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An American National Standard

# Standard Guide for
# Forensic Analysis of Geological Materials by Powder X-Ray Diffraction[1]

This standard is issued under the fixed designation E3294; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ($\varepsilon$) indicates an editorial change since the last revision or reapproval.

## 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.*

## 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

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:*[3]

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, $\lambda$ is the wavelength of the X-ray, $d$ is the crystal plane separation, also known as *d*-spacing, and $\theta$ 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 arrangement that can be outwardly expressed by plane faces (adapted from Ref (**1**)).[4]

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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 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. Guidance for the analysis of forensic geological materials can be found in Refs (**2-4**).

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 $2\theta$ 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 ($\lambda$) 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 (**5**).

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 (**6**). Adaptations to achieve parallel beam optics include:

6.1.4.1 Göbel mirrors,

6.1.4.2 Polycapillary collimators (**7**),

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 Mill[5] (**9**), or other mills;

6.2.3 Filtration apparatus (**10**).

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 $2\theta$ (for a specified X-ray wavelength); tables of diffraction peaks listing the degrees $2\theta$ 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) (**11**).

6.5.1.2 NIST Inorganic Crystal Structure Database (ICSD) (**12**).

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

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[5] 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 (**8**) 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.

6.5.2.1 The RRUFF Project (**13**) integrating the American Mineralogist Crystal Structure Database.

6.5.2.2 The Crystallography Open Database or COD (**14**) 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 (**15**).

6.5.3.2 Common soil minerals in Table 4-1 of Ref (**16**).

6.5.3.3 Common minerals in clay-sized material (**17**).

6.5.3.4 Clay mineral-specific diffraction data (**16, 18-21**).

6.5.3.5 Cement- and concrete-specific data (Ref (**22**), 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 (**23**)) and no cost software packages (for example, CrystalSleuth (**13**), ReX (**24**), or GSAS II (**25**); see review in Ref (**26**)).

## 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 (**27**).

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 (**28**), 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 (**16, 29**).

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 (**2**).

8.5 *Sample Particle Size*—An optimal sample for powder XRD data acquisition consists of fine particles, typically less than 10-20 µm diameter (**8, 16, 29**).

8.5.1 *Reduction of Particle Size*—Samples of limited quantity are often ground using a mortar and pestle (**16, 29**).

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 (**29, 10**).

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 (**8**) 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 $2\theta$ 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 (**9, 10, 16, 21**).

8.7.3 Use of a side-loading sample holder can minimize these effects (**9, 10**).

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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 (**19**, **21**).

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 (**10**, **18**, **19**, **21**, **30**; section 7A1 in Ref (**20**); Table 4.2 in Ref (**16**)). Common treatments include:

8.8.4.1 Saturation with $Mg^{2+}$, $K^+$, 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 (° 2*θ*). 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 (**31**).

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 (**29**, **28**, **32**).

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 (**29**).

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.

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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 (9).

8.12.1.5 Use of parallel beam optics can mitigate the artifacts of an uneven sample surface (6).

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 6, 32-34).

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 6, 32-35)

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 (36).

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-Kα X-rays, 29 Å to 1.3 Å (31).

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-Kα 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 (37), but these facilities are not easily accessible to most forensic examiners.

9.2.2 Scan rate of the diffractometer (typically expressed in ° 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.