Accuracy In Powder Diffraction: Are We There Yet ?

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In the 12 years since the last Accuracy in Powder Diffraction meeting, there have been significant advances. Just an example: a search of the Protein Data Bank for “powder” shows just 2 hits for before 2000, 19 for 2000-2005, 27 for 2005-2010 and 31 for 2010-present. The current Cambridge Crystallographic Data Base (CCDC) shows 2354 molecular crystal structures determined via powder diffraction (out of some 0.6M structures determined by single crystal methods!); most have been determined in the last 10 years Similarly, most synchrotron sources now have high resolution multi-detector powder diffractometers either in operation or under construction; 10 years ago there was only one (at ESRF). Software developments have also kept pace with, for example, the addition of extensive restraints and rigid bodies in GSAS for support of protein refinements and the continued development of the fundamental parameters approach (FPA) in TOPAS. These developments come with a new set of questions about accuracy. For example, what is the impact of constraints/restraints on the results; should restraints be considered as “observations”? What instrumental deficiencies now appear with high resolution multi-detector data? Are they accurately modeled in Rietveld refinements? Is our approach to validate powder diffraction results adequate? This talk will summarize these and other developments and their impact on the accuracy of powder diffraction results.

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Development and Certification of NIST Standard Reference Materials for Powder Diffraction

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The powder diffraction method accesses a considerable breadth of sample characteristics. Each application presents a specific challenge with regards to the development of a standard, both in the context of the character of the standard itself and the method by which it is certified. The success of an SRM is often critically dependent on obtaining feedstock of the appropriate microstructure. We typically will attempt to locate a material from pre-existing commercial products or, failing this, develop a custom fabrication method that we hope to farm out to an intrepid vendor. Failing this, we will, indeed, fabricate the material in house. The certification procedures vary in accordance to application, but often is one of two methods: The majority of powder diffraction SRMs are certified with an SI traceable measurement of lattice parameter to yield a standard for calibration of line position. The second method quantifies the crystalline phase purity, or conversely the amorphous content, and yields SRMs certified for quantitative analysis. The overall technical approach can be divided into three subtopics: (i) microstructure engineering or evaluation to obtain SRM feedstock suitable to address the measurement issue at hand, (ii) the design and commissioning of the equipment that embodies the unique features required for SI traceable measurements, and (iii) the design of experiments, measurement methods and data analysis strategies that allow for a valid assessment of systematic uncertainties of the measurement quantities.

For example, the LaB_6 of SRM 660b was prepared in a custom, dedicated processing run using the ^{11}B isotope enriched to a nominal 99% concentration. The native ^{10}B isotope is essentially opaque to neutrons and, as such, this isotopic enrichment renders this SRM relevant to the neutron diffraction community. The resulting powder was then annealed to "remove" microstructural defects and produce a uniform crystallite size of approximately 0.5 µm.

Owing to the specialized requirements placed on our equipment, all of our machines are designed, built and commissioned in house and located in the temperature controlled, subterranean laboratory. A high-resolution parallel beam diffractometer was commissioned to perform SI Traceable measurements of lattice parameters and layer spacings on powders and thin film structures. A second diffractometer is configured with a divergent beam is also used for SRM certification, homogeneity testing, microstructure and quantitative analysis. Additional equipment includes a double crystal diffractometer used to evaluate diffraction optics and a dedicated X-ray reflectometer. A NIST SRM must include valid estimates of uncertainty on the certified measurement values. While “Type A” uncertainties are determined through statistical analysis, the “Type B”, systematic uncertainties are assessed through a technical understanding of the measurement method(s). Therefore, the design of the experiments and data analysis procedures imparts the experimentalist with the information necessary for a meaningful assessment of “Type B”, systematic errors.

SI Traceable Diffraction Measurements on the NIST Parallel Beam Diffractometer

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Construction of the NIST Parallel Beam Diffractometer (PBD) was initiated some 15 years ago. The machine embodies a range of features that render it capable of performing SI traceable measurements of powder and thin film structures. These include: rotating anode X-ray source, a full range of interchangeable optics and a Theta / Two-Theta goniometer assembly featuring optical encoders and vertical rotation axes. We have just completed a series of upgrades which improve not only its measurement capability but will also address maintenance and reliability issues. This lays the groundwork for a facility which will provide full-circle angular accuracy on both Theta / Two-Theta stages provable to better than 0.05 arcsec. Critical X-ray optics of the instrument have been characterized with the NIST lattice parameter comparator, the “delta d” machine, to establish SI traceable character. These, intern will be used to characterize the performance of the mirror optic(s) used for incident beam preparation, providing an SI traceable spectrum and known geometry. The unique feature of this instrument will be its ability to carry out diffraction measurements anywhere in angular space in which every step of the measurement is completely traceable to primary standards.

The work so far has been on establishing the angular measurement scale via circle closure for measuring long-range errors and a continuous-motion data collection technique to measure the short-range errors. We will discuss how the circle closure is carried out using a 'virtual polygon' provided by a permanently installed third stage. This permits the long range errors to be re-measured in a few hours without disturbing anything else on the instrument setup, allowing the state of the calibration to be ascertained whenever a critical measurement is provided.

The establishment of the spectrum and shape of the X-rays transmitted through the incident beam optics is the critical second step towards SI traceable measurements. This will be done by passing the beam through a pair of three bounce Si 440 channel-cut crystals, one on each of the two diffractometer stages and, using the angular scale we have established, and a Dectris detector, observe the shape and position of the transmitted beam as a function of the two crystal angles. The result of this can be analyzed to provide detail about the spectrum and geometry of the beam. The first crystal is mounted on the Theta axis while the second is fixed on the detector arm of the Two-Theta axis. The motion in either axis will then result in an angular change between the two optics; however the beam will “walk” across the face of the optic and the detector. The optics were designed with this in mind to provide a band pass more than sufficient to characterize the Cu Kα emission spectrum. The silicon used for these crystals has a lattice parameter which is directly traceable to an iodine-stabilized laser primary standard, through a measurement of the WASO 4.2 material via the NIST lattice comparator.

The Powder Diffraction File:
Recent Developments In Quality Control

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The new Powder Diffraction File™, housing more than 760,000 diffraction patterns and 200,000 crystal structures, has a wealth of information that a materials scientist can take advantage of in various ways, from materials identification,characterization to design. Various structural and chemical classifications implemented in the database will be presented in detail. These classifications are important in data mining studies and optimizing pattern search/match methods. While using any database in materials characterization, it is important to know the quality of the crystal structure or diffraction pattern found in the database. With varying quality of published data in the literature, database editorial review processes had to adopt rigorous data evaluation methods to classify data based on its quality. Every entry in the Powder Diffraction File™ has a quality mark and editorial comments describing the error and the correction. Results of the analysis of the quality of the crystal structures (~500,000) published over the years will be discussed along with the most common errors found. The recent developments in Powder Diffraction File will be presented. International Centre for Diffraction Data has been encouraging its Grant-in-Aid recipients to use NIST SRM while submitting powder diffraction patterns to the database. The quality enhancement in such submissions will be presented.

Developments in Synchrotron Instrumentation

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Since the last APD conference in 2001, synchrotron powder diffraction beamlines continue to be constructed in line with the opening of new national sources around the world. As is well understood, the combination of high flux, collimation, and wavelength tunability of synchrotron radiation allows powder diffraction to be optimized for a wide range of high quality crystallographic, analytical, and in-situ studies on diverse materials, from those that can be classified as hard condensed matter through to protein crystallography. The ability of powder diffraction to investigate systems of fundamental physical and chemical interest and also those of direct technological relevance makes a powder diffraction beamline an essential component for a modern central facility carrying out materials research. Powder diffraction beamlines are often among the most productive at their home institute.

Whereas superficially a powder diffraction experiment needs no more than a beam, a sample and a detector, dedicated beamlines are designed to produce high quality data. The last decade has seen significant progress in a number of areas that enhance instrumental performance. These include, for example, building powder diffraction beamlines on dedicated insertion devices such as undulators where they benefit from the very high brightness of these powerful sources, and very high flux density at the sample. This is generally an advantage, though radiation damage or beam heating effects can be a worry. Powder diffraction is also being exploited at harder energies than before, with ≈0.4 Å now a respectable wavelength for a high resolution beamline where capillary geometry can be adopted without concerns about sample absorption. A spinning capillary sample reduces the tendency for preferred orientation effects significantly. The use of hard energies has also been exploited by the PDF community where measurements to high Q are essential. Detectors have made significant progress, with very fast position-sensitive detectors, either one-dimensional or two-dimensional, making significant improvements to time resolution for in-situ studies, and throughput for crystallographic investigations. High throughput has required the development of robotic sample changers to make efficient use of beamtime. Focusing of the beam via compound refractive lenses has also contributed to instrumental resolution and performance. Use of the pulse structure of the synchrotron source is not usually considered an attribute, more a hindrance as it can cause pile-up problems with photon-counting detectors. Nevertheless, specialized pump-probe powder diffraction experiments have exploited the pulse structure to give time resolution below 1 ns.

Neutron Powder Diffraction with Long Pulses at the European Spallation Source (ESS)

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Powder diffraction is the cornerstone of materials characterisation, determining where atoms are in space, without which it would be impossible to relate structure to physical properties. Neutron powder diffraction is highly complementary with X-ray powder diffraction for structure determination and refinement. Optimization of powder diffraction instruments at neutron sources has lead to the predominance of angle dispersive instruments at reactors and the use of the wide wavelength band time-of-flight (t-o-f) technique at sharp-pulse spallation sources. With the unique long pulse neutron time structure of ESS we have the opportunity to rethink this paradigm.

The European Spallation Source will be a 5MW long-pulse spallation source, the first of its kind. The long-pulse offers unparalleled source brilliance, while at the same time a time-averaged flux commensurate with the most powerful research reactors available today. This means that instrument concepts based on either the t-o-f technique or crystal monochromators are possible. Within the ESS reference instrument suite there are 5 powder diffractometers: thermal powder diffractometer, bispectral powder diffractometer, pulsed monochromatic diffractometer, extreme conditions instrument and the materials and engineering diffractometer. Other concepts are also under consideration that combine powder diffraction with other neutron scattering techniques such as SANS, imaging and/or inelastic scattering. The motivation behind each instrument concept will be presented, highlighting the advantages over existing instrumentation and limitations that the long-pulse time structure imposes.

The ESS is a European large-scale facility project with 17 international partners based in Lund, Sweden, with construction planned to begin in 2013. It is scheduled to deliver its first neutrons to target in 2019 and have its full design complement of 22 public instruments by 2025. The ESS will offer new opportunities to all areas of scientific research, as well as complementing the existing neutron sources, both reactor and spallation-based, in Europe. The instrument suite is currently under development and provides an opportunity to investigate and evaluate novel instrument concepts that fully utilise the possibilities presented by a long-pulse source.

Laboratory Powder Diffraction: The Last 10 Years

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The last 10 years have seen many developments in the field of laboratory powder diffraction – both hardware and software. High speed detectors in particular have seen rapid development with new, improved models appearing every year so it seems. The increase in speed and reduction of noise is undeniable, but in some circumstances the higher backgrounds can adversely affect the accuracy of results. Back in 1994, results from the CPD round robin set the benchmark of a peak/background ratio of 50 to obtain accurate structural information.

Some other 'improvements' in instrumentation had an adverse effect on some aspects of accuracy whilst striving to improve another. As is often the way, a decision has to be made as to the priority in terms of data characteristics. Conversely some configurations with highly desirable characteristics are very rare due to the cost compared with more conventional setups.

The inevitable compromises required for multi-user environments can impact on data accuracy for some or all of the users. Sample fluorescence is an issue that preoccupies labs where functional oxides are the bread and butter. Consider what configuration would be best where you have users with both Fe and Mn-containing samples – it is a serious headache. Very recent detector developments may provide an option other than MoKα radiation, but might not be available to all. One should also be aware that some apparent improvements in data quality may hide underlying issues that impact accuracy. Secondary monochromators and energy discriminating detectors may improve the appearance of the data in terms of much-improved peak-to-background but any underlying sample fluorescence is still there impacting the particle statistics due to a lower sampling volume.

The specifications of purchased systems are often driven by factors other than simply data quality and accuracy. In the current budgetary climate, unscientific aspects such as price and 'political' justification of spending in organizations play have an increasing impact on decisions and may indeed affect developments in in-house instrumentation over the next 10 years.

High Perfomance Hybrid Pixel Detector and its Applications

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High quality of experimental data is of fundamental importance for accurate and precise data analysis. Quality of the data has been improved by introducing higher intensity X-ray sources, coupled with sophisticated multilayer optics and the detectors with high sensitivity. In the field of powder diffraction, more than a decade has passed since the conventional zero-dimensional detectors were replaced with one-dimensional silicon strip detectors for faster data acquisition. These detectors have been used for measuring the powder diffraction intensity in the equatorial plane on the assumption that the specimen is of ideal. Two-dimensional detectors make possible to measure the areal intensity distribution of the Debye-Scherrer ring, giving the information such as of in-homogeneity of the specimen.

Various kind of two-dimensional detectors have been used for diffraction measurements; imaging plates, CCD cameras, CMOS cameras, gas detectors, semiconductor detectors etc. Silicon hybrid pixel detectors show outstanding dynamic range, positional resolution, frame rate, energy resolution, and signal to noise ratio compared to the others. Moreover, they can be operated with air fan cooling system. In the present talk, the latest type of area detectors, a silicon hybrid pixel detector, and its applications to powder diffraction measurements will be presented.

Critical Parameters for Instrument Alignment and Performance Verification of XRD Instrumentation

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The requirements for alignment accuracy and reproducibility of XRD instrumentation increased significantly in the past decades. This increasing demand is caused by several circumstances:

1. XRD systems evolved from single purpose dedicated instruments into multi-purpose, multi-user analytical facilities. The introduction of advanced optics has opened the path for performing measurements that require a high accuracy, reproducibility and stability of the system's alignment.
2. Modern fast detectors allow for more accurate data collection by using narrower slit settings.
3. Next to this, concepts for fast interchanging factory pre-aligned optics and stages without the necessity for the user to perform an alignment have been developed and integrated in modern XRD systems. These concepts have created the possibility of more and more applications possible on a single instrument, but they have also created new requirements for manufacturing tolerances and alignment procedures in system assembly and manufacturing.
4. The new applications that are added to the powder diffractometer often have more stringent demands than the powder diffraction application itself.

Users benefit from the increasing range of applications. The ease-of-use of a state-of-the-art XRD system allows also non-expert users to get access to perform advanced applications. They trust that the system performs as guaranteed by the manufacturer without any prior system adjustment and performance check. To fulfil this high expectation level a highly reproducible and stable system alignment is required.

In this presentation we give an overview of X-ray optics properties, instrument settings and sample properties that influence peak positions and peak shapes in a diffractogram. We discuss consequences for manufacturing tolerances of a multi-purpose system and required accuracies in X-ray instrument alignment procedures in lean manufacturing. In addition, we discuss possible strategies for the verification of the instrument alignment accuracy with e.g. NIST calibration standards by end-users.

Parametric Rietveld Refinement

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The introduction of linear position sensitive detectors and area detectors on laboratory powder diffractometers means that high quality diffraction patterns can be routinely obtained in home laboratories in a time scale of a few minutes. With high intensity/brilliance synchrotrons Rietveld-quality data can often be obtained in a few seconds. It is therefore increasingly common for a series of diffraction patterns to be recorded on a given system as a function of time, temperature, pressure, chemical environment or a range of other external variables.

Refining a structural model against multiple data sets has been common practice for many years: on a time-of-flight neutron diffractometer one typically fits data from multiple banks simultaneously; combined refinement against X-ray and neutron data sets can give better precision on coordinates fo systems such as heavy metal oxides where the contribution of the metal sites may dominate X-ray data. The advent of modern “programmable” refinement programs such as Topas and Topas Academic and increases in computational power of desktop computers means that it is now possible to simultaneously refine structural models against tens or thousands of data sets using user defined models to describe the evolution of the system – parametric Rietveld refinement.

In this overview presentation I will discuss the pros and cons of parametric Rietveld refinement and try to highlight when the approach should and should not be used. In appropriate cases the method can be used to: obtain more precise information from ensembles of diffraction data; to ensure that one extracts the “correct” answer from the data in cases where the “incorrect” answer gives a better Rietveld fit; to rapidly extract “non-crystallographic” information from data; or to reveal when the behaviour of an evolving system is more complex than had been expected.

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Developments in Detector Technology for X-ray Diffraction

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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. These new technologies offer improvements in both data quality and also acquisition throughput. The principles and characteristics of recently developed sensors will be reviewed including hybrid pixel array detectors, microgap gaseous detectors, monolithic CMOS sensors and energy dispersive imagers.

Multilayer Optics for X-ray Diffractometry

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Even 100 years after the first publication of the Bragg equation, there are still developments which are mainly based on this fundamental law. One of these developments are multilayer mirrors which are used for beam shaping of X-rays. The multilayer mirrors act as an artificial two-dimensional crystal with the typical distance d of the Bragg equation. It is advantageous that this distance can be changed and thus adapted to the specific application and setup.

Using a parabolic form for a multilayer mirror a divergent x-ray beam will be collimated. With an elliptical mirror the beam will be focused. The substrate is usually made of e.g. Si, fused silica, quartz, or zerodur. It is either bend to the desired form or it is prefigured and the form is polished into the material. The substrate is coated with the multilayer; usually about 100 layers of spacer and absorbing material are applied. As spacer, materials like C, B4C, or Si are used, to absorb X-rays W or Ni are mainly used. The multilayer on a curved substrate must have a lateral gradient to fulfill Bragg's equation at all points along the mirror. The last step in the production of a multilayer optics is often the combination of mirrors, e.g. to get a Kirkpatrick-Baez or side-by-side setup.

A multilayer mirror for home-lab systems is up to 150 mm long, for use at synchrotron beam lines up to 500 mm. The maximum available length of a mirror is often limited by the size of the coating chamber.

The quality of the X-ray beam behind a multilayer mirror depends on the quality of the substrate curvature, its roughness and the precision of the coating. The shape tolerances are below 100 nm, the thickness deviation of a multilayer from its designed value must be below 1%. This means that a deposition precision in the picometer range is needed.

In the last ten years, the multilayer optics reached such a high quality and reliability that they are not anymore a limitation of the needed instrument quality. In XRD for a lot of instrumental set-ups multilayer optics became indispensable. For high-end applications at synchrotrons the multilayer showed their potential by focusing beams down to 50 nm and below. At the same time, several commercial companies and scientific groups also improved the cost-effectiveness within a fruitful and fair competition.

In the future optics for X-ray sources like microfocus sources, liquid metal jet sources, and synchrotron experiments with sub-micrometer sized beams and energy ranges of 5 keV to several 10th of keV will be routinely designed and manufactured. The quality of the substrates will increase to fulfill the demand of very small spots of focusing mirrors and very homogeneous spots of collimating mirrors.

Structure Validation in the Submission, Review and Publication Process

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The International Union of Crystallography (IUCr) publishes eight journals covering a range of crystallographic disciplines. This requires a variety of approaches in dealing with the submission, validation, peer review and publication of research articles and their associated data. We will present an overview of this process from the pre-checking of crystal structure data through to the online publication of the article, with an emphasis on how data checking and validation are integrated into the submission and review process. The tools that are available to authors, reviewers, referees and readers will be discussed.We will investigate the improvements that can be made to this process for powder-diffraction studies.

Reliable and Highly Accurate Molecular Crystal Structures from a Combination of XRPD and DFT-D

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Dispersion-corrected Density Functional Theory (DFT-D) has been shown to reproduce small-molecule crystal structures very accurately. In a validation study against 225 high-quality single crystal structures, the average Root Mean Square (RMS) Cartesian displacement upon energy-minimisation with the unit cell allowed to relax was only 0.084 Å (Van de Streek & Neumann, 2010). Crystal structures containing errors were shown to consistently give RMS Cartesian displacement values greater than 0.30 Å, whereas for correct crystal structures this value never exceeded 0.25 Å. This makes DFT-D highly suitable as a source of complementary data for confirming the correctness of a crystal structure determined from powder diffraction data, or for selecting the correct structural model from a set of alternatives that cannot be distinguished based on the experimental powder diffraction data.

However, there is another use for DFT-D calculations in crystal structure determination from powder data. Experimental X-ray powder diffraction data, especially laboratory data, is often limited to a real-space resolution of about 1.5 Å: enough to locate a molecule as a whole very accurately, but not enough to refine bond lengths and bond angles with great accuracy. In this presentation, we will show that molecular geometries from DFT-D reproduce high-quality single crystal geometries within about 2%. With bond lengths being of the order of 1 Å, this means that DFT-D calculations can achieve an accuracy of around 0.02 Å on bond lengths. The DFT-D calculations can be used as an independent source of information that can be fed into the Rietveld refinement in the form of polymorph-dependent restraints, for example in the program TOPAS (Coelho, 2007).

The combination of XRPD and DFT-D is therefore able to produce molecular crystal structures that are both more reliable and more accurate than would be possible through the use of XRPD alone (see e.g. Brüning et al., 2011, Naelapää et al., 2012, Van de Streek, 2012).

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Application of Maximum Likelihood Method to Powder Structure Refinement

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A mathematical formula for a new analytical method based on maximum likelihood estimation for structure refinement using powder diffraction data has recently been proposed [1]. The results of the structure refinements from the powder diffraction data of fluorapatite $Ca_5(PO_4)_3F$, anglesite $PbSO_4$ and barite $BaSO_4$, available as test data for Rietveld refinement programs, have been demonstrated. The structure parameters of $Ca_5(PO_4)_3F$ and $BaSO_4$ optimized by the new method have become closer to single-crystal data than those optimized by the Rietveld method, while the structure parameters of $PbSO_4$ are almost unchanged by application of the new method. It has been suggested that the diffraction data of $Ca_5(PO_4)_3F$ and $BaSO_4$ are strongly affected by the particle statistics but the data of $PbSO_4$ are not.

In this study, fine (~1μm) and coarse (50~100μm) powder samples of $BaSO_4$ were prepared and characterized by SEM observation. It has also been confirmed with a single-crystal X-ray equipment (Bruker AXS, SMART APEXII, MoKα-source) that the particles in the coarse powder sample of BaSO4 are fundamentally single crystals. Two sets of powder diffraction data for stationary and rotating specimens for each sample powder were collected with a CuKα-source laboratory powder X-ray diffractometer (Rigaku RAD2C). The penetration depth (reciprocal of linear absorption coefficient μ) of bulk $BaSO_4$ for CuKα X-ray is estimated at $\mu^{-1} = 10.7\mu m$.

No significant differences in atomic coordinates optimized by the Rietveld method and maximum likelihood estimation are found for the fine powder samples and rotating coarse powder specimen. The structure derived by the Rietveld refinement from the powder diffraction data of the stationary specimen of the coarse $BaSO_4$ powder was heavily deviated from a reasonable structure, but the structure optimized by the maximum likelihood estimation from the same diffraction data were coincided with the single-crystal data almost within the statistical errors.

Attempts to apply the current method extended to (i) multiphase crystalline powder mixture and (ii) possible errors in mechanical or model diffraction angles will also be presented.

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Crystal Structures from Powder Diffraction: Principles, Difficulties and Progress

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Structure solution from powder diffraction has undergone an intense evolution during last 10 years, but is far from being a routine. The methods are generally divided into two groups: intensity extraction based algorithms working in the reciprocal space (RSM), and pattern modeling based algorithms (global optimization methods) working in the direct space (DSM) and using the chemical knowledge from that space. Hybrid methods iterating between both spaces are known too, but a decisive criterion to classify a method is whether it requires integrated intensities of individual peaks in a powder pattern (intensity extraction) or not (pattern modelling). For a comprehensive review on the methods see [1].

Powder diffraction uses same methodology for structure solution regardless the nature of the compound to be investigated, but the careful selection of the solution algorithm according to the compound may considerably improve the success rate. The separation of compounds by inorganic/organic boundary is of less importance for the diffraction than the knowledge how the atoms build up larger building units and the crystal itself. This does not mean a particular difference for RSM, however, it becomes important for DSM. The structure solution algorithm working in the direct space has to know how to define basic structural units (BU) of the crystal which are then manipulated (optimized) by the algorithm. A molecular/non-molecular boundary is therefore relevant for the choice of a structure determination method. A molecule is naturally a BU that can be moved in the unit cell, and deformed from its planar form. No sharing of atoms between the molecules occurs. Non-molecular compounds – also called extended solids – are constructed by bonds that extend “infinitely” in three dimensions through a crystal. These non-molecular crystals usually crystallize with higher symmetries, and atoms often occupy special Wyckoff positions. Moreover, the presence of high-order symmetries leads to a fragmentation of BUs, as any group of atom (e.g. an octahedron) can be located on a symmetry element, so that only part of the atoms of a symmetry-constrained BU are truly independent. Finally, the actual arrangement in space between BU and relatively to the symmetry elements of the unit cell, are a priori unknown. To cope with this Deem and Newsam used a merging term in the cost function [2], which has then evolved in a general and simple algorithm called Dynamical Occupancy Correction (DOC) implemented in the DSM program FOX [3].

Current challenge of powder crystallography is ab initio crystal structure determination on real samples of new materials with specific microstructures, characterization of intermediate reaction products from in situ, *in operando* studies, and novel phases from in situ studies of phase diagrams. On the other hand the intense evolution of electron diffraction in last years, especially providing experimental (precession) and theoretical (still under intense development) solution to strong dynamic scattering of electrons, smears the traditional frontier between poly- and single-crystal diffraction. Finally, the computational chemistry, theoreticians hand-in-hand with crystallographers, have developed a tool called DFT based crystal structure refinement, which becomes unavoidable step in the validation of crystal structures obtained from powder diffraction.

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Accuracy in Powder Diffraction: New Methods for High Resolution *in-situ* Data

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Due to recent upgrades of synchrotron- and laboratory sources and the parallel development of new position sensitive detectors and reaction cells, it is now possible to collect a vast amount of powder diffraction patterns *in situ* in dependence on external variables (i.e. temperature or pressure) with a time resolution in the second or even sub-second regime thus allowing to track many structural changes in detail [e.g. 1]. The real challenge is to get the maximum amount of information from these high quality data. In the first part of this presentation, some advances concerning parameterization of the temperature/pressure dependence of spontaneous strain, symmetry modes, polyhedral tilts, order parameter, strain-order parameter coupling etc. are presented. In the second part, the application of the method of maximum entropy to *in-situ* XRPD data as a complementary method to Rietveld refinement is introduced. Under the simple assumption that structural changes within a crystalline phase vary continuously upon external variables like temperature or pressure, it is possible to parameterize certain parameters by a suitable function in dependence of the external variable(s). In this so-called surface or parametric refinement, all powder patterns are refined simultaneously, drastically reducing the number of

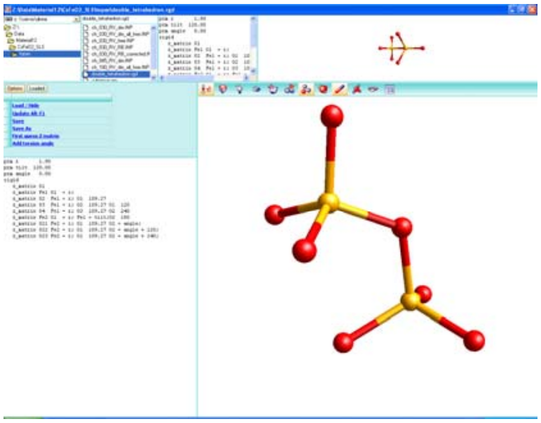

Figure 1: Flexible description of a double tetrahedron via z-matrix notation using Topas (Bruker AXS).

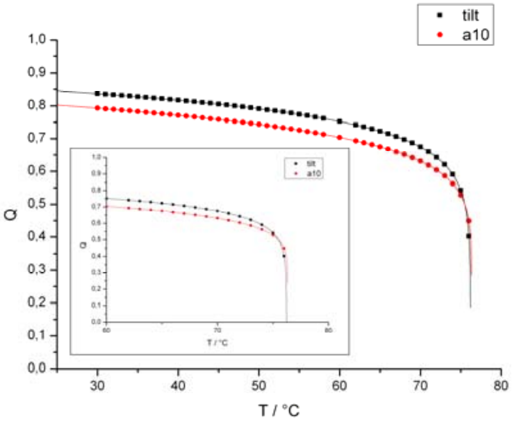

Figure 2: Example for a parameterized symmetry mode (red) and the equivalent polyhedral tilting (black) revealing the temperature dependence of the order parameter.

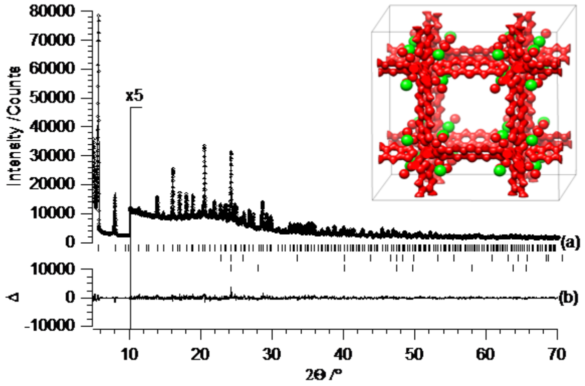

Figure 3: Scattered X-ray intensity for MFU-ML MOF loaded with Xe at T= 110 K as a function of diffraction angle 2 Θ and three-dimensional MEM electron-density maps based on F_{obs}+G-constraints.

parameters, thus leading to higher stability of the refinements and more accurate results. Suitable variables which can be subjected to parameterization are spontaneous strain, atomic coordinates, polyhedral tilting (Fig. 1), symmetry modes, magnetic modes etc. In case of displazive phase transitions, the application of this techniques allows for the direct determination of physical quantities like order parameters (Fig. 2) [2, 3].

As a complementary approach to Rietveld analysis, the Maximum Entropy Method (MEM) is a powerful tool that can be used for reconstruction of the accurate electron-density distribution in particular for powder diffraction data in dependence on external variables like temperature [4] or gas pressure [5] etc (Figs. 3, 4). Application of this method to powder X-ray diffraction data opens new possibilities in crystallography, since a parameter-free distribution of the electron density in the crystal structure can be obtained. MEM also allows the extraction of novel information from powder diffraction data that cannot be obtained from standard Fourier analysis [1-3].

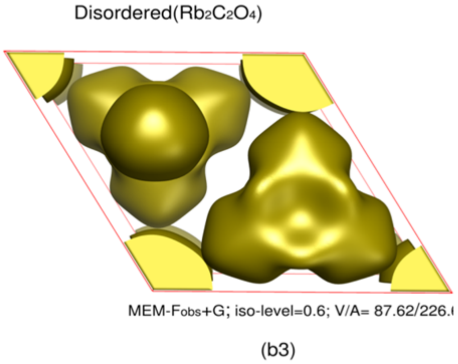

Figure 4: Three-dimensional MEM electron-density map of disordered rubidium oxalate at T = 860 K based on F_{obs}+G-constraints.

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Non-ambient Diffraction in the Laboratory Environment

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Non-ambient diffraction in the laboratory poses challenges above and beyond those required for conventional, ambient diffraction. The quest to optimize systems to be fit-for-purpose or beyond becomes more complicated when non-ambient measurements are required, often on the same instrument as conventional measurements.

A number of commercial developments in the area of non-ambient cells have been made in the past 10 years such sample displacement compensating mounts in high temperature ovens and pressure cells for hydrogen storage studies. However, many non-ambient cells are still designed and built ‘in-house’, so it up to the experimentalist to choose the design and materials of the stage as well as the instrument and experimental strategy to produce the best data possible. In extreme cases improved ‘accuracy’ may simply be the difference between getting data and zero data.

The design of the some of the more challenging sample environments may dictate the use of higher energy X-rays such as Mo$K\alpha$ and Ag$K\alpha$, which then impacts on the optics and detectors that may be used. For instance, high-energy setups using beta-filters have to contend with severe absorption-edge effects that greatly hinder accurate peak fitting. Algorithms to model these effects expand the options available while maintaining reasonable data accuracy. A trend towards the use of parallel-beam optics in reflection geometry to avoid sample roughness and displacement artefacts has an impact on the data resolution and peak shapes, degrading the accuracy of the data that can be obtained. Some unusual optical configurations such as the ‘twin mirrors’ regains much of the resolution with an improvement in the accuracy that can be obtained but has different issues. One thing that hasn’t changed over the last 10 years is that the ideal setup to do everything still doesn’t exist – weighing up priorities and compromise are still an integral part of the process.

A number of examples will be presented to highlight the considerations that can be required to optimize the experimental design. They will demonstrate the additional repertoire of hardware and software choices that are at the experimentalist’s disposal.

Temperature- and Time-Dependent Cell Parameters During Order-Disorder Phase Transitions

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In situ powder diffraction studies to study the phase evolution of reacting systems or to monitor structural phase transitions as a function of temperature or pressure are now relatively common place. In most cases the time spent collecting data under a given set of experimental conditions is determined by the rate at which statistically acceptable data can be collected. For synchrotron or neutron experiments, timescales are often simply determined by the length of beamtime allocated divided by the number of experimental conditions that need to be explored.

In this presentation I'll describe how for inorganic functional materials it can be extremely important to obtain a full picture of the time evolution of diffraction patterns for systems that undergo structural phase transitions, particularly for systems with transitions at temperatures where the kinetics of the process may be slow. I'll discuss how for some materials it is vital to monitor the diffraction patterns over a period of days or weeks to gain a complete picture of the structural changes that can occur. For these systems in-house in situ experiments can be far more informative than experiments at central facilities. Examples will be drawn from a range of materials including frameworks that show negative thermal expansion, the $SnMo_2O_8$ zero-expansion system and transition metal oxychalcogenides.

Current State of Quantitative Phase Analysis

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Quantitative phase analysis (QPA) is one of the most useful aspects of powder diffraction and separates it from many other analytical techniques in its ability to characterise the contents of a sample. Identification and quantification of the individual components of a multi-phase sample is achieved directly from the structural information contained in a diffraction pattern rather via inference from its bulk chemistry. This reliance on structure enables, for example, the direct quantification of polymorphs which may not be distinguished by chemistry. Powder diffraction patterns may be collected rapidly in a variety of sample environments making the technique suitable for industry and research alike.

Sounds too good to be true? It is. The reality is that powder diffraction, whilst capable of fast, accurate analyses under specific conditions, is too often poorly performed and interpretations are made which extend well beyond the reach of the data. It is far from being a “one-size-fits-all” technique and not all samples and experiments are created equal. Whole pattern (Rietveld) techniques routinely report “errors” in the analyses. However, these are errors only reflect the measure of fit between the model and observed data. Accuracy is the agreement between the analytical result and the true value, while precision is the agreement between results if the analysis is repeated under the same conditions. Precision may further be split into (i) repeatability which is the agreement between repeated measurement and analysis of the same specimen, and (ii) reproducibility which additionally includes re-preparation of the sample. Hence, the Rietveld errors never represent the real error in the quantification and consequently provide a misleading impression of the true accuracy of the determination.

A very important thing with QPA via powder diffraction is to have realistic expectations regarding the result. This is achieved by understanding the factors associated with the sample and the data collection strategy which may introduce errors to the analysis. These may be mitigated to some extent but must often be allowed for in the interpretation of the results. Determination of the absolute accuracy of QPA from powder diffraction in isolation is virtually impossible.

Do not despair though! A measure of accuracy can be achieved if the contents of the sample can be verified in some other way; for example, by comparing the total chemistry of the sample calculated from the QPA and micro-chemistry of each phase with the bulk analysis derived using conventional chemical analysis. However, absolute accuracy, whilst nice to have, is not always necessary in the provision of valuable information. QPA via powder diffraction routinely provides precise results which are correct in a relative sense. That is to say, that comparison of differences between samples is valid within the level of precision. This is particularly useful in in situ studies where changes in the sample are observed in successive diffraction patterns and used to interpret reaction mechanisms.

This presentation will discuss accuracy in QPA as assessed within the diffraction community and explore the factors which affect this. Determination of the accuracy of any given measurement will be considered as will the pitfalls which await the unsuspecting analyst (and feature in many publications).

Accuracy in Quantitative Phase Analysis of Complex Mineral Assemblages: A Decade of Reynolds Cup Round Robins

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Since the Accuracy in Powder Diffraction – III meeting in April 2001, The Clay Minerals Society have conducted biennial quantitative mineralogy round robins. The Reynolds Cup competition, as it is called, is named after Bob Reynolds for his pioneering work in quantitative clay mineralogy and exceptional contributions to clay science. Established in 2000, the first contest was run in 2002 with 40 sets of 3 samples prepared and composed of mixtures of purified, natural and synthetic minerals commonly found in clay bearing rocks and soils that represent realistic mineral assemblages.

2012 marked the 6th Reynolds Cup quantitative mineralogy competition where a total of 74 sets of three samples were distributed to participants from 25 countries. Samples were made available to individuals in commercial, industrial, government, or academic laboratories. Any method or a combination of methods could be used to obtain the most accurate quantitative phase analysis. X-ray diffraction was dominantly the method of choice for quantifying the mineralogy of the sample mixtures, however, a multitude of other techniques were also used to assist with phase identification and quantification.

A summary of the 6 contests between 2002 and 2012 are given in Table 1. The number of participants, and more importantly, the return rate has steadily increased since 2002 despite the highly complex mineral assemblages. The accuracy of a particular quantification is judged by calculating a “bias” for each phase in an assemblage. Determining exactly the true amount of a phase in the assemblage would give a bias of zero. Average biases per mineral phase for the winners of the first 4 contests between 2002 and 2008 remained relatively constant at a little under 1%. Since 2010 the contest was assessed in greater detail with the clay minerals in particular being judged to a higher level. For example, dioctahedral 2:1 clay minerals (muscovite, illite, illite-smectite and smectite) and trioctahedral 2:1 clays minerals (saponite, biotite and vermiculite) were grouped together prior to 2010 but were assessed separately in 2010 and 2012. As a result of this closer scrutiny the average bias per mineral phase for the winners of the 2010 and 2012 contests had doubled to 2%.

Generally the higher placed participants correctly identified all or most of the mineral phases present. Conversely the worst performers failed to identify or misidentified phases. Several contestants reported a long list of minor exotic phases, likely reported by automated search/match programs but mineralogically not possible. Not surprisingly, clay minerals were the greatest source of error reported.

Plaques are presented to the top 3 finishers and the perpetual Reynolds Cup Champion’s trophy is presented to the winner during the annual meeting of the society. Winners of each contest are also given the opportunity to chair the organizing committee and prepare the sample mixtures for the following Reynolds Cup contest to be run in 2 years time.

Table 1. Summary of the 6 Reynolds Cup round robin contests 2002 to 2012

Year	*Number of participants*	*Returned results*	*Return rate (%)*	*No. of mineral phases*	*1st place total bias (%)*	*1st place average bias per mineral (%)*	*Average total bias for all participants (%)*
2002	40	15	37.5	36	32.4	0.9	90.5
2004	60	35	58.3	34	14.0	0.4	102.4
2006	64	37	57.8	42	33.8	0.8	138.1
2008	53	42	79.2	35	35.2	1.0	162.3
2010	76	63	82.9	42	87.8	2.1*	269.2
2012	74	62	83.8	40	72.0	1.8*	213.4

* the method for assessing the clay biases were changed for the 2010 and 2012 contests

Rietveld Refinement of Real Structure Parameters of Disordered Clay Minerals in Phase Mixtures

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X-ray diffraction (XRD) of powdered materials is one of the most common methods used for structural characterization as well as for the quantification of mineral contents in mixtures. The presence of clay minerals in mixtures makes the application of the Rietveld method difficult due to frequently occurring disorder effects. These effects can be divided in two groups. The first one affects the hk reflections and consists of randomly occurring translations and/or rotations of the layers relative to each other. The amount of these translations or rotations may be well defined (e.g. b/3 translations or n 120° rotations) or totally random (turbostratism). The second group of disorder effects consists of irregular sequences of layers with different thicknesses and affects the basal reflections. It was shown recently that structural models describing hk affecting disorder effects can be combined with models for disordered mixed layering for a quantitative phase analysis based on the Rietveld method (Ufer et al., 2012).

Another difficulty which has to overcome is the structural alikeness of layer silicates, e.g. smectites and mixed layered illite/smectites. These two minerals both consist of stacks of 2:1 layers and differ only partly by the content of the interlayer space. The similar lattice constants lead to strong overlapping of the reflections and consequential correlations, which is a general problem in powder diffraction. Due to this, it is necessary to restrain or fixate certain real structure parameters for a reliable determination of phase contents. The possibilities and the limitations of this approach were demonstrated by the refinement of simulated data and by preparing different mixtures of standard minerals.

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Powder Diffraction with Proteins

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Many proteins form microcrystals that are perfect for powder diffraction measurements. Powder methods can help to discover new polymorphic forms and study changes where single crystals do not survive, because a powder can often be produced under a wider range of growth conditions. The powder method can be used to measure unit cell parameters, identify phases, detect impurities and analyse mixtures of polymorphs. While many of these tasks seem routine, the properties of protein crystals can make it difficult to get reproducible results. Protein crystals contain a lot of liquid water, so the unit cell parameters depend not only on the protein molecule but also on the details of preparation. Changes in the mother liquor solution (pH, salt, humidity etc) and also exposure to X-ray radiation can all perturb the unit cell.

Some proteins give exceptionally good powder patterns at room temperature; the intrinsic line shape from the sample is very narrow. Protein samples stretch current instrumentation as the unit cells are large and the materials are very sensitive to radiation damage at room temperature. Synchrotron powder patterns are sufficiently rich to refine the molecular structure of small proteins, with as many as a thousand atoms, if the refinement also uses stereochemical restraints. Multiple datasets help these refinements if the unit cell changes slightly as this helps to untangle the accidental peak overlaps in the data. Parameter reduction constraints can also greatly improve the data to parameter ratio. So far all of the structures refined from powder data have been built from similar molecular structures that were already known. An approximate model for the molecule is located in the unit cell before the structure is refined. Attempts at *de-novo* structure solution have so far revealed the shape of a protein molecule but not the internal details.

Structure refinements do improve as the data improve, but for larger proteins the powder overlaps seem to be a limiting problem. The resolution of the structures in real space, coming from the minimum d-spacing in the diffraction patterns, scales with the size of the structures. Small proteins (diameter of ~30 Å) can be refined at a resolution of ~3Å, where meaningful details emerge, and it seems the structural resolution we can obtain is about 1/10 of the diameter of the molecular complex.

Structure Solution From Powder Diffraction Data: How Reliable Are Our Structures?

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Over the last two decades, the development of crystal structure solution techniques from powder diffraction data has revolutionised our expectations of what can be achieved within this field. Advances in instrumentation, the development of algorithms and a change in ethos and approach to structure solution has taken us from the determination and refinement of small molecules to the structural investigation of proteins. In this lecture, the key advances and the impact of recent developments will be discussed, with a focus on those that have led directly to significant breakthrough in the complexity and number of organic crystalline structures determined by powder diffraction data [1-3].

Examples will be presented to demonstrate the current state-of-the-art in application, including forms from across the pharmaceutical and biochemical sciences, and the structure elucidation of molecular materials designed with structure-property relationships in mind. With the boundaries of structure determination from powder diffraction data still expanding, these new developments will also be discussed in the context of data limitation, and the accuracy and precision of structures obtained. Specific examples will be presented from the area of crystal engineering and molecular adducts, in which structure solution from powder diffraction data has been utilised, but where reliable structural details regarding hydrogen bonding networks, and the interpretation of protonation and isomerisation are vital.

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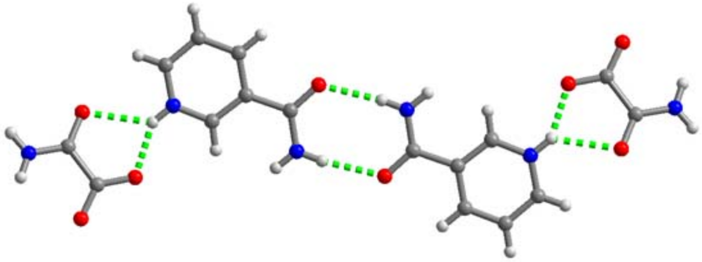

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The Impact of Powder X-Ray Diffraction on Mineral Science, Mineral Processing and Process Optimization

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Powder X-ray diffraction (XRD) has seen an increased application in the field of mineral science and mineral process optimization. With the increased emphasis on ore body characterization (geometallurgical evaluation) before mining and processing actually commences, the mineralogy and mineral behaviour of the ores are evaluated using a number of analytical techniques, including XRD methods. The method is however limited to ores that contain appreciable amounts (>1% of valuable minerals). This effectively excludes the base and precious metal ores.

Accuracy in mineral and phase quantification by XRD has been the focus of a number of round robin studies and these have highlighted the problems associated with the method, and the need for careful attention to aspects such as micro-absorption and preferred orientation, among others. However, the minerals industry deals with large numbers of samples that need to be analysed rapidly and accurately. Mass balance calculations assessing mineral processing operations quickly identify shortcomings in the method and its compatibility with chemical analysis must be continually assessed. Usually the problem lies with XRD and there is a need for more reproducible and accurate analysis.

XRD analysis is also used in process optimization and examples of its application in iron ore assessment are given. The removal of certain key elements is dependent on the ore mineralogy and this is variable for different ores. Mass balance analysis is key to the assessment of different ores with regard to their upgrading. Progress in on-stream analysis using XRD is also discussed.

Analysis of high temperature reactions by *in situ* XRD methods is key to the understanding of the sintering behaviour of iron ores. Recent work using both laboratory XRD and synchrotron sources have contributed significantly to our understanding of the role of different phases in the sintering reactions and their contribution to the strength and reducibility of the resultant sinters. Important aspects such as the need for accurate structural data for the major phases are highlighted.

High temperature XRD methods have also been used in kinetic studies of oxidation reactions in titania slags containing single phase pseudobrookite. These studies have shown that some reactions take place at relatively low temperatures and are accompanied with extensive decrepitation of cast slag blocks that impact negatively on subsequent fluidised bed processes. Again, since the reactions are driven by the development of anisotropic stresses, accurate measurement of lattice parameters are required. There is therefore a need for reliable methods of phase characterization at high temperature and also for the development of high-temperature diffraction standards.

XRD suffers from a number of shortcomings that limit its routine use in the minerals industry. The method suffers from poor mineral or phase sensitivity below ~0.5% by mass,

(high detection limits compared to quantitative SEM techniques). It is sensitive to preferred orientation, especially of layer silicates as well as micro-absorption effects. Comparability between sample minerals and crystallographic standards sometimes are problematic, complicating the choice of suitable crystal structures to use. Attention should be given to methods to quantify phases at low contents (less than 0.5%) , and development of more robust quantification methods dealing with preferred orientation, especially of layer silicates, and micro absorption.

Quantitative Rietveld XRD Mineralogy of Copper and Molybdenum Ore Products

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At Freeport-McMoRan and its predecessor Phelps Dodge, X-Ray Powder Diffraction has developed from a method used to provide qualitative data on occasional curiosity samples to a routine method to provide quantitative mineralogy on hundreds of samples/per day. Advances in instrumentation such as high-speed detectors have made it possible to provide XRD data at the same turnaround time as chemical data for daily production samples such as blast hole samples from current mining production benches and daily feed and concentrate samples from froth-flotation mills. Longer term projects such as feed and tail mineralogy from leach residue experiments and mineralogy of exploration diamond drill holes are also performed along with the ever-present troubleshooting and curiosity samples.

The laboratory has developed from the part-time attention of microscopy mineralogists in 2000 to a single full time XRD mineralogist in 2002 to today's lab of 4 mineralogists and 3 technicians doing Rietveld analysis supported by 1 mineralogist, 1 LIMS coordinator, 1 supervisor and 10 technicians performing XRD and NIR sample preparation. In 2009 a robotic sample prep circuit with automated belt feed to diffractometers and NIR analyzers was commissioned with a design capacity of 550 samples/day. The system was designed around sample presses that were developed specifically for XRD (back-loading at low pressure against a frosted surface) rather than using XRF presses (front loading at high pressure against a polished surface).

The development of the laboratory using sound scientific principles and practices learned from former APD conferences, ICDD (and SUNYA) X-ray Clinics and the Denver X-ray Conferences will be discussed. QA/QC and method development will be addressed.

Use of Cluster Analysis of XRD Data for Ore Evaluation

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The use of high speed detectors let X-ray diffraction (XRD) become an important tool for quality and process control in mining industries. Decreasing ore qualities and increasing prices for raw materials require a better control of ore grades and a more efficient use of energy for processing. Therefore more frequent analysis of samples for optimization of the mine planning and exploration as well as tools for fast translation of changing ore qualities into adaptations to processing (flotation, separation, sintering etc.) are required.

Traditionally grade control of ores has relied on elemental analysis of sampled materials such as blast cone drill cuttings. This analysis provides a standard elemental suite that is used in grade control to assign mined material as grade blocks to high grade, low grade or waste destinations. Assessment of the mineralogical composition of such samples is currently more subjective however, relying on visual inspection of collected samples and interpretation of the elemental data.

X-ray diffraction (XRD) analysis in combination with data clustering has been successfully trailed to establish the mineralogical composition of a sample to supplement the elemental data and supply the mine planner with more details information about the ore distribution and possibility of ore up-grading.

Case studies for grade control of ores and sinter material using cluster analysis in combination with full pattern quantification will be demonstrated.

Main features and benefits of the theory of the statistical cluster analysis approach used to process XRD data and the possible use within an automated environment are subject of the presentation as well.

Complex Modeling: Towards More Robust Nanostructure Refinements

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Many modern materials under study for technologies from energy to the environment to health, are highly complex, often heterogeneous and nano structured. A full understanding of the structure requires us to go beyond crystallography and to study the local structure, which is a major experimental challenge. There are recently emerging powerful experimental developments, for example, using the atomic pair distribution function technique (PDF), among others. However a general problem is that the information content in the data is limited, and often decreases with increasing structural complexity of the problem, whereas the degrees of freedom needed to fully describe the structure increase. This can lead to an information gap. We discuss modeling approaches to study local structure in general, and describe Complex Modeling which is an attempt to close the information gap in cases where the inverse problem is ill posed. The concepts will be illustrated with examples from our recent scientific studies in areas from superconductors to pharmaceuticals.

Modeling Biomolecules in Solution: Pitfalls and Challenges

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Local structural neutron diffraction is a technique by which the local structure present in liquids and solutions can be determined. Using isotopic substitution techniques information concerning the atomic structure on the Angstrom length scale can be directly determined experimentally for systems which contain only a small number of unique atomic components - such as water or HF. For more complex systems, such as biomolecules in solution, only a subset of atomic sites can be isotopically labelled and as such a full set of atomic correlations cannot be determined by experiment alone. For these more complex systems, in practice a variety of isotopomers for each solution are measured and then the data is subsequently 'fit' by reverse Monte Carlo techniques. The pitfall to these techniques is that model is always necessarily under-constrained with respect to the variables in solution and as a result a variety of models which are consistent with the experimental data can emerge. Using other experimental techniques to feed into modeling of the neutron data is imperative for the future to provide more physically realistic models of the solutions in question. The challenge for the future of investigations on more complex biological molecules - such as proteins and DNA - is to not only add new techniques to the modeling regime but also to develop better more highly constrained types of computation to address these complex problems.

Total Scattering Developments for Nanoscale Research

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Pair distribution function (PDF) analysis, based on spallation neutron or synchrotron x-ray total scattering data, has emerged as a very promising characterization method for nanomaterials in recent years. Total scattering methods can provide information about every pair of atoms probed in a diffraction experiment, however data analysis and interpretation remain challenges as grand as the materials are complex. In this contribution we present progress in several methods developement areas that push the boundaries of extracting quantitative information from nanoscale systems. We will introduce methods for treating neutron scattering data with significant incoherent contributions from hydrogen, and describe the effects the corrections have on atomic pair distribution function data sets. We will also demonstrate determination of amorphous and crystalline phase fractions with PDF data and present recent work benchmarking particle size, shape, and surface structure signatures in total scattering analysis. Along the way we will showcase examples from a number of nanoparticle, amorphous, and disordered crystalline material systems where these developments have impacts and emphasize related challenges and software development needed for the future.

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Microstructure From Diffraction: Progress in Line Profile Analysis

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Line profile analysis is one of the fields of diffraction that received a huge boost in the last decade or so. This has not been the mere effect of the availability of faster computers. The limits and risks of the traditional line profile analysis methods (Scherrer formula, Williamson-Hall plot, Warren-Averbach method and their modification) for a quantitative analysis of the microstructure have been identified and critically discussed. The need for an accurate information on the nanoscale, where each particle matters, has lead to an elegant mathematical inclusion of a distribution of shape, size and microstrain in the most complete Fourier approach of line profile analysis. The main revolution, however, has been in the way data is handled. We moved from a deconvolutive single peak analysis to the analysis of multiple peaks with analytical profile functions (Multiple Whole Profile method) and then to an ab initio convolutive full pattern approach (Whole Powder Pattern Modelling) that can be considered the microstructural complement of the Rietveld method. An overview of those changes and their impact on the accuracy of the quantitative microstructural result, as well as some caveats for potential users will be presented and discussed.

Microdiffraction to Analyse Polycrystalline Materials

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In the last decade, x-ray methods have been developed to treat polycrystalline specimens as an ensemble of individual crystals. Crystallographic techniques developed for single crystal data have been generalized to simultaneously characterize each of the crystals in such samples. Examples of application areas are structure solution and refinement [1,2], reciprocal space mapping, characterization of sizes and strains [3,4,5] and defect populations [6]. Furthermore, methods such as 3DXRD microscopy [7,8] and DCT [9] have allowed 3D mapping of the morphology, phase, orientation, and strain of the crystals. In this way, 3D movies of the structural evolution within samples comprising up to 20,000 crystals have been made. We provide a short overview and compare the accuracy and potential of the multigrain methods to classical powder diffraction in terms of :

Strain measurements: Uniquely, the single grain methods enable the characterization of intra- and inter-grain stresses [3]. The spatial resolution of maps is improved, as averaging over an ensemble of grains is not required [4]. The resulting strain accuracy for the two methods vary, as powder diffraction tends to provide a better S/N ratio, while the multigrain methods give rise to three observables per diffraction spot; in comparison only the radial strain is observable by powder diffraction.

Grain sizes: In comparison to line-broadening studies, the grain size distribution can be studied. Furthermore size and strain is decoupled. The accuracy on grain properties such as volume, aspect ratio and assignment of nearest neighbors is discussed.

Multigrain crystallography: We will summarize a comprehensive study on the quality of multigrain crystallography solution and refinement for small crystal as well as protein work is given in [2]. As an example in an analysis of Cupric Acetate Monohydrate multicrystal data gave R_1 of 0.057, and included positions and anisotropic mean square displacement parameters of all non-H atoms. It was not possible to refine the model to anywhere near the same level of detail from powder data, A comparison of the thermal parameters showed that the parameters obtained from multigrain refinement were about 10 times more accurate than the ones obtained with the powder experiment. Furthermore, the deviations in bond distances are 2-3 times smaller for the multigrain structure compared to the powder structure.

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Internal Stresses in HCP Metals

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Hexagonal close packed metals typically exhibit elastic, thermal and plastic anisotropy at the single crystal level. When used In the polycrystalline state, the local misfit between crystals arising due to this anisotropy will lead to the generation of internal stress, even in the as-fabricated state. The effect of such internal stress can be considered in two ways, depending on the goal of the researcher. Firstly, internal stresses affect the measured lattice position (d-spacing) of the various (*hkil*) diffraction peaks, meaning that in the measured diffraction pattern, peaks do not fall in the expected location based on the c:a ratio of the HCP crystal. This has an impact on subsequent full pattern (e.g. Rietveld) refinements that might wish to explore e.g. texture, peak width or other crystalline parameters, since the deviation from ideal c:a location influences the quality of the fit. Secondly, such internal stresses can provide information about the single crystal level anisotropy that gave rise to them. This is in particular of interest in the case of plastic behaviour since such information can be impossible to obtain on a single crystal sample. The talk will give examples of both effects considering both thermal and mechanical stressors. Results are compared with some models of polycrystalline deformation to assist in interpretation.

Description and Interpretation of Microstrain(-Like) Line Broadening

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The perhaps most prominent source of microstrain broadening in powder-diffraction patterns is strain fields around dislocations. These strain fields are long-range but nevertheless inhomogeneous within coherently diffracting grains. There is, however, also a couple of other microstructure scenarios which may (in an ideal case) lead to constant strain in each grain of the microstructure. Thus, in the absence of other sources of line broadening, each grain contributes with a delta-shaped function to each reflection in the powder diffraction pattern. Variation of the strain from grain to grain then leads to the microstrain broadening, which can be anisotropic in case of anisotropic distribution (in the crystal frame of reference) of the strains, i.e. the microstrain is *hkl*-dependent. Taking the variance of the microstrain measured along the diffraction vector as measure for the microstrain broadening, one obtains

$$\left\langle \left(\varepsilon_{hkl} - \left\langle \varepsilon_{hkl} \right\rangle \right)^2 \right\rangle = \sum_{i,j,p,q=1}^{3} Z_{ijpq} x_i x_j x_p x_q \qquad \text{................................ (1)}$$

where **x** is a unit vector parallel to the diffraction vector of the reflection *hkl* in the crystal frame of reference, and where Z_{ijpq} are the at maximum 15 independent coefficients. Note that equivalent formulations exist with *hkl* with coefficients most frequently called S_{HKL}.

The scenarios leading microstrain broadening compatible with Eq. (1) are:

- inhomogeneity of the composition of the sample leading to inhomogeneous compositional strains.
- inhomogeneity of the temperature of the sample leading to inhomogeneous temperature strains.
- inhomogeneity of the stress of the sample (2nd kind stresses) leading to inhomogeneous elastic strains.

For these scenarios the values of the coefficients Z_{ijpq} (as they can be determined e.g. by Rietveld refinement) can be related with originating inhomogeneities via property tensors (compositional expansion, thermal expansion, elastic compliance).

The following main points will in particular be addressed:

1. Quantitative interpretation of the Z_{ijpq} parameters for different microstructure scenarios.
2. Analysis of the anisotropy of tensor properties by analyzing the anisotropy of the microstrain broadening.
3. Microstrain broadening can be asymmetric and need not be Gaussian, as frequently believed.

4. One may misinterpret certain types of anisotropic microstrain broadening in terms of a reduced crystal symmetry.

Diffraction Analyses of Mineralized Tissue

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Mineralized tissues are based on diverse inorganic phases ranging from calcite in echinoderms to carbonated apatite (cAp) in vertebrates and typically employ a hierarchy of structures across a wide range of spatial scales. Many of these tissues have been studied by X-ray diffraction, and the focus of this presentation is on cAp-based tissues of mammalian bone and tooth studied with transmission high energy X-ray diffraction (E > 60 keV).

Bone is a composite of collagen discontinuously reinforced with cAp nanoplatelets which achieves a remarkable combination of strength and toughness. Tooth consists of dentin (composition similar to but structure different from bone) covered by a layer of enamel (dense cAp) on its crown or of cementum (composition similar to dentin) on its roots. Dentin provides toughness to the structure; enamel a hard, abrasion resistant covering and cementum an attachment layer for periodontal ligaments.

The collagen-cAp composite material of bone and dentin is intrinsically variable, and its properties change with position within a given bone or tooth, between tissues in an individual (e.g. femur vs scapula) and between individuals or species. This variability and the effect of nanoscaled constituent dimensions complicate evaluation of the accuracy of diffraction (WAXS, wide angle x-ray scattering) and small angle scattering (SAXS) data. This presentation focuses on the cAp-collagen composite and on a) analysis of internal strain in bone and tooth during in situ loading and b) WAXS tomography for 3D mapping of phase distribution, crystallographic texture, strain, etc.. The in situ loading studies employ simultaneous WAXS and SAXS data collection to quantify response of the cAp and collagen phases, respectively. The same signals are used for diffraction tomography. The focus is on what can be learned and on the limitations of this analysis.

Powder Diffraction:
The Best Opportunities Are Yet To Come, But …

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Over the past decade of powder diffraction, we have witnessed improvements in instrumentation that have led to increased resolution, higher intensities, faster measurements and more complex and realistic experiments. The next decade holds a similar promise with hardware developments of novel laboratory-based diffractometer systems and major source and instrumentation advances at both synchrotron and neutron facilities.

The best opportunities are yet to come, but … improved hardware, ranging from miniaturised in-situ reactors to massive fourth generation synchrotron sources, may lead to better precision but do not necessarily guarantee improved accuracy.

In keeping with the conference theme, this talk will focus on the future fate of accuracy in powder diffraction. What determines the accuracy of a phase fraction or a lattice parameter? How close can the accuracy of a parameter estimate be to its precision? How do we deal with uncertainties of measurement? How confident can we be of the accuracy reported for a crystal structure determined or refined from powder diffraction data?

These questions raise significant issues, ranging from the necessity of basic crystallographic training to the mathematical aspects of theoretical crystallography and statistics, that must be tackled before we can be sure that the best in powder diffraction is indeed yet to come.

The First X-Ray Diffraction Results From the Mars Science Laboratory

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The Mars Science Laboratory (MSL), one of the most ambitious planetary missions ever launched, landed in Gale Crater on August 5, 2012. The crater contains a thick section of sedimentary rocks holding a story billions of years old. MSL carries ten instruments on or inside the Curiosity rover, including CheMin, a miniature X-ray diffraction (XRD) and fluorescence (XRF) instrument. To-date, no XRD data were available for martian soil nor has XRD ever been used on another body apart from Earth. CheMin measures XRD and XRF data simultaneously using Co radiation in transmission geometry. It operates in single-photon counting mode so that at most one photon strikes each CCD pixel between readouts, giving both the photon energy (XRF) and 2-D position (XRD). The 2-D distribution of Co Kα pixels in rings represents the XRD pattern, and integration of these rings gives a conventional 1-D XRD pattern. This energy and positional information is summed over repeated 10-sec measurements to improve counting statistics.

Curiosity delivered sieved (150 μm) samples of soil to both Kapton and Mylar cells in CheMin. The first XRD data were successfully measured on Mars in October, 2012, coinciding with the 100th anniversary year of the discovery of XRD by von Laue. Data were measured for 3.8 hrs (scoop 3), 15.7 hrs (scoop 4), and 26.9 hrs (scoop 5, Fig. 1). XRD data revealed plagioclase feldspar, forsteritic olivine, augite, and another pyroxene. The comparatively large instrumental peak widths for the CheMin instrument limited determination of minor phases (<3 wt. %). Data were analyzed via Rietveld methods (Bruker AXS Topas), and refinements using numerous potential phases revealed the likely presence of pigeonite with augite. Refinements using augite with orthopyroxene or clinopyroxene were inferior to an augite-pigeonite model. A single plagioclase model was as good as a model with two plagioclases. Refinements also clarified the minor phases and allowed exclusion of many possibilities. The presence of minor phases was evaluated individually by including each in the model and evaluating their effect on the fit. We found no evidence for any perchlorate, carbonate, sulfate (apart from anhydrite), or phyllosilicate with this approach. Phase compositions were estimated from refined unit-cell parameters for all phases.

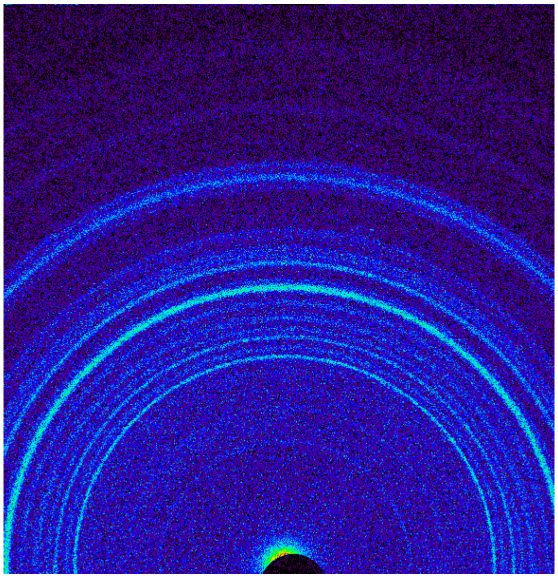

Fig 1 2-D XRD pattern of scoop 5; 26.9-hour data integration; black semi-circle at the bottom is the beam stop.

The elevated background in the XRD patterns suggested the presence of one or more amorphous or poorly ordered components, and data were also analyzed using the FULLPAT program, giving ~27% amorphous content. The exact nature of the amorphous component remains unclear, and SAM and MER Mössbauer data support the presence of a hydrated amorphous phase containing Fe^{3+}. The uncertainty on this value may be as high as 50% relative. These first XRD data from another planet reveal a rich mineralogic inventory in these soil samples, showing that the mineralogy is remarkably similar to that found on Earth in places such as soils on the flanks of Mauna Kea volcano, Hawaii. It is also noteworthy that the crystalline component is very similar to normative basalt mineralogies predicted from Gusev and is also qualitatively similar to mineralogies of martian basaltic meteorites. Combining these XRD results with compositional estimates from unit-cell parameters and bulk chemistry will allow determinations of individual phase compositions, including that of the amorphous components, thereby providing valuable ground truth information on Martian soils.