I. SCOPE

X-ray diffraction is used for the identification of any crystalline material, including inorganic and organic crystalline explosives, residues, and raw materials. Samples may be either individual substances or mixtures. X-ray diffraction is an identification technique for individual phases.

Limitations: Similar diffraction patterns can result from different compounds, and very complex patterns may result from mixtures. Amorphous (non-crystalline) substances, which would not give a diffraction pattern, could also be present. Compounds that comprise less than 1 % of a mixture may not be detected.

II. REFERENCES

Introduction to X-Ray Powder Diffractometry, by Ron Jenkins and Robert L. Snyder, published by John Wiley and Sons, Inc.

Elements of X-Ray Diffraction, First and Second Editions, by B. D. Cullity, published by Addison-Wesley Publishing Company, Inc.

ICDD X-Ray Clinic Instruction Manuals, International Centre for Diffraction Data

X-Ray Diffraction Procedures, by Harold P. Klug and Leroy E. Alexander, published by John Wiley and Sons, Inc.

Reference Intensity Method of Quantitative X-Ray Diffraction Analysis, by Briant L. Davis, Institute of Atmospheric Sciences, South Dakota School of Mines and Technology

Practical X-Ray Spectrometry, by Jenkins and deVries, distributed by Springer-Verlag

X-Ray Spectrochemical Analysis, by L.S. Birks, published by Interscience Publishers

Visual Lines for Spectroscopic Analysis, by D.M. Smith, published by Hilger and Watts, Ltd.

An Introduction to X-ray Spectrometry, by Ron Jenkins, published by Heyden and Son, Ltd.

Worked Examples in X-ray Analysis, by Jenkins and deVries, published by The Macmillan Press Ltd.

Forensic Investigation of Explosions, Edited by Alexander Beveridge, published by Taylor & Francis Ltd.

III. VALIDATION

X-ray diffraction is a well-known, proven technique. The 1912 work of Max von Laue confirmed the wave character of X-rays by diffraction experiments from a single crystal. The field of X-ray crystallography followed from that work, with X-ray powder diffractometry being developed in 1935 by

LeGalley and the first commercial equipment introduced by North American Philips in 1947. Changes since then have been primarily in the areas of detection and counting systems, automation, and the X-ray tubes themselves, with very few changes in the construction and geometry.

IV.   APPARATUS/REAGENTS
An X-ray diffractometer, as available in the laboratory. The instrument should be equipped with an ICDD database and appropriate software to allow automatic analyses including measuring, recording and comparison of patterns acquired with the desired databases.

Standards and/or Reagents
The calibration standards (Quartz, Silicon, and Corundum) are permanently prepared for analysis and should be stored appropriately. Any user database patterns generated should be from known, properly documented sources or confirmed analytically by at least two other methods. Patterns from the commercial ICDD database are from validated sources, mathematically calculated, or both. New bottles of adhesion solvents should be tested by dropping several drops onto a zero-background plate, letting the solvent evaporate, and running the sample. New samples of other adhesion substrates should be applied to the sample holders in the manner normally used, and a sample run.

V.   CALIBRATION
The calibration procedure will vary depending on the type of detector used with the instrument. A check of the calibration should be done within one month prior to analysis for casework, and following any instrument maintenance procedures. Calibration procedures will be specified in work instructions for each instrument and the results will be recorded in the instrument logbook.

VI.   SAFETY PRECAUTIONS
Safety precautions should always be used when grinding any substance, especially considering the potentially explosive nature of many of the samples normally encountered. For example, grinding small samples in a solvent such as hexane may lower the risk involved. Safety glasses should be worn when working with powdered substances. Sample preparation should be such that a minimum of sample can be scattered inside the instrument during the sample spinning. The inside of the instrument should be checked monthly and cleaned as needed to prevent sample build-up.

Also see radiation safety manual.

VII.   SAMPLE PREPARATION
All samples should be run with as little sample preparation as possible to avoid rearrangement of anions and cations in a mixed sample. The specimen analyzed must be representative of the entire sample. Small particle size (allowing for a more random orientation of particles in the sample) is desired, so all samples should be well ground. Care should be taken when grinding potentially explosive materials.

Several different types of sample holders are available. An adhesion substrate such as methanol, ethanol, hexane, or vaseline may be used to affix the sample to the holder.

In cases where crystal shape may result in "preferred orientation" of the crystals, additional steps may be taken to prepare the samples for analysis. Preferred orientation results in not all of the planes being detected in their predicted ratios (as in the case of long, flat crystals or fibers). More information can be found in the references, especially SPECIMEN PREPARATION FOR THE DIFFRACTOMETER from Chapter 2

of the ICDD X-ray Clinics manual.

VIII. ANALYTICAL PROCEDURE

After confirming that the calibration is current, samples are prepared by one of the methods addressed in Section VII. Using the apparatus and conditions given in the attachments, a diffractogram is obtained. See the instrument manuals for further details on actually running the samples. The raw data is then transferred into a format suitable for comparison to the commercial databases, and a search program is used to generate a list of possible matches. A manual search, using the Alphabetic, Fink, or Hanawalt Method, may also be used, either in addition to, or in place of, a computer search program.

The diffraction patterns of the computer-suggested or search-found matches are then viewed by the examiner as a tool to help determine whether or not suggested components are actually present. Subtraction programs (either manual or computer based) may need to be used when multiple phases are present. A residue search (performed on remaining peaks) can be performed on peaks, which may aid in their identification. The diffractogram can also be compared to any standard diffractogram in the commercial or user-generated database to check for the presence of any individual phase. If possible, all lines should be accounted for. In the lab's experience, having only 1 or 2 matching lines is insufficient by itself to identify a compound. Therefore, at least 3 lines are required for pattern identification. For compounds having between 3 and 5 lines (such as aluminum), an attempt should be made to identify all lines in the pattern. Refer to "Using the Powder Diffraction File," published by ICDD, for guidelines on the criteria for a match.

The ICDD commercial databases utilize IUPAC nomenclature for the naming of chemical phases. Because this system is based on the atoms present, care should be taken to assure no confusion between different chemicals, which are given the same IUPAC name. A commonly found example is $KClO_3$ and $KClO_4$, both named potassium chlorate in the databases. Different phases of the same chemical, such as anatase, rutile and brookite phases of TiO_2, should also not be confused.

Peak displacement errors can occur if the sample is not level/flat or offset from the plane of the beam focus causing a consistent shift to the right. An example of this would be using too much sample in a low background slide. This displacement could hinder sample identification and may necessitate re-preparing and reanalyzing the sample. However it is possible that the software can compensate for this shift and re-preparing and reanalyzing can be avoided.

As discussed in Section VII, preferred orientation of samples can result in changes in peak intensity ratios from what is expected. This should be taken in account when identifying phases or performing subtractions. These samples with multiple phases may need to be prepared again, and rerun.

IX. NON-ROUTINE EXAMS

Different samples may need to be handled in a non-routine manner. Solid objects, hard materials, and other non-routine samples can be handled using different sample holders. Specifically looking for a certain phase may require extending the region scanned, or may allow for a much quicker scan through a certain specified region. Any change from the stated operating parameters, as well as a description of the need for the change, should be noted on the instrument parameter sheet included with the case notes. The type of sample holder (and the sample preparation method) is always included with the case notes.

X. QUALITY ASSURANCE/QUALITY CONTROL

When identifying a certain phase as being present, the diffractogram of that phase needs to be shown in the notes. This will assist in peer review of the results. This is required by our Standard Method of Analysis, and helps to assure quality results.

Variations in instrument performance will be demonstrated and adjusted, as necessary, during monthly calibration procedures.

GLOSSARY

Antiscatter slit - Controls the unwanted radiation that may pass through the receiving slit and strike the detector

Beam mask - Retains a constant beam width, aiding the divergence slit in maintaining a constant exposure area

Bragg's Law - Describes the relationship between the wavelength of the incident radiation, the angle of incidence, and the distance between the planes of the crystals

Crystal lattice - Regular, repeating three-dimensional arrangement of atoms, resulting in predictable distances between the planes formed by the atoms

Debye rings - Diffraction cones from a crystalline material that produce a set of concentric circles. Smooth and continuous rings indicate a fine-grained polycrystalline material. Continuous but spotty rings indicate a large-grained polycrystalline material. Individual spots and no rings indicate that the material is a single crystal.

Detector slit - Aids beam monochromation

Diffractogram - Pattern resulting from scanning a sample over a specified range of angles of incidence (2θ values). Will include contributions from diffraction, scatter and fluorescence from the sample.

Direct-beam center - X and Y coordinates (unwarped centroids) of the direct beam at a swing angle of zero

Divergence slit - Adjusts aperture to maintain the same area of exposure on the sample during data collection

GADDS - General Area Detector Diffraction System

Göbel mirror - Graded multilayer mirror that creates a highly parallel incident beam while suppressing K_β radiation

Hi-Star detector - 2-dimensional multiwire proportional counter. The chamber is filled with Xe/methane gas. An X-ray photon enters the detector and interacts with the Xe near the front window. The gas is ionized, creating a cloud of electrons. This electron cloud is then accelerated into a detection grid, which consists of a fine plane of anode wires located between two planes of cathode wires. The signal is collected on the anode wire surface and converted into X-Y positions for each X-ray photon. The Hi-Star

detector has a large imaging area (11.5 cm), which allows 18° to 65° 2θ to be collected at one time (depending on the location of the detector).

Monochromator - Gives improved peak/background ratios and suppression of K_β lines

Phase - A unique arrangement of atoms in a regular, repeating arrangement. More than one phase may exist for the same chemical formula (e.g. rutile, brookite and anatase phases of TiO_2).

Phi rotation stage - Motorized circular stage that mounts to the XYZ stage and can rotate during sample collection. The rotation minimizes preferred orientation effects and is useful for small samples.

Receiving slit- Controls the 2θ angle measured (resolution)

Sample holder - Holds sample during analysis. Options include a low background slide, frosted glass slide, and cavity slide. The holder can vary depending on sample size and consistency. An automated version rotates at a predetermined constant rate to help compensate for surface effects and non-random crystal orientation.

Sample-to-detector distance - Distance between the goniometer center and the flat front surface of the detector (where the fiducial plate mounts)

Scintillation (proportional) detector - X-ray photon is converted into flashes of blue light by a phosphor (scintillator). The phosphor absorbs radiation at a certain wavelength, and then re-emits it at a longer wavelength. The blue light from the phosphor is amplified and converted to voltage pulses by a photomultiplier tube.

Snout and pinhole slits - Similar to a collimator in that it focuses the X-ray beam. A snout and corresponding slit are attached to the Göbel mirror, which is attached to the X-ray tube.

Soller slits - Contribute to reduced background and improved resolution by "straightening out" the X-ray beam

X-ray diffraction - Utilizes a monochromatic beam of radiation to yield information about the d-spacings (distances between the planes) and their intensities from a single crystal or crystalline powder

X-ray source - Tungsten filament emits electrons that bombard a target (in current operation – Cu anode is used). The target emits X-rays (Cu K_α =0.154 nm) through beryllium windows towards the sample. Since the wavelength of Cu K_α emission is similar to the interatomic distances in many crystalline materials, diffraction can occur.

XYZ stage - Motorized, flat surface on which samples are placed. The stage is approximately 100 mm x 150 mm and can move in the X, Y, and Z (height) direction to align the sample. Motion of the stage in the XY direction during sample analysis can reduce the effects of preferred orientation.