand and evaluate all the work performed, and independently interpret the data.

12.3 Refer to Practices E1492 and E620 for further guidance.

13. Keywords

13.1 cement; concrete; forensic; geology; soils minerals; X-Ray diffraction

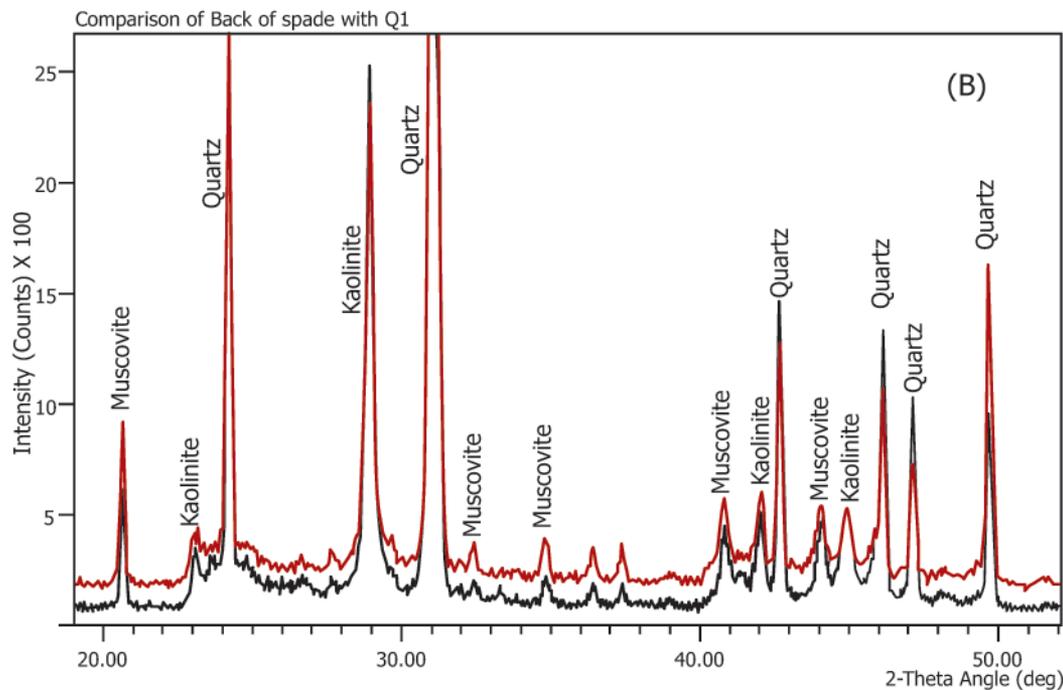
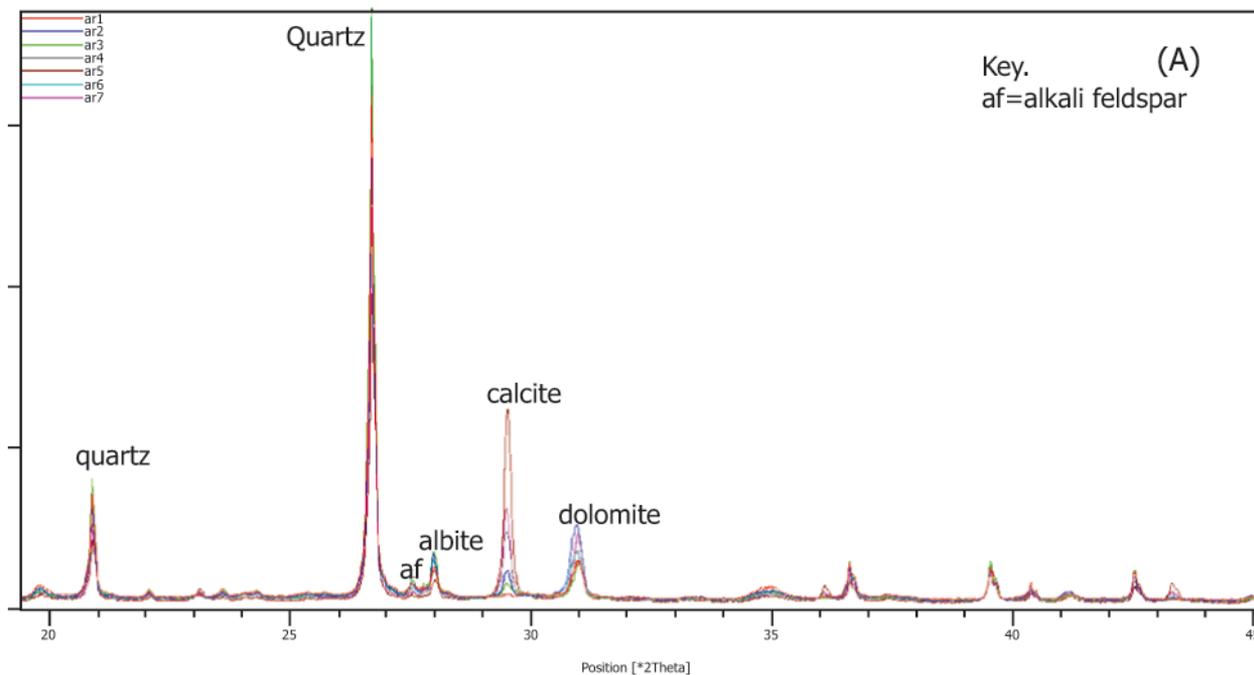


FIG. 3 Examples of Comparison of Geological Materials by XRD patterns Where No Exclusionary Differences Were Found; Therefore a Common Source of Samples Cannot be Excluded, and Thus Further Analysis is Recommended by Orthogonal Methods (For Example, Polarized Light Microscopy of Coarse Fraction Grains, SEM-EDS, Palynology). (A) Samples ar1, ar2, and ar3 are from the Questioned Item; Samples ar4, ar5, ar6, and ar7 are from the Known Samples (in This Case, the Crime Scene). The Peak Size, and Thus Modal Abundance Varies Among the Samples, but the Same Peaks and Minerals are Detected in All Samples. $\text{CuK}\alpha$ X-rays Were Used to Generate the Diffraction Patterns. (Figure provided by Alastair Ruffell). (B) XRD Patterns from a Questioned Soil Sample Collected from the Back of a Shovel (Black Trace) and a Known Soil Sample Collected from a Quarry (Red Trace), Sieved to < 0.4 mm Were Compared and are Quite Similar, Consistent With Being Derived from the Same Location. XRD Patterns Were Recorded With a Philips PW1800 Microprocessor-Controlled Diffractometer Using $\text{CoK}\alpha$ X-rays, Variable Divergence Slit, and Graphite Monochromators. Further Details of This Comparison of Geological Materials, Including Case Circumstances and Other Soil Properties for Comparison, are Described in Ref (44)

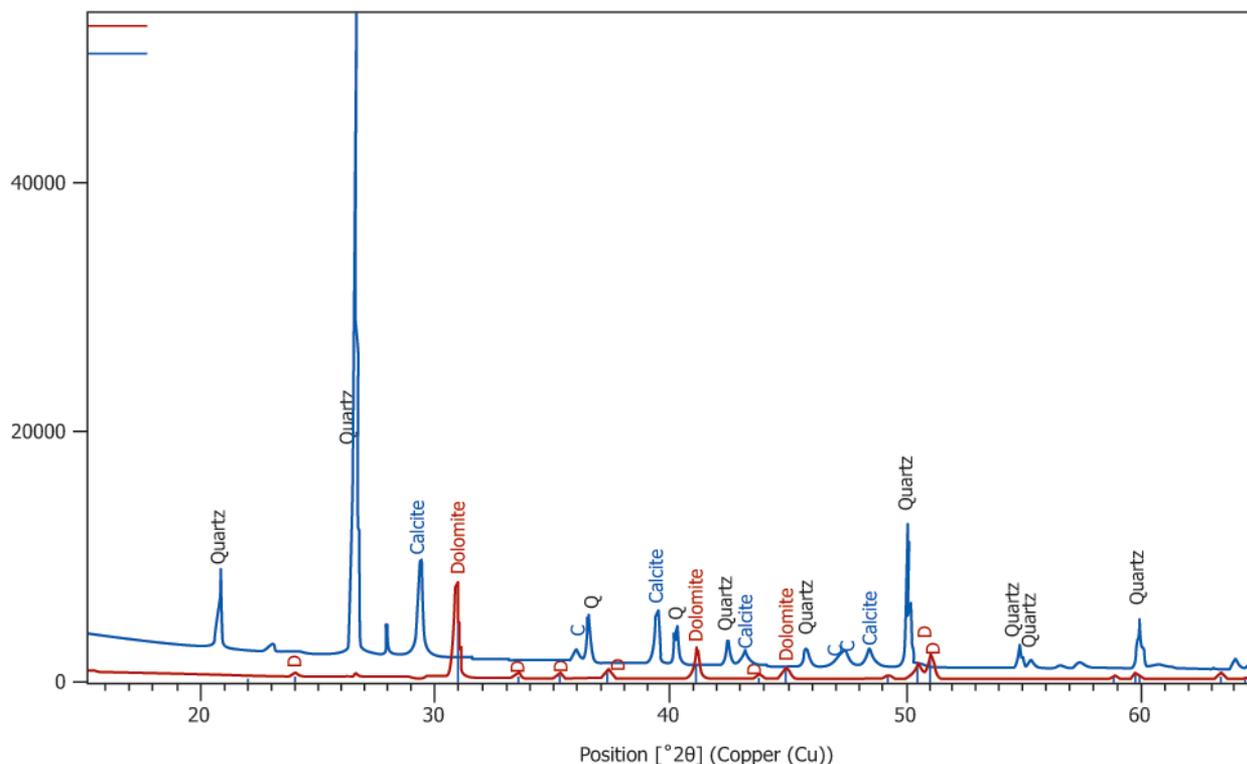


FIG. 4 An Example of Two Diffraction Patterns With Distinct Minerals in Each. The Red Diffraction Pattern Contains Peaks Derived from Dolomite ($\text{CaMg}(\text{CO}_3)_2$, D) and The Blue Diffraction Pattern Contains Peaks Derived from Calcite (CaCO_3 , C) and Quartz (SiO_2 , Q). These Diffraction Patterns Have Been Smoothed for Clarity in Print. These Two Diffraction Patterns Have Exclusionary Differences

APPENDIX

(Nonmandatory Information)

X1. SUMMARY OF SELECT INTER-LABORATORY STUDIES USING XRD FOR PHASE IDENTIFICATION WITHIN MIXTURES

X1.1 The suitability of modern powder XRD software for phase identification within mixtures was assessed in a search-match round robin study including 25 laboratories and 10 software systems (46) and in a forensically-focused validation study by Ekhardt et al. (36). Both studies demonstrated that modern software is suitable for phase identification within mixtures by powder XRD, but that the experience of the analyst improved the ability to detect peaks and thus identify phases present within mixtures. The most frequent error was failure to identify a phase, whereas misidentification was rare. In one experiment in Ref (36), phases were always correctly identified when the 5 peak detection threshold was met.

X1.2 Modern inter-laboratory comparison studies (the Reynolds' Cup; see Refs (47) and (48)) focus more on the accuracy of quantification of quite complex mixtures of phases in addition to the identification of phases. Most participants in these studies use combinations of analytical approaches and therefore the results of these inter-laboratory studies are not directly relevant to the use of XRD in isolation. In most cases, the analyst has some general or highly specific information about the material being subjected to powder XRD, which greatly limits the possible crystal identification.

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