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Advances In XRD Instrumentation, Data Analysis/Interpretation and Applications in Science and Technology

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ABSTRACT

X-ray diffraction (XRD) analysis is the main tool in the analysis of crystal structures of polycrystalline materials. When a more accurate mineral phase information is sought, X-ray powder diffraction (XRPD) is the technique that is traditionally used. The use of XRD data as a quantitative tool has been considerably enhanced in recent years following the development of purpose-specific computer processing systems and improvement in instrumentation. XRPD data can also be used for the identification of unknown substances, measurement of precise lattice parameters, determination of crystal size and lattice strain and detection of long-range ordering and evaluation of textures in polycrystalline solids. Other information encoded in XRPD pattern include whether a material is single phase or a mixture of phases.

Keywords*:* X-ray diffraction, quantitative phase analysis, Instrumentation, modern Diffractometers.

INTRODUCTION

X-ray diffraction (XRD) technique is used for structure determination of inorganic and organic solids and the identification of crystalline solids. XRD techniques are some of the most useful in the characterization of crystalline materials such as metals, intermetallics, ceramics, minerals, polymers, plastics, or other inorganic and organic compounds [1]. The compositional and physical descriptive analysis of a material make X-ray unique among other analytical methods [2]. The decisive advantage of XRD methods is based on the unique character of diffraction patterns of crystalline substances, the ability to distinguish between elements and their oxides, and the possibility to identify chemical compounds, polymorphic forms and mixed crystals [3].

Powder XRD is a versatile, non-destructure analytical technique that is used to characterize samples in the form of loose powders or aggregates, of finely divided material (Jenkins and Haas, 1973)[1]. These techniques cover various investigations, including qualitative and quantitative phase identification and analysis, determination of crystallinity, micro-identification, lattice parameter determination, high-temperature studies, thin film characterization, and in some cases crystal structure analysis [1]. The most important parameters in X-ray diffraction studies are intensity of diffraction peak, interplanar distance (d) and full width at half maximum (FWHM) which can be accurately estimated by using sophisticated instruments and profile fitting programme [4].

In the field of material analysis, there is a constant demand for sophisticated tools, which can process enormous number of data in a short time, deal with cases showing sample-induced anisotropy and extract more information about sample. New instrumental developments such as flexible diffracting geometrics (Theta-Theta-movement), high temperature XRD chambers with homogenous temperature distribution and parallel beam optics provide much better application to a wide range of specimen [5]. The recent advance of rapid detector systems, conjointly with the increasing computational abilities of hardware and quantification software, drastically shortened data collection and processing times, allowing accurate and precise on-line monitoring of phase content in well-calibrated systems [6].

Modern computer-controlled diffraction systems use automatic routines to measure record and interpret the unique diffractograms produced by individual constituents in even highly complex mixtures [7]. The software system is a complete suite of applications including instrument control, data acquisition and data analysis. Phase analysis softwares include profile fitting, search-match for phase identification using data bases, and quantitative phase analysis involving a choice of several algorithms for pattern refinement [7].

The most common use of powder diffraction is the identification of polycrystalline phases (search/match) from peak positions and intensity related to unique crystal structure, and the determination of phase amounts in polycrystalline materials related to peak intensity and shape related to concentration.

Due to high degree of automation and digital control [8], XRD has endeared itself as an ideal solution for a variety of industrial and research applications especially in the following areas: mineralogical studies, material research, university and educational laboratories, pharmaceuticals, geology and mining, industrial by-products, engineering process and quality control, ceramics and factories, environmental monitoring, alloys and process metallurgy, cement, chemical and fertilizer industries, forensic science and archeology and art studies. The aim of this contribution is to highlight on the powerfulness of XRD technique in material analysis especially with the advent of modern technology.

X-RAY POWDER DIFFRACTION (XRPD)

Powder XRD represents a fast and highly automated method which has been used across many fields of material science for decades and has found many industrial applications [9]. The laboratory X-ray powder diffractometer offers several virtues that have rendered it a principal characterization device providing critical data for a range of technical disciplines involving crystalline materials (Cline *et al.,* 2015) and with advanced data analysis methods, it can provide a wealth of information concerning sample character (Cline *et al.,* 2015)[10]. Because of the relative ease with which information about submicroscopic structure of any sort of material may obtained by XRD, this method of crystal structure analysis has become indispensable to modern industry. Modern X-ray diffractometers are capable of multiple applications for example., powder diffraction, thin film analysis, small angle X-ray scattering, residual stress and texture to name a few [11].

MODERN X-RAY DIFFRACTOMETERS

The instrument used for X-ray diffraction measurements is called the Diffractometer. Basically it consists of the following basic components.

i) X-ray tube - (the source of X-rays);
ii) Incident beam optics - which condition the X-ray beam before it hits the sample;
iii) the Geniometer -a platform that holds and moves the sample and sample holder;
iv) receiving-slide optics -which condition the X-ray beam after it encounters the sample and;
v) thedetector - which counts the number of X-rays scattered by the sample. (source: http://xray-tamu.edu/pdf/notes/introzxrd.pdf)

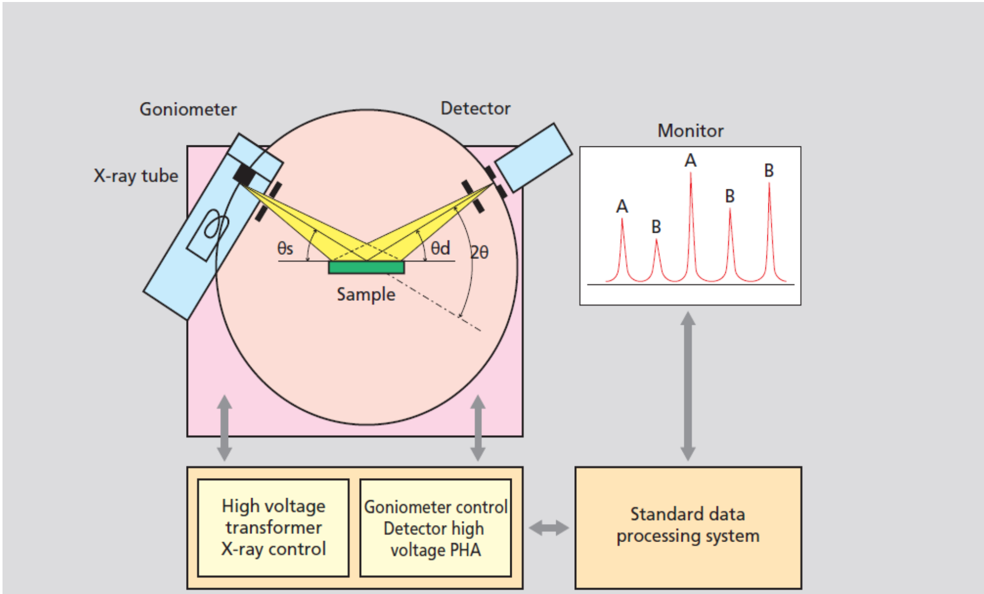


Figure 1: Schematic diagram of an X-ray diffractometer (XRD, 7000).

Source: Shimadzu, 2015

X-RAY DETECTORS

X-ray detectors can be classified as point, linear, or area, depending on whether they record the diffraction pattern in zero, one or two spatial dimensions [12]. X-ray detector technology has advanced rapidly over the past decade, driven in part by new technology borrowed from areas as diverse as high energy physics, astronomy and medical radiography (Durst, n.d). Modern fast detectors allow for more accurate data collection by using narrower slit settings [13]. The introduction of linear position sensitive detectors and area detectors on laboratory powder diffractometers means thathigh quality diffraction patterns can be routinely obtained in a time scale of few minutes (Evans,n.d). The two most common types of area detectors used for X-ray diffraction include charged coupled devices (CCDs) and image plate (IP) detectors. After a slow start with plate (IP), area-detectors systems made impact, the first commercial area-detector instruments based on charge-coupled devices (CCDs) was introduced in 1994 (Blake *et al.,* 2009)[14]. Modern area detectors for X-rays exploit image plate and charge-coupled device (Cockroft and Fitch, 2008)[12]. CCDs have enormously improved the quality and speed of X-ray data acquisition for many scattering and imaging applications (Nobarzard *et al.*, 2014)[15]. Data collection has advanced from film based to serial detector-based systems, thus speeding up this stage by at least an order of magnitude (Spek,2009)[16]. Modern CCD detector-based systems can easily collect 1000 small-molecule data sets in a year[16].

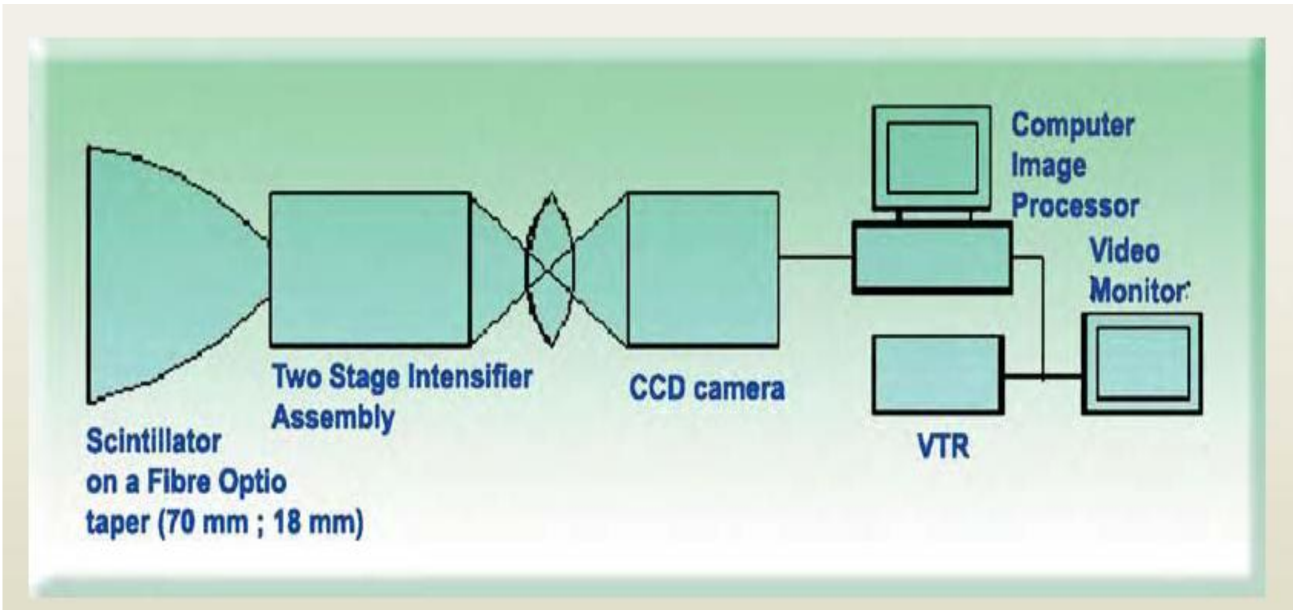


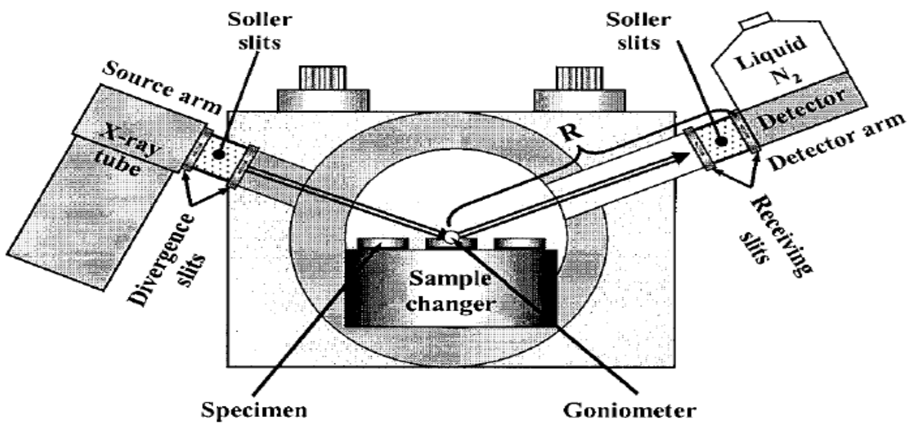
Figure 2: Schematic diagram of ICDD-based area detector for online diffraction imaging. Source: Sinha, 2007

Solid-state detectors have good energy resolution, and can be designed to work as individual devices or arrays [17] in commersurate crystals. High performance X-ray diffractometers have been built around position-sensitive detectors (PSD), since a PSD detects X-rays at many angles simultaneously, it can minimize data acquisition times and improve counting statics [17].

The replacement of single-point by area detectors has brought with it both advantage and disadvantages [14], the advantages include: simulteneous recording of many reflections; fast data collection possible; data-collection time independent of structure size; high redundancy of symmetry-equivalent data possible; rapid screening of samples, not necessary to obtain correct orientation matrix and unit cell before data collection; complete diffraction pattern measured, not just around Bragg reflection positions; poor crystal quality and weaker diffraction can often be tolerated, minimal crystal movement necessary, so easier to use low temperature and other accessories; easy visualization of the diffraction pattern, so good for teaching and training and; can obtain data on twinned or in commensurate crystals.

The disadvantages according to Blake,(2009)[14] include: possibly high capital and maintenance cost; high computing requirements, especially processing power and data storage; need for useful correction for non-uniformities and other effects; usually poor discrimination against other X-ray wave lengths for example; harmonics; restricted detector size may lead to problems with large unit cells and with Cuka X-rays; it may be expensive and difficult to change radiation; upper limit on counting time per frame for CCD detectors and; they are not efficient for very small cell.

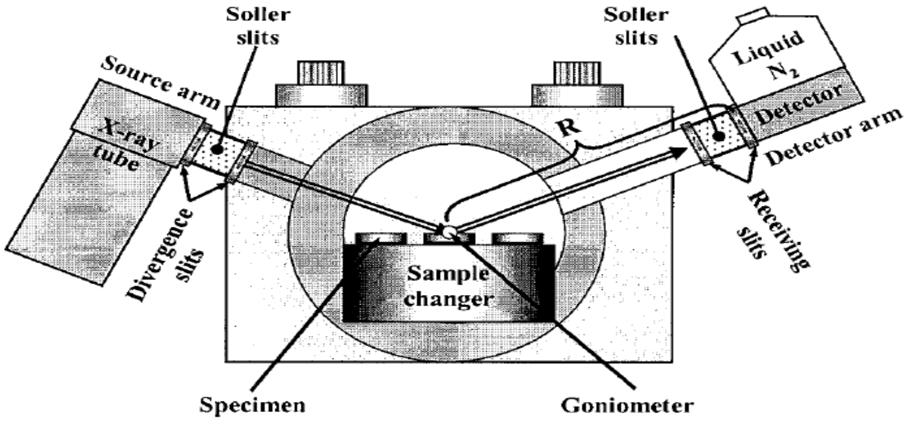
GENIOMETER



Source: Pecharsky and Zavalij, 2003

Figure 3: Schematic Diagram of a Geniometer (geniostatof scintag XDS - 2000 Powder Diffractometer)

The Debye-Scherrer type requires, a geniometer that performs precise mechanical movements of the detector and specimen with aspect to the source of monochromatic X-rays (Fultz and Howe, 2013). Geniometers can be programmed to analyse specific elements (quantitative analysis) or scan the X-ray spectrum to detect elements present in a given sample (quantitative analysis) [7].



Source: Girgsdies, n.d

Figure 4: a Simplified Representation of the Debye-ScherrerGeometry.

INSTRUMENTAL CONFIGURATIONS

There are two types of X-ray powder diffraction methods differentiated by the relative position of the specimen and the film. The two types of laboratory powder diffractometers: reflection mode which is the basis of Bragg-Brentano geometry and transmission mode which is the basis of Debye-Scherrer configuration [12], in reflection geometry, the sample is in the Form of a flat plate, while in transmission geometry a glass capillary or thin foil is used.

Debye-scherrer method: The film is placed on the surface of a cylinder and specimen on the axis of the cylinder. In the transmission geometry the capillaries are ideal for light atoms (polymers, pharmaceuticals), small atoms, hazardous materials and air-sensitive materials [18].

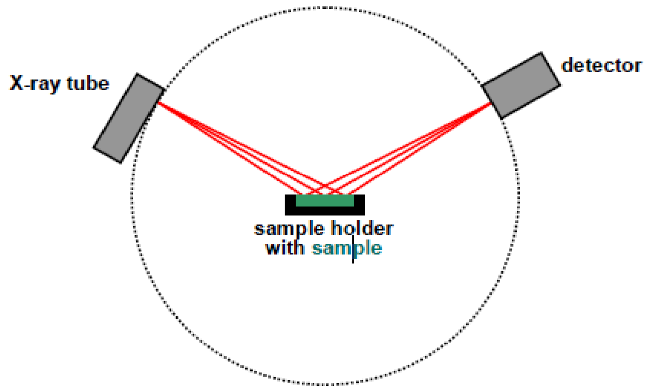


Figure 5: a Simplified Representation of Bragg-Brentano Geometry

Source: Girgsdies, n.d

i) **Bragg-Brentano configuration.**

It works best for samples with low absorption, and capillaries can be used as sample holders. Reflective geometry is ideal for absorbing materials (ceramics and metals), thin films and texture analysis (Dobelin, 2013)[18]. The Bragg-Brentano optics enables easy acquisition of high resolution and high intensity data by the reflection method (Smartlab, 2010)[19]. The majority of commercially available diffractometers use the Bragg-Brentano arrangement, in which the X-ray incidents beam is fixed but a sample stage rotates around the axis perpendicular to the plane [15].

The result of an XRD measurement is a diffractogram, showing crystalline phase present (peak positions), phase concentrations (peak areas), amorphous content (background hump) and crystallite size/strain (peak widths) (PANalytical, 2009)[7]. The figure 6.0 below shows the information contained in an XRD pattern.

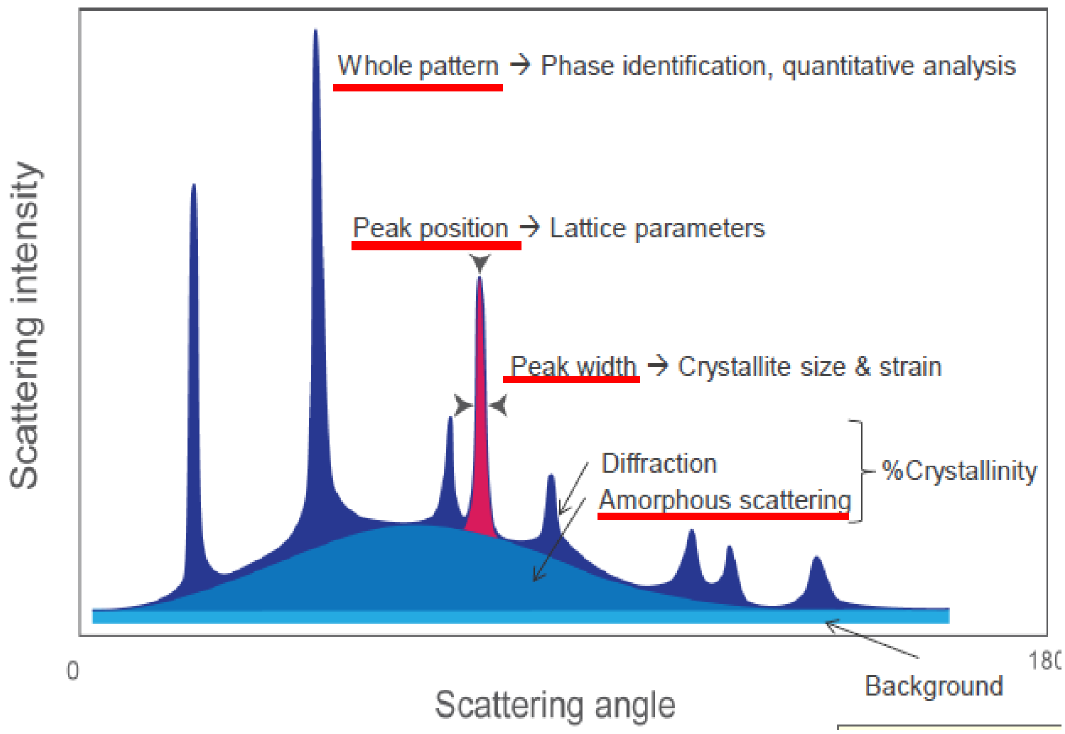


Image source: Connolly, 2012

CONCLUSIONS

X-ray diffraction (XRD) analysis is one of the most powerful tools in the analysis of crystal structures of solid materials. The role of powder diffraction in structural characterization of materials has expanded dramatically during the last thirty years (Cheetam, in press), as evidenced by the number of developments in QPA which include:

i) The advent of Rietveld method;
ii) Improvements in laboratory X-ray instrumentation;
iii) The availability of high resolution powder diffractometers;
iv) Advances in computational methods for structure solution and;
v) Improvements in computer hardware (for example. personal computers that are capable of running Rietveld codes.)

In most cases XRD provides an unambiguous phase determination. Data interpretation is relatively straight forward. It is a very good method for the identification of homogenous and single phase materials. A wider application of this techniques [15] include detecting crystalline minority phases (at concentrations greater than > 1%). Crystal size for polycrystalline films and materials, percentage of material in crystalline form versus amorphous, measuring sub-milligram loose powder or dried solution samples for phase identification, analyzing films as thin as 50Å for texture and phase behaviours; strain and composition in epitaxial thin film, surface of flat in single materials and measuring residual stress in bulk metals and ceramics.

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