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Environmental Consequences of Nanotechnologies

Characterization of Nanosized Crystallites Using X-ray Diffraction (XRD)

Standard Operating Procedure Series: Characterization (C)

E. Rae Reed-Gore, Robert D. Moser, and Charles A. Weiss, Jr.

July 2018



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Standard Operating Procedure Series: Characterization (C)

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Abstract

Characterization of nanoparticle phase composition is an important attribute that cannot be determined by using many different chemically based analysis methods. X-ray diffraction (XRD) is a ubiquitous technique that can be used to determine the phase composition of materials, quantify phase proportions in multi-phase materials, as well as to estimate crystallite size. In this Scientific Operating Procedure, the use of XRD methods to analyze nanomaterials and products containing nanomaterials is discussed. Specialized sample preparation procedures that are used to produce test specimens for analysis are also discussed. Analysis procedures to identify phase composition are presented along with an introduction to approaches to quantify phase composition and particle size by using various whole pattern fitting routines.

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Preface

This study was conducted under the Environmental Consequences of Nanotechnologies Research Program. The technical monitor was Mr. Alan J. Kennedy.

The work was performed by the Concrete and Materials Branch (CMB) of the Engineering Systems and Materials Division (ESMD), U.S. Army Engineer Research and Development Center-Geotechnical and Structures Laboratory (ERDC-GSL). At the time of publication, Mr. Christopher M. Moore was Chief, CMB; Dr. Gordon W. McMahon was Chief, ESMD; and Dr. Michael K. Sharp was Technical Director for Civil Works Infrastructure. The Deputy Director of ERDC-GSL was Dr. William P. Grogan, and the Director was Mr. Bartley P. Durst.

COL Bryan S. Green was the Commander of ERDC, and Dr. David W. Pittman was the Director.

1 Introduction

The Standard Operating Procedure (SOP) described herein for assessing the properties of nanotechnologies was developed under Task 2: Optimized Scientific Methods of the U.S. Army Engineer Research and Development Center/Environmental Laboratory Environmental Consequences of Nanotechnologies Research Program. The primary goal of this task was to develop robust SOPs for investigating the environmental health and safety (EHS)-related properties of nanotechnologies, including nanomaterials and products incorporating nanomaterials.

X-ray diffractometry is typically used to identify mineralogy in a sample and determine weight percentages of minerals in an unknown sample (Jenkins and Snyder 2012; Langford and Wilson 1978; Weidenthaler 2011; Whittig and Allardice 1986). However, X-ray diffractometry can be used to determine the size of crystallites in a material. This can be a useful tool in determining the size and mineralogy of nanoparticles. This SOP describes how to determine the mineralogy, crystallite size, structural characteristics, and number of nanoparticles in a material by using X-ray diffraction (XRD). First, a quick look at the background or history of XRD analysis, possible pitfalls that are associated with analysis, and available software for analysis is presented. Liquids, gels/ creams, polymers and solids, are only a few of the many types of materials that contain nanoparticles. There are various supplies and apparatus needed to analyze these materials and procedures for sample preparation may vary. Finally, methods for reporting the data obtained are discussed.

2 Scope

This SOP is used to characterize a nanomaterial by means of XRD. The two main properties identified by XRD are (1) the phase composition / mineralogy of the material in question and (2) the determination of crystallite size. Other properties that may be determined are atomic arrangement or crystallographic arrangement of ions in the substance, the shape of the nanoparticle, and the presence of lattice stress or strain. Identification of the nano-sized materials can give insight into the behavior of the substance: for example a carbonate mineral will be more soluble, or a heavy metal could be toxic (Harris et al. 2001; Jenkins and Snyder 2012; Langford and Wilson 1978; Uvarov and Povov 2007; Weidenthaler 2011; Whittig and Allardice 1986; Zhu et al. 1987).

3 Terminology

3.1 Related documents

The following documents are current standards used for characterization of particle size, reporting particle size analysis and terminology used. These documents are used to guide current research and preparation of materials for testing:

- National Institute of Standards and Technology. 2013. *Preparation of nanoscale TiO₂ dispersions in an environmental matrix for ecotoxicological assessment*. Special Publication 1200-5.
<https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.1200-5r1.pdf>
- ASTM International. 2014. *Practice for reporting particle size characterization data*. Designation E1617. West Conshohocken, PA: ASTM International.
- ASTM International. 2014. *Standard guide for size measurement of nanoparticles using atomic force microscopy*. Designation E2859-11. West Conshohocken, PA: ASTM International.
- ASTM International. 2014. *Terminology related to nanotechnology*. Designation E2456. West Conshohocken, PA: ASTM International.

3.2 Acronyms

The following acronyms and initialisms will be used throughout the text:

- SEM – Scanning electron microscopy
- XRD – X-ray diffraction
- ZBP – Zero background plate
- wpf – Whole pattern fitting
- PDF – Powder diffraction files
- SOP—Standard Operating Procedure

4 Materials and Apparatus

4.1 Materials

- Zero background plate (ZBP) (s): Used to hold dispersed nanoparticles for XRD analysis.
- Methanol (reagent grade): Used to clean substrates.
- Sample holder (s): 32-mm internal diameter sample holder with spring pin used to hold zero background plate
- Loose powder sample holder: 32-mm internal diameter sample holder used for loose powder
- Reverse mount stage: Used to hold 32-mm sample holder to loosely pack powder samples
- Small brush: Used to brush off excess powder in reverse mount sample preparation
- Calibration standards: May be used as an internal standard in quantitative mineral analysis (TiO_2 , Al_2O_3)
- Evaporating trays: Used to hold ZBP for ease of transport
- Disposable pipette (s): Used to drop liquid onto ZBP
- System monitor: Si chip used as a known standard before and after every XRD run to ensure proper measurements
- Scissors: Used to cut polymer or fabric to fit into sample holder

4.2 Apparatus

An X-ray diffractometer instrument to perform XRD measurements and collect diffraction patterns – The instrument discussed herein is an X-Pert Pro Multipurpose Powder Diffractometer system that uses standard techniques for phase identification (Panalytical, Inc.). The run conditions included Co-K α radiation and scanning from 2 to 70 $^{\circ}2\theta$ (standard run) with collection of the diffraction patterns, accomplished by using the PC-based Windows version of X-Pert Pro Data Collector. Other XRD instruments can be used for this analysis along with other X-ray sources (e.g., Cu X-ray tube). Instrument-specific considerations for voltage and current settings, sample holders, etc. should be considered if using a different XRD instrument. However, the procedures described herein are generically applicable to multiple instruments.

5 Procedure

Liquids, gels/ creams, polymers and solids, are only a few of the many types of materials that contain nanoparticles. The various supplies and apparatus needed to analyze these materials and procedures for sample preparation vary. The following procedures were used to characterize the nanoparticles:

Evaluate the material to be analyzed:

- Type of material to be analyzed
- Amount of sample available
- Background information to determine scan range (i.e., metallic mineral or nonmetallic mineral)
 - Follow sample Preparation Procedures for Liquids - 5.1.2.1
 - Follow sample Preparation Procedures for Gels or Creams - 5.1.2.2
 - Follow sample Preparation Procedures for Polymer or Fabric Films - 5.1.2.3
 - Follow sample Preparation Procedures for Solids - 5.1.2.5

5.1 Specimen preparation

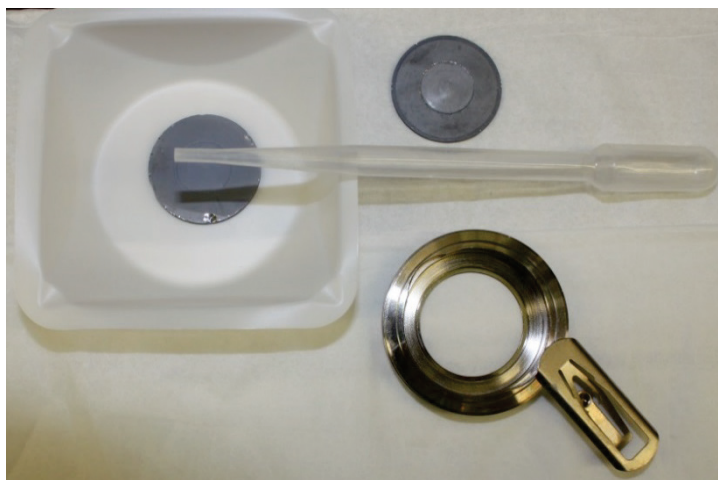
5.1.1 Extraction of nanoparticles for XRD

When a liquid is being prepared for XRD, the concentration of nanoparticles needs to be determined. If the levels in the sample are in the parts-per-millions range, the sample will need to be centrifuged to obtain enough nanoparticles for evaluation. It is important to evaluate the amount of sample received to determine the proper steps to be taken. Creams/gels and other types of material will have a specific way of sample preparation for the type of XRD being used and the amount of material received for analysis. Preparation techniques for polymers/plastics, fabrics, and solids are similar but also depend on the type of machine being used.

5.1.2 Specimen preparation for analysis

5.1.2.1 Liquids

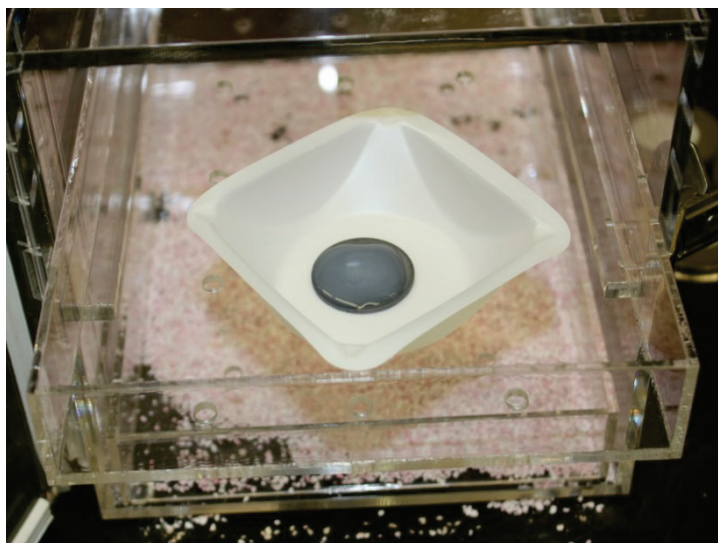
1. Gather equipment needed: ZBP or glass slide, ZBP sample holder, sample boat or petri dish, and plastic pipette.



2. Drop liquid onto ZBP until a meniscus forms and covers most of the plate.



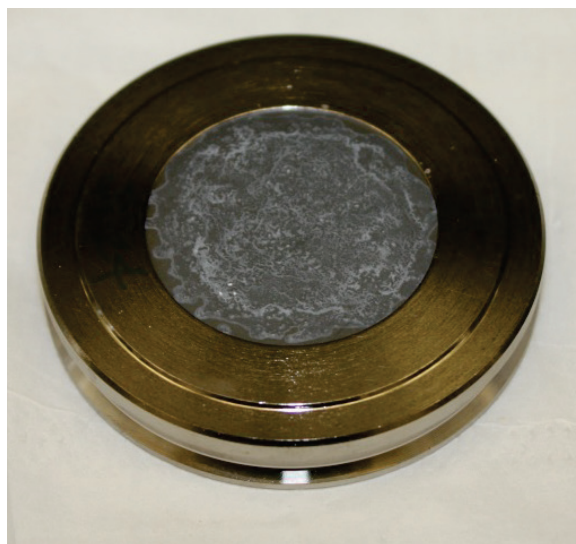
3. Place petri dish into decant box or an oven at no higher than 50°C and allow water to evaporate. (50°C temperature ensures no crystallographic damage will occur to the sample).



4. Repeat steps 2 and 3 until a thin layer of evaporate can be seen on the ZBP.

Note: This sample may be used for scanning electron microscopy (SEM) analysis after the XRD pattern is obtained.

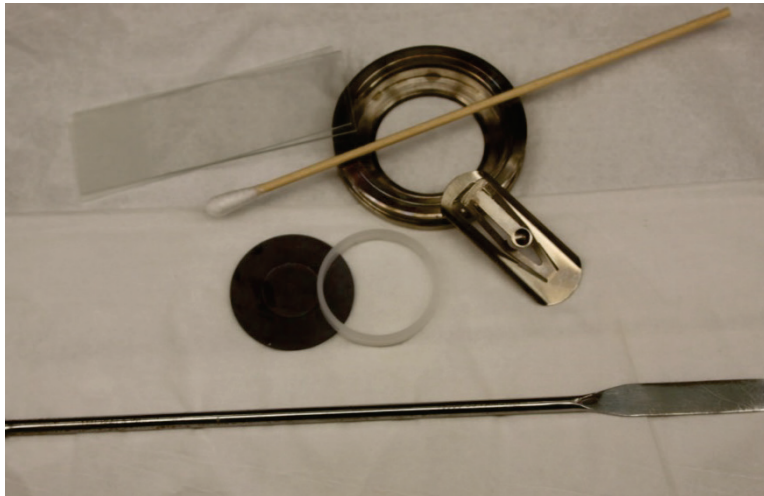
5. After all liquid has evaporated, place the ZBP into the sample holder and place into rack.



6. Proceed to step 5.1.2.6-1

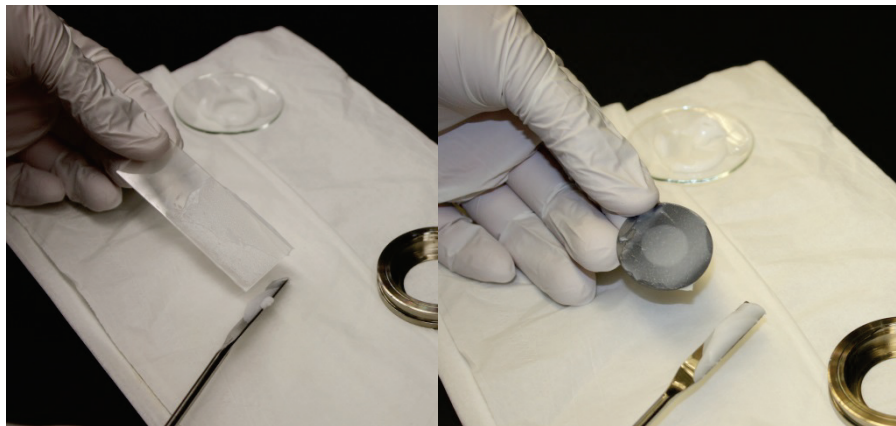
5.1.2.2 Cream or gel

1. Gather equipment needed: ZBP or glass slide, a flat spatula, a cotton swab, a ZBP sample holder, and a plastic spacer.



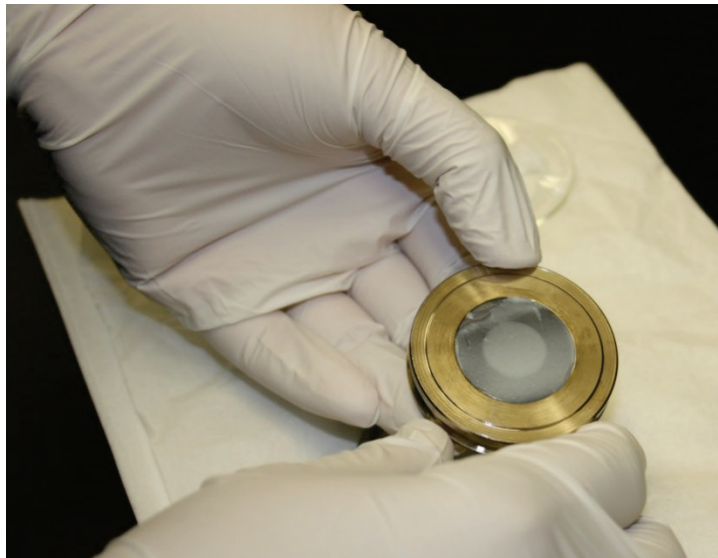
If only a small amount of material is received or the equipment is limited, use steps 2 to 4; if there is more material, go to steps 5 to 7.

2. Apply a thin coat of cream/gel with the spatula; try to maintain a smooth, even height across the glass slide or ZBP.



Note: If the material is too thick or higher than the sample holder, a pattern shift can occur.

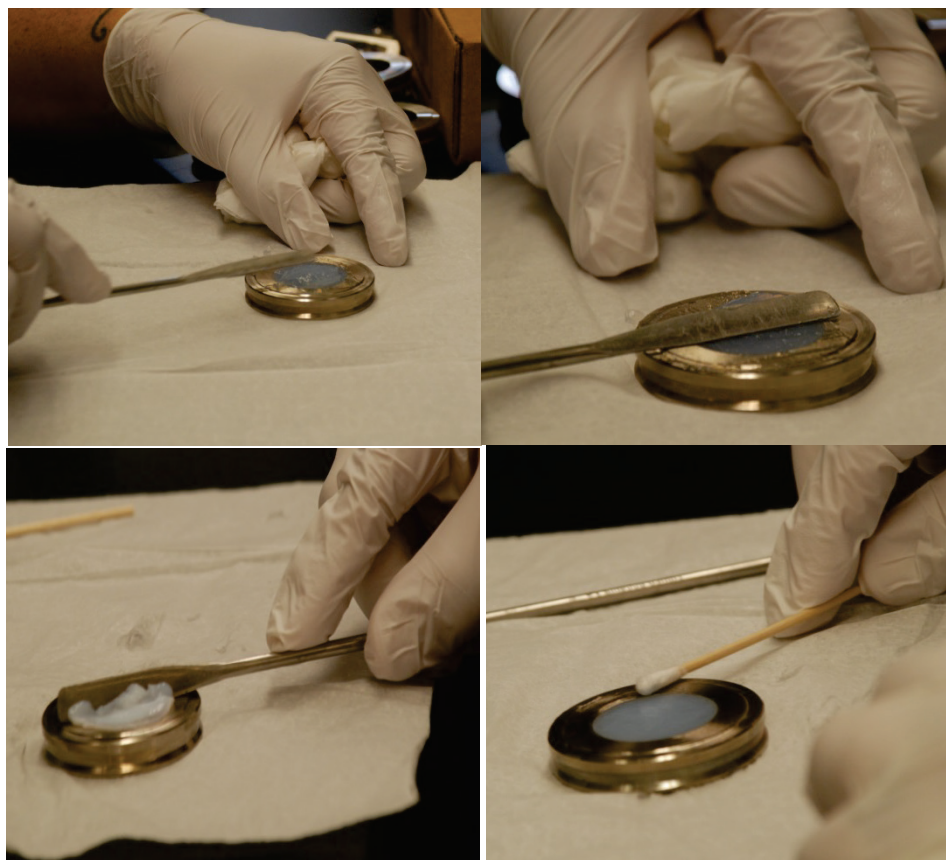
3. Place the ZBP or slide into the sample holder.



4. Place the sample holder into the sample rack.
5. Proceed to step 5.1.2.6-1.
6. Place the plastic spacer into the ZBP sample holder. Carefully place the ZBP in place and secure with the clip.

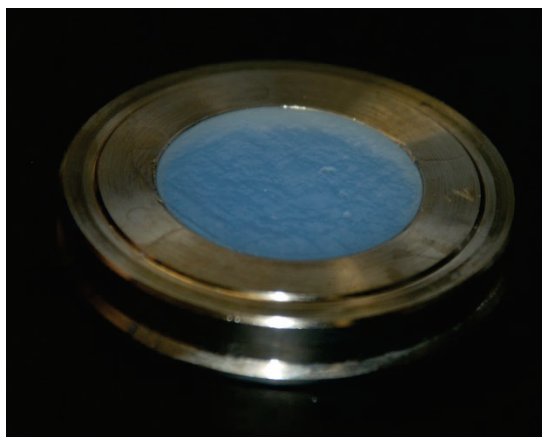


7. Turn the ZBP sample holder over and fill with gel or cream, smooth out sample until level with the sample holder, and use a cotton swab to remove excess material from the sample holder.



Note: If the sample is higher than the sample holder, the XRD pattern may shift

8. Place into sample rack.



9. Proceed to step 5.1.2.6-1.

5.1.2.3 Plastic or polymers and fabric

1. Gather equipment needed: ZBP, ZBP sample holder, and scissors or cutting apparatus.



2. Cut material into the shape of the ZBP; adhering is not necessary as long as the ZBP holds the sample properly in place. (If the material is higher than the sample holder, a pattern shift can occur.)



3. Place the polymer into the ZBP sample holder and secure the ZBP in place.



4. Place the sample holder into the rack.
5. Proceed to step 5.1.2.6-1.

5.1.2.4 Powders

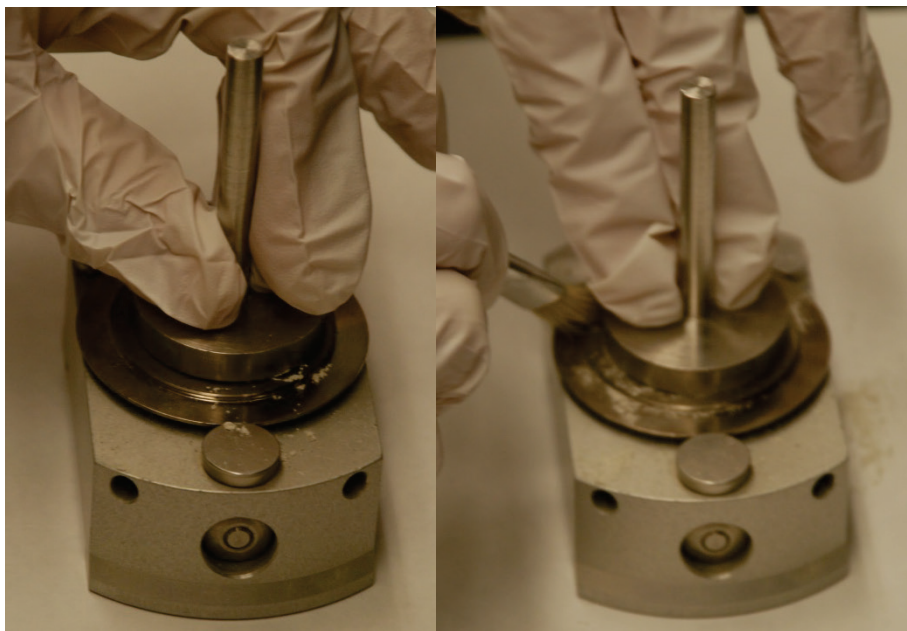
1. Secure equipment needed: reverse pack sample mount, loose powder sample holder, small brush, and sample press.



2. Place the sample holder into the reverse pack sample mount; place the loose powder into the open slot.



3. Lightly press the powder to fill the slot completely, and place the sample press over the sample and brush excess away.



4. Place the sample back over the sample holder and remove from sample mount.



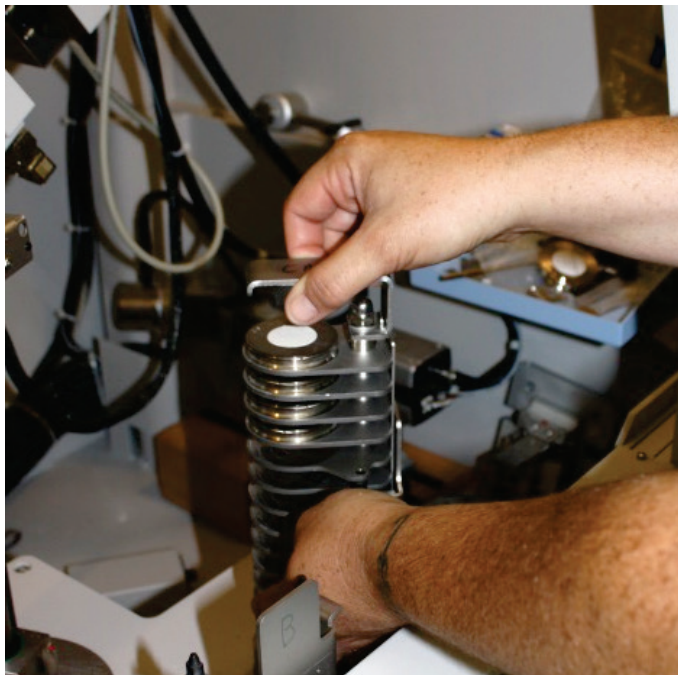
5. Place the sample into the sample rack.
6. Proceed to step 5.1.2.6-1.

5.1.2.5 Solids

1. Use a ZBP holder, a drill press with the appropriate core bit size for the sample holder, and a precision saw to cut a 2- to 5-mm slice from the extracted core.
2. Core out the sample to fit into the ZBP sample holder; cut the core to a height that will fit into the sample holder.
3. Place the sample into the rack.
4. Proceed to step 5.1.2.6-1.

5.1.2.6 *Gather XRD pattern*

1. Place the sample rack into the XRD.



2. Bring the XRD tube up to the proper voltage, 45kV 40mA.
3. Program scan criteria, such as sample names and scan range.
4. Gather data.

5.1.2.7 *Analyze data*

1. Export .xrdml files.
2. Analyze data with available software or computation.
3. Report results.

5.2 **Analysis**

5.2.1 **Obtaining XRD data**

A key element to gathering XRD data is to understand the settings of the X-ray machine being used and the capacity to which the machine can yield reliable data. There are many types of X-ray machines on the market, from hand-held field units to stand-alone units able to run multiple samples in a session.

5.2.1.1 *Type of tube*

The type of anode material, located in the X-ray tube, has specific wavelengths of the $K\alpha$ radiation produced. Shorter wavelengths will lead the d -spacing to become less accurate and have less resolution. The most common anode used is copper ($\text{Cu} - 1.54\text{\AA}$), but chromium ($\text{Cr} - 2.29\text{\AA}$), iron ($\text{Fe} - 1.94\text{\AA}$), cobalt ($\text{Co} - 1.79\text{\AA}$), molybdenum ($\text{Mo} - 0.71\text{\AA}$), and silver ($\text{Ag} - 0.56\text{\AA}$) tubes are available. Depending on the type of samples that are typically run in the XRD being used, a tube that will yield the least amount of fluorescence should be selected (School of Crystallography, 2014).

5.2.1.2 *Filtering for $K\beta$ and $K\alpha_1$ reduction*

A white spectrum of X-rays is produced when the anode is excited, and filters are needed to reduce the spectra to a monochromatic spectrum. A metal foil filter is needed to remove the $K\beta$ line from the spectra. Depending on the type of anode being used, the proper filter is usually a metal with one less atomic number than that of the anode. For example, a copper (Cu) anode needs a nickel (Ni) filter. Molybdenum (Mo) is an exception: it needs a zirconium (Zr) filter that has a 2 less atomic number. To reduce $K\alpha_1$ radiation, a monochromator can be used. The most common types of monochromators are made from pyrolytic graphite, silicon, germanium, or quartz. These filters help to reduce background noise and allow for the $K\alpha_2$ spectrum to be the primary band used to satisfy Bragg's Law (School of Crystallography 2014).

5.2.1.3 *Scan settings*

It is also important to understand the scan parameters when gathering an X-ray pattern. If a scan is taken too quickly, there will be too few data points gathered to allow for statistical soundness. Too many data points can cause excess overshadowing and cause run times to be unnecessarily long. A step size of less than or equal to 0.02 allows for adequate data points and statistically viable data to calculate full width half maximum (FWHM).

The scan range should be set to the type of material being evaluated. Clay mineral scans are typically taken between 2 and $35^\circ 2\theta$. Soil sample scans are taken between 2 - $70^\circ 2\theta$, while metals are measured from 30 - $100^\circ 2\theta$. Scans can take 45 min to 2.5 hr, depending on the range and step size being used.

5.2.2 Using software for data analysis

Many programs, such as the Jade2010 program (Materials Data, Inc.) or High Score plus (PanAlytical, Inc.), are available for analysis of X-ray patterns. Prior to the advent of these computer programs, phase identification was performed by using a list of observed peaks from the obtained pattern and comparing it to a database of d-I (d spacing and intensity) such as the ICDD-PDF reference database. Computers can now search and match the PDF files and compare them to the entire pattern more quickly and efficiently. Once minerals and/or amorphous material are identified to one's satisfaction, a whole pattern fit (wpcf) can be performed to obtain the percentages of each mineral identified. Some programs can also be used to identify crystallite size, strain, and stress.

6 Reporting

6.1 Analysis of results

Analysis techniques have changed over time with the advent of technology. Prior to computers, patterns and crystallite size were all calculated by hand using Bragg's law and Scherrer's equation, etc. (Langford and Wilson 1978). Computer programs, such as Jade 2010 (MDI) and High Score Plus (Panalytical), now allow for quick computation of mineral identification, crystallite size, and stress/strain. The advancement of these programs has allowed the analysis of one component at a time (e.g., mineralogy) or various components simultaneously.

(Note: The following procedures are based on the use of Jade2010 software, the software the authors typically use. Other programs may have variations in the steps taken in analysis of X-ray patterns.)

When analyzing X-ray patterns, one should first look at the pattern itself and ascertain that the peaks identified are valid. Adjustments to the peak height threshold may be needed to remove or add peaks. In some instances, the program does not differentiate broad short peaks or the presence of amorphous humps from background noise.

A search match for mineral identification is then started. The program uses the PDF databases to compare known patterns to the pattern obtained. At this point, knowing as much as possible about the sample (i.e., where the sample came from) will help with the selection of minerals. For example, Calcite, Aragonite, and Vaterite are all CaCO_3 ; but they do not form under the same conditions. After all peaks are accounted for, the wpf is started.

During wpf analysis, many variables have to be considered. Not all patterns are the same, and some settings will vary based on the pattern obtained.

6.2 Key results provided

The main principle one should obtain from this SOP is that techniques for sample preparation vary for different material types. Identification of the mineral constituents and the determination of crystallite size will be dependent on the instrumentation and software used during analysis.

6.3 Quality assurance/Quality control considerations

Identification of minerals present in samples, especially unknown samples, is dependent on the software and PDF databases available to the user. The more one knows about the origin of the materials, the easier it is to eliminate unlikely minerals present in the sample. With regard to nanoparticles, knowing the behavior of polymorph stability and phase transformation helps when fitting patterns. Having the proper scan parameters during data acquisition, using standards for monitoring peak position and intensities, and using internal standards increase the precision of wpf analysis. When calculating crystallite size, it is a good practice to validate calculations with microscopy by using methods laid out in the Scanning Electron Microscopy (SEM) SOP.

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