ITWG

Nuclear Forensics

International Technical Working Group

NUCLEAR FORENSICS INTERNATIONAL
TECHNICAL WORKING GROUP

ITWG GUIDELINE
ON POWDER X-RAY DIFFRACTION (XRD) —GENERAL OVERVIEW

EXECUTIVE SUMMARY

X-Ray Diffraction (XRD) is an analytical technique used to identify crystalline compounds. It is a bulk technique, though the volume of material sampled is relatively small (approximately 0.01 cm^3). Specimens are typically examined in the form of powders or solid pieces. XRD analysis produces diffraction patterns which can be compared to large open databases of crystal diffraction patterns to give precise information about the crystal structure of the material examined. The quality of matches of the analyte data to the database can be rigorously quantified. In the case of mixtures of compounds, the relative amounts of each compound can be calculated, although significant errors may exist. In general, XRD is a rapid, easy to use, robust, and largely nondestructive way to identify materials. It is a widely used and mature technology, with considerable flexibility.

1. INTRODUCTION

X-Ray Diffraction (XRD) is a well-established analytical technique that has its roots in the early part of the 20th century. It has been developed over the intervening years into a highly sophisticated and robust technique with many applications[1]. For the purposes of Nuclear Forensics, the main application is the identification of compounds or mixtures of compounds in samples of interest.

XRD operates by scattering a collimated beam of x-rays off of a specimen over a range of angles, and measuring the intensity of the scattered beam as a function of angle with an x-ray detector. The intensity and direction of the scattered beam strongly depends on the crystal structure of the specimen, which is the diffraction phenomenon at the root of the XRD technique. Figure 1 shows schematically the most common geometry for XRD instruments, the "θ-2θ" configuration. In this configuration, the specimen remains fixed, while the x-ray generating tube and detector are simultaneously rotated by a goniometer. The rotation is constrained such that the angle θ is held the same for both the x-ray tube and the detector as it is increased. The detector continuously records the diffracted x-ray intensity as a function of θ. The data output is a diffraction pattern (sometimes referred to as a diffractogram), which is typically plotted as x-ray counts vs. 2θ. A diffraction pattern for the compound LaB_6, a common reference standard, is shown in Figure 2.

Fig. 1. Schematic of the θ-2θ goniometer configuration widely used for XRD analysis.
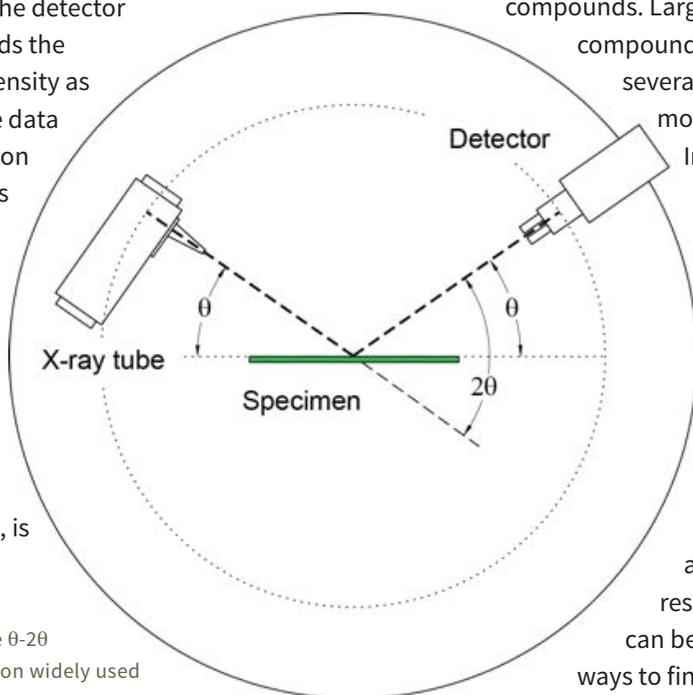
The diffraction pattern contains a large amount of information. Most valuable for the identification of unknown compounds is the position of the peak centers, from which the lattice parameters and crystal structure of the unknown can be determined. The peak positions can be compared to large databases of known compounds using sophisticated search-match software. The diffraction peaks for the majority of known compounds are positioned differently enough to uniquely identify the compound. Typical diffraction patterns contain 15-25 peaks, so matching each peak in a diffraction pattern to a known compound is a convincing identification. In addition, the quality of the match can be quantified using goodness-of-fit measures such as simple standard deviation or complex measures such as the Smith-Snyder figure of merit[2]. With appropriate care, XRD can determine the crystallographic parameters for powder or fine-grained material to an accuracy of < 500 ppm. In fact, it is among the most precise measurements that can be performed on materials.

Identification of unknowns by XRD is a software driven search-match procedure, so it is only as good as the state of knowledge about known compounds. Large databases of known compounds are maintained by several organizations, the most prominent being the International Centre for Diffraction Data, and a consortium of FIZ-Karlsruhe and National Institute of Standards and Technology. These organizations continually update their databases, which contain >340,000 and >140,000 entries, respectively. The databases can be searched in multiple ways to find compounds with

diffraction patterns that match a given set of peaks, such as those in Figure 2.
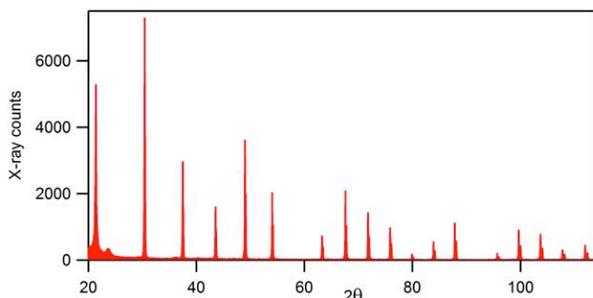

Fig. 2. A typical XRD powder diffraction pattern. The sample is the compound lanthanum hexaboride, a widely used standard reference material.

The relative amounts of each compound in samples containing mixtures of compounds can be quantified using whole pattern fitting routines[3,4]. Once the identity of each compound present in the sample is well-established by matching the positions of each peak, whole pattern fitting routines adjust a wide variety of parameters to fit every aspect of the diffraction pattern, in particular, peak height and width, and background. One fundamental adjustable parameter is the relative amounts of each identified compound, giving the quantification sought. However, the accuracy of this type of fitting procedure for quantification of compounds is quite variable, as there are many sources of error. For example, large errors can result from mixtures of compounds which have crystal structures with very different degrees of symmetry, or if the constituent powder particles of the compounds differ significantly in size. In general, quantification of the compounds in a sample by XRD should be viewed as an estimate only.

X-ray diffractometers have been developed over the past 100 years, so there are numerous manufacturers and many types of instruments. The power (intensity) of the x-ray beam varies widely. At one extreme are the rotating anode type instruments with x-ray tube powers of ~15 kW. These are expensive, and have significant power and laboratory safety requirements. Their advantage is deep penetration of the specimen and detection of weak diffraction peaks. At the other extreme are the newest generation of bench-

top XRD instruments, which are approximately 1 m³ in volume, with modest power and cooling requirements. The x-ray tube power for such units is typically in the 1 -3 kW range. These bench-top units are portable, although it should be recognized that the goniometer of any XRD instrument must move with extreme precision, and this limits the environment in which XRD instruments can be used. XRD instruments can easily be installed in gloveboxes or other special enclosures. However, water cooling is required for x-ray tubes, so hazards associated with having water in a special nuclear material glovebox must be mitigated.

2. USE OF XRD FOR NUCLEAR FORENSICS

Material for nuclear forensics is frequently interdicted in the form of powders or small solid pieces, which are easily analyzed by XRD. The identity of the compounds present in the sample can be determined, and this can be key information for making attribution and intended use conclusions about the material. XRD is a bulk technique which analyzes ~0.01 cm³ of the sample (typically $1.0 \times 1.0 \times 0.01$ cm³), therefore giving a reasonable picture of the contents of a well-mixed powder specimen.

The utility of XRD can be increased significantly by using it in parallel with other analytical techniques, in particular scanning electron microscopy (SEM) and x-ray fluorescence (XRF). SEM and XRF use spectroscopic techniques to identify the elements present in a sample. Once the elemental composition of the sample is known, the task of identifying the compounds present in the sample by XRD is simplified enormously. Searching the large databases can be reduced by many orders-of-magnitude in scope if the elemental constituents of the compounds are known. In addition, knowledge of the elements present in the sample can be used to explain anomalies in crystal structure that occasionally arise during XRD analysis.

Identifying the compounds present in a sample can give forensic information on a variety of levels. For example, analysts can look for precursor compounds

to specific nuclear fuel chemical processes, to learn about the degree of sophistication of the processor. Analysts might also identify site-specific minerals or compounds that give information about possible sources and origins of interdicted materials. Additionally, sophisticated physical-chemical information can be derived, such as metal-to-oxygen ratios in complex oxides.

3. XRD SAMPLE REQUIREMENTS

XRD analysis works best on specimens with a flat surface, approximately 1 cm^2 in area. If the sample is fine powder, it can be sprinkled onto adhesive on a specimen mount and flattened with a press so that the powder particles are coplanar. Solid specimens must have a flat ~1 cm^2 surface that can be oriented parallel to the XRD goniometer rotation axis. Deviation from planarity results in peak broadening and shifting in the diffraction pattern, and to some extent these can be mathematically corrected. Specimens that are smaller in area than 1 cm^2 can often be meaningfully analyzed, but the full power of the x-ray beam will not be exploited, and the beam will potentially strike the sample stage surrounding the specimen causing artifacts in the diffraction pattern.

While XRD is essentially non-destructive, excessively coarse powder specimens (roughly, particles greater than 500 μm) are commonly crushed into finer form using a mortar and pestle. An ideal size is in the 1 – 100 μm diameter range. One downside of crushing is that there can be significant specimen loss, so it is not suitable when only small amounts of sample are available. Solid specimens are commonly cut to size and ground flat using standard materialographic techniques, with good results. Again, there is loss of material involved in shaping specimens in this way.

Moisture in a powder specimen is a potential problem, as water will form an amorphous film on the powder particles and reduce the amount of x-ray scattering from the particles. Dry powders produce the best results, although useable diffraction patterns can be derived from slightly moist specimens.

Radioactive specimens are typically contained by sealing them with polypropylene film after mounting. The film is a simple and effective containment for potentially airborne contaminants, but the film sits in the x-ray beam path and therefore contributes to the diffraction pattern, and attenuates the x-ray intensity. The effect of polypropylene film can be seen in Figure 2. It produces a broad low-intensity peak at 10° < 2θ < 30°, and more distinct peaks at 2θ ~ 21° and 24°. Generally, no problems arise from using polypropylene film containment except in rare cases of peak overlaps or weakly diffracting samples.

4. PRO'S AND CON'S OF THE TECHNIQUE

A major strength of XRD analysis is its simplicity of use. Samples can be easily mounted and examined in a variety of forms. Diffraction patterns can be generated in a matter of hours, with minimal user intervention. Analysis of the diffraction patterns is more complex, but numerous software packages are available to simplify the analysis steps. The compounds present in a moderately complex specimen could easily be identified in less than a day in a properly outfitted laboratory. Coupled with a complementary technique like SEM or XRF that is capable of identifying the elements present in the sample, XRD analysis is a powerful identification and characterization tool.

XRD analysis can become very complex if the sample contains 3 or more compounds in similar volume fractions. In such cases, there are frequently peak overlaps and other difficulties in cleanly identifying peaks associated with a given compound. Additional SEM/XRF analysis is often required to characterize such specimens, and even then there may be ambiguities.

Impurities at a low level can significantly alter the crystallography of some compounds. Thus, an identification might be missed due to a shift in lattice parameter. In such cases, operator knowledge is a must. Generally speaking, confident

identification of complex multi-component samples requires the skills of an expert, experienced analyst.

5. FAQ

– Cost: XRD instruments suitable for forensic analysis are currently in the $150,000 - $500,000 range, depending on accessories, size, power, etc.

– Laboratory requirements: XRD instruments require active cooling for the x-ray generator, so a chiller is needed nearby, capable of maintaining the x-ray tube at 15 – 25 °C. X-ray shielding is required for operator protection.

– XRD has a detection limit of ~1% by volume, i.e. if a compound is present below this level, no peaks above noise will be detected in the diffraction pattern. The exact detection limit depends on the density, Z number, and crystal structure of the compounds in the sample.

– XRD can be performed on very small amounts of material. A sample in the 10^{-2} to 10^{-3} cm^3 range will give a useful x-ray diffraction pattern. However, it should be noted that there are difficulties with mounting very small powder samples, which can be hard to manipulate and spread on an XRD specimen holder.

– Quantification of relative amounts of compounds present in a sample is achievable. However, the accuracy depends on many factors, including powder size, crystal structure, and density of the compounds in the sample. Errors in quantification can be quite large.

– XRD analysis is not useful for glassy (amorphous) specimens. Diffraction patterns from such specimens, e.g. glasses, most polymers, and rapidly solidified metals, are not well-defined enough for compound identification. However, XRD analysis will show immediately whether the sample is crystalline or amorphous, which can be useful information.

– XRD instruments are easily and safely operated with minimal training. However, identification of compounds in a sample from diffraction patterns is an expert operation, made easier by diffraction analysis software, but nonetheless requiring significant knowledge and experience.

6. USEFUL REFERENCES

1. B. D. Cullity, S. R. Stock, "Elements of X-ray Diffraction", 3rd edition, Addison-Wesley Publishing Co, Inc. , 2001. A classic text for advanced undergraduates and graduate students.

2. G. S. Smith, R. L. Snyder, J. Appl. Cryst., 12 (1979) pp. 60-65.

3. Jade™ software, Materials Data, Inc. Livermore, CA, (www.materialsdata.com). A powerful, commonly used software package for XRD analysis.

4. GSAS (General Structure Analysis System) is non-commercial software for the refinement of structural models for x-ray and neutron diffraction data. Available at: https://subversion.xor.aps.anl.gov/trac/EXPGUI.

DOCUMENT REVISION HISTORY

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