COMMISSION ON POWDER DIFFRACTION

INTERNATIONAL UNION OF CRYSTALLOGRAPHY
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(Rob Delhez, Editor)

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CPD Chairman’s Message

Powder diffraction is a manifold technique and it is exciting to learn that there is always a new field for which powder diffraction can make a major contribution. In this regard, I am happy to announce that we are back on track with our CPD newsletter with an interesting issue edited by Rob Delhez on extraterrestrial XRPD. Also the second topic of the newsletter on pharmaceuticals is of interest for a broad readership. The next issue will be edited by myself and will focus on 2D powder diffraction using image plates or CCD detectors, as well as on the CPD workshop “Watching the Action, Powder Diffraction at non ambient conditions” which will be held October 6-7, 2005 in Stuttgart. This will probably be one of the last issues of the newsletter in its paper form. Increasing costs and the need for more flexibility will convert the CPD newsletter to an electronic paper like the CompComm Newsletter. My triennium as chairman of the CPD is almost over and it is my pleasure to announce that Bill David from Rutherford Appleton Laboratory has been elected as the new chairman of the CPD for 2005-2008.

Robert Dinnebier

CPD projects

RIETVELD REFINEMENT OF ORGANIC STRUCTURES

Increasing numbers of organic crystal structures are being solved and refined from powder diffraction data. The basic arrangement of the molecules in the structure can often be determined by direct methods, or by direct-space approaches. However, experience shows that problems can arise in the subsequent Rietveld refinement. For example, unless restrained by appropriate bond distances and angles molecules can distort unrealistically from a reasonable molecular structure. So how good are these Rietveld refinements? Is the problem a fundamental one of powder diffraction? eg. the ambiguities and correlations caused by peak overlap or defining the background etc. lead to inaccurate structures. Or can some of the blame be attributed to poor refinement practice? We plan to put onto the CPD web site a number of good quality powder diffraction patterns from organic compounds of known crystal structure and of different complexity. These can be downloaded, and powder crystallographers can try out their own prowess at Rietveld refinement, by comparing their refined structures with the accepted single-crystal structures. This should be a learning exercise for us all. Any suggestions as to compounds that would appear particularly appropriate for this project are very welcome. Please contact the CPD chairman.

From the Editor of Newsletter 30

Powder diffraction goes into space

Powder diffraction is a technique that originated on Earth and has settled there. Almost a century ago it came to life in its first "incarnation": the X-ray camera. About four decades later one could meet the first X-ray diffractometers, almost at the same time as the first astronaut escaped from the Earth's gravity. Just like mankind X-ray powder diffraction aims at spreading its wings and it is expected that the first one or two X-ray powder diffractometers will be launched to Mars as the first X-ray diffractometers to explore extra-terrestrial soil and rocks *in situ* in 2011. NASA is creating an X-ray powder diffractometer, just as ESA does. Clearly right from the start X-ray diffraction does not want "to bet on one horse" - like the Dutch proverb says. At present the NASA team is well ahead of the ESA team. However, it is no question who will be the real winner of the race: X-ray powder diffraction.

Also in this Newsletter: Computer Corner, Pharmaceuticals

Powder diffraction would not be alive as much as it is, if the Computer Corners in your laboratories and in the CPD Newsletters would be obsolete issues. I take this opportunity to compliment Lachlan Cranswick -whether he likes it or not- with his ardour and persistence with respect to "his" Computer Corner, and with his knowledge and expertise of and insight in so many computer programs. Further a sequence of three contributions on Pharmaceuticals from the USA are incorporated.

The Editor's Apologies to the Powder Diffraction Community

"Misfortunes never come single" holds for this very CPD Newsletter. It was expected that the early issuing of Newsletter 31 by Norberto Masciocchi would elegantly take away possible concerns about the delay of Newsletter 30. Notwithstanding all efforts the delay increased and it was decided to try to merge the CPD Newsletter 30 and the one edited by me. The result of this merger is visible in this issue in the form of the contributions on Pharmaceuticals. Strongly stimulated by the CPD Chairman the completion of the present Newsletter was planned for December 2004, and the contributions by Lachlan Cranswick and some others were received in due time and in good order. It was my very diverse and high workload and my personal circumstances that blocked the direct way to the finish until recently. For this delay I would like to apologise to the Powder Diffraction Community, with the main purpose of making clear that it is not the CPD to blame for the late, but (I hope) satisfying and appreciated appearance of the present CPD Newsletter 30.

Rob Delhez

WWW sites related to powder diffraction

The Commission on Powder Diffraction (CPD): http://www.fkf.mpg.de/cpd
The International Union of Crystallography (IUCr): http://www.iucr.org/
The International Centre for Diffraction Data (ICDD): http://www.icdd.com/
The International X-ray Analysis Society (IXAS): http://www.ixas.org/
CCP 14: http://www.ccp14.ac.uk/

Submitting a proposal for neutron diffraction or synchrotron radiation X-ray diffraction is possible at many (publicly funded) large scale facilities in the world. It represents an important and frequently unique opportunity for powder diffraction experiments. A useful guide and information can be accessed through the following web-site, maintained by R. Dinnebier at http://www.fkf.mpg.de/xray

This list is far from being complete and needs input from users and readers of the CPD Newsletter. Please send comments to *R. Dinnebier* (r.dinnebier@fkf.mpg.de)

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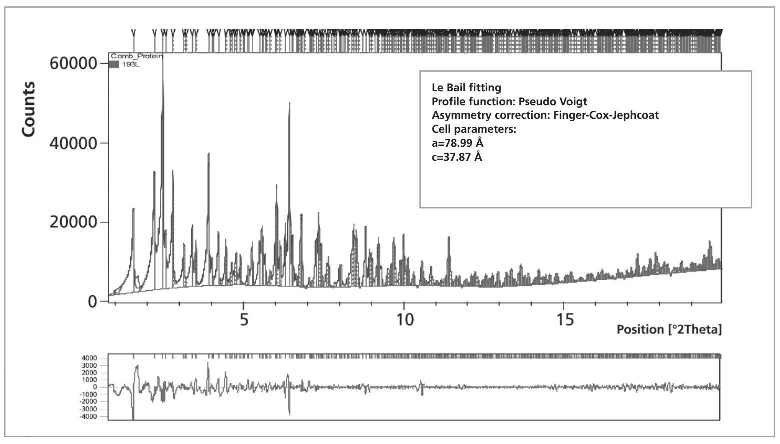
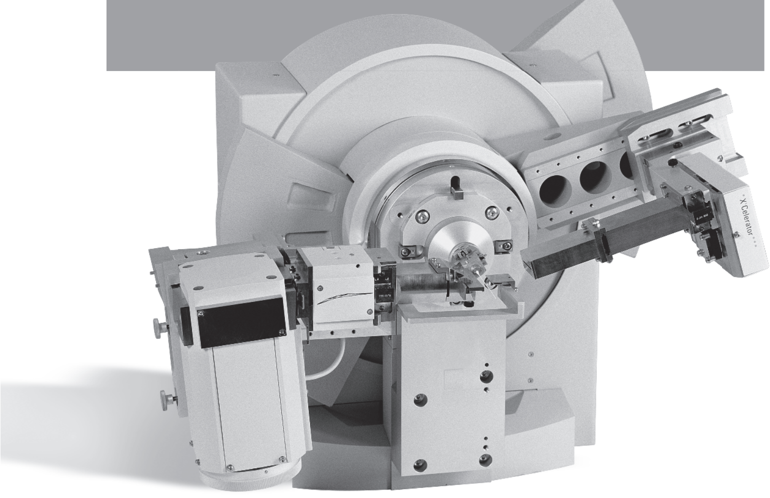
ANOTHER FIRST FOR PANALYTICAL!

New X'Pert PRO for transmission allows for diffraction measurements on proteins



Indexing was carried out using X'Pert HighScore Plus software. Further processing using Le Bail fitting method provided excellent agreement with the cell parameters achieved by single crystal diffraction.



The X'Pert PRO MPD fitted with the focusing mirror, capillary spinner and X'Celerator detector

Using PANalytical's new transmission geometry with PreFIX focusing mirror, in conjunction with the X'Celerator detector, diffraction experiments on macromolecules such as proteins can now be carried out with an X'Pert PRO MPD X-ray diffraction system. Characterized by weak scattering and small sample volumes, these materials have previously been considered 'difficult' for X-ray diffraction. Instead, protein structure determination traditionally relied on the use of single crystal systems, or beam lines for the extraction of powder patterns. Here, we show for the first time that protein powder data measured on a laboratory X-ray diffraction system can be used for crystallographic analysis.

Emphasis on the research and development of macromolecules – especially in areas such as protein pharmaceutics – has increased strongly in recent years. By offering researchers the potential for pre-screening and investigation of protein-based medicines within the laboratory, use of the transmission setup represents a significant technical advance.

As a PreFIX optic, the focusing mirror is interchangeable with all other available incident optics for the X'Pert PRO MPD without the need for any re-alignment. From a technical perspective, it means:

- the size of the capillary tube no longer governs resolution
- peaks narrower than 0.05 degrees are easily resolved.

Use of the X'Celerator detector, meanwhile, ensures fast data collection.

Transmission experiments on hen egg white lysozyme using an X'Pert PRO MPD fitted with the new mirror and the X'Celerator detector, provided high resolution data sufficient to enable cell searching, indexing and unit cell refinement. The lattice parameters determined were in good agreement with literature data obtained from single crystal measurements.

To find more about PANalytical's X'Pert PRO for transmission, contact PANalytical.

Acknowledgement:
We thank Dr. B. Prugovečki, University of Zagreb, Croatia for the lysozyme crystallization, sample preparation of capillary and stimulating discussions.

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X-ray Powder Diffraction on the Red Planet

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Why X-ray powder diffraction?

A very considerable part of the solid material in the universe is crystalline. Chemists, geologists, mineralogists and materials scientists consider X-ray powder diffraction [XRPD] analysis of solid materials as a basic method for their fields. An X-ray powder diffractionist might even say that XRPD is the most powerful analytical method to identify and quantitatively characterize crystalline solids.

An important issue in the exploration of space is the search for life, i.e. the presence of organic molecules. Such compounds are to be identified by other methods than XRPD. But, because life and organics will be hiding from the high UV radiation dose at the surface of Mars, XRPD is an effective method to identify environments that probably contain life or remnants of it. Then XRPD is applied within a sequence of instruments that "zoom in" in three "stages": (i) remote analysis by satellite to find promising areas, (ii) local analyses by the Mars-XRD to identify the minerals present in those areas which yields information on the overall geology of that location, monitors the presence of bio-generated structures and in particular minerals that can host molecules of life, and (iii) detection of specific organic molecules like amino acids, bases, etcetera by appropriate analyses like GC/MS and HPLC.

Why X-ray powder diffraction on Mars?

It is assumed on good grounds - but the dispute is still going on - that Mars is comparable to our Earth with respect to its chemical composition and the compounds present. It appears that a few billion years ago Mars and the Earth were rather alike - not regarding their mass and size of course. Probably Mars had oceans like the Earth. Observations from satellites in orbit around Mars revealed fine details of surface structures on Mars that corroborate the geologically recent occurrence of large quantities of streaming water. Therefore it is rather likely that life could have developed on Mars too. In fact small amounts of methane were observed recently that are presumably not generated by volcanism, but more likely by some form of life. If so, then there must be remnants of those life forms, maybe as minerals or as organic molecules or traces of biologic materials.

Considering minerals, we know structures exist on Earth consisting of minerals that are very old and that were generated by bacteria or algae, e.g. the BIF's (Banded Iron Formations) that consist of alternating layers of iron(hydr)oxides and aluminiumsilicates. The oldest layers are a few billion years old, probably from the time that Mars and Earth were still in the same stage of evolution.

Considering bio-organics we know that clay minerals can contain products of life forms. If life occurred or occurs on Mars -and if it was based on aminoacids-, species may have evolved that resemble those on Earth and therefore remnants comparable to those we know from Earth may be found on Mars. If other species have evolved on Mars we may find remnants, or even minerals still unknown to us. However, the basic simple organic molecules that can be stored in clay minerals are expected to be identical to the ones found on Earth.

Another interesting phenomenon on Mars is the weathering of surface rocks. The Mars atmosphere consists mainly of carbon dioxide and atmospheric pressure is only a few percent of that on Earth. Heavy dust storms occur frequently over very large areas and may persist for weeks. Therefore weathering on Mars is probably more important than in deserts on Earth where rocks and stones obtain a patina by the bombardment with dust particles. This may also lead to mineralogical discoveries. To illustrate this: XRD analysis of a lunar highland meteorite showed the presence of a new natural mineral Fe_2Si, called Hapkeite[1]. Bruce Hapke predicted thirty years ago[2] that high-velocity impacts of meteorites and micrometeorites on planetary bodies may yield Fe_2Si and related compounds by deposition from the vapor phase created by such energetic bombardments. Although involving much less energy than these high-velocity impacts, comparable impact processes occur on Earth in deserts during dust storms, but such processes will produce oxides, hydroxides or silicates due to the air and water present. Is it far-fetched to expect that the dust storms on Mars will yield different, i.e. new, weathering patinas?

X-ray powder diffraction on Mars: *How* & *Who*?

Most laboratory X-ray diffraction systems have a mass of about 1000 kg and a power consumption of several kW. For a system that can be launched to Mars these numbers must be reduced by a factor 100 to 1000, whereas the performance must remain almost the same. This asks for radical changes in design.

Moreover, severe and unusual requirements are added because the instrument has to survive the extreme vibrations during its launch, the high radiation dose during its journey to Mars and the landing shock. Moreover it has to function properly under the harsh conditions at the Martian surface: low temperatures and low atmospheric pressure.

At present NASA as well as ESA have projects underway to construct an X-ray powder diffractometer that contains a two-dimensional CCD detector that is also capable to perform X-ray spectrometry. Here the resemblances end.

The NASA instrument is called CheMin (Chemical composition and Mineralogy) and it belongs to the Mars Science Laboratory (MSL '09). A specimen preparation device is incorporated which prepares specimens for analysis in transmission. The X-ray source emits cobalt-K radiation: it is a miniature micro-focus tube with a cobalt anode. Its development is well ahead of the ESA project: a third prototype has been used for tests already[3]. For the flight instrument a mass of 6.8 kg is envisaged, a power consumption of 18 W, and a volume of 10.6 litres. Its launch is planned for 2009.

The ESA instrument is called Mars-XRD and is to be launched in 2011 as one of the instruments on board of the rover of the ExoMars mission. ESA just started the project to construct a first prototype diffractometer[4]. The target mass of the prototype is about 1 kg in a volume of approximately 1 litre, with a power consumption of 2 W. These numbers are so low, because it is planned that specimens supplied by a central specimen preparation device will be analysed by several instruments, including the X-ray diffractometer/spectrometer. A radioactive source irradiates the specimen and a reflection geometry is applied, because large lattice spacings play an important role in the identification of many materials, in particular for clay minerals.

Conclusion

NASA and ESA are developing XRD instruments that will be used for mineralogy and materials research on Mars, because the mineralogy as well as the structure and arrangement of the surface materials of Mars are key issues to disclose its present and past life and climates. In addition these instruments will help to characterize the biological environment on Mars in preparation of robotic missions and human exploration.

As X-ray diffraction analysis is a rigid, unique, simple and fundamental method in the search for minerals, it is amazing that no X-ray diffractometer has been launched yet.

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Mars-XRD: the X-ray Diffractometer for Rock and Soil Analysis on Mars in 2011

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Abstract

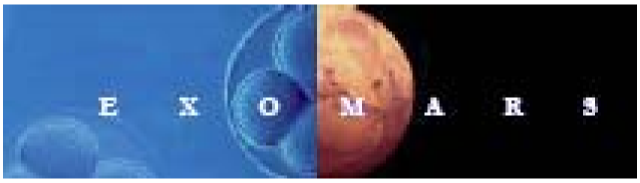
"Mars-XRD" is a reflection mode X-ray diffractometer that includes an XRF for in-situ Martian rock and soil analysis: one of the instruments on board of the Mars rover in the ESA ExoMars mission planned for 2011.

A so-called breadboard instrument - a working prototype and "proof of principle" - has to be ready for testing in the autumn of 2006. It has to be approximately a factor 1000 smaller, lighter, and less power consuming than usual laboratory X-ray diffractometers. Yet its performance must be comparable to such an instrument.

The instrument has been proposed by a consortium of European institutes which includes Italy, the Netherlands, and the United Kingdom along with the involvement of other scientists from Spain, Portugal, and the USA. The Mars-XRD will help to disclose the mineralogy and aspects of the geology of Mars, as well as signs of the presence of water and -hopefully- life at or near its surface.

Last but not least, X-ray powder diffraction has not been used in a planetary environment yet.

The ExoMars mission.



The ExoMars mission is a mission in the Aurora program of ESA, a program mainly devoted to Space Exploration for future Human missions. It is the first European attempt to develop a complex and mobile lander for in situ planetary exploration. In this framework, a mission dedicated to the search of life on Mars, ExoMars, and to the definition of the level of environmental hazards for the humans has been studied to assess a first step of a long term programme. ExoMars will consist of a fixed lander station and a rover capable to move for a few kilometers on the surface of Mars. A scientific payload, Pasteur, will be carried by the rover to perform analyses in different areas, collecting information on the different Martian environments. The Pasteur model payload will include cameras, spectrometers (IR, Mossbauer, LIBS), an XRD, ground penetrating radar, a gas-mass spectrometer, and a couple of instruments for the detection of organic molecules. In addition the ExoMars rover will be equipped with a microdriller to core rocks upto 2 meters depth to avoid the sterilization of organic molecules at the surface by UV light. Pasteur will also include a package of instruments to record the radiation environment, dust density and monitor the meteorological conditions. The fixed lander will host a long-term (a few years) geophysical package to monitor the frequency of quakes and measure the thermal status of the subsurface. In the near future a technical and scientific review will be undertaken for the model payload of scientific instruments which may result in a slightly different configuration of the system as a whole and the individual instruments of which it is composed.

This complex robotic mission is planned to be launched in May 2011 and will reach Mars after a trip of two years.

Once it reaches Mars, ExoMars will be walking and analyzing the surface rocks and soils for six months.

The Mars X-ray diffractometer "Mars-XRD"

"Mars-XRD" will be a reflection mode diffractometer with a CCD detector system. A CCD detector additionally enables elemental analysis by X-ray fluorescence spectroscopy (XRF) when working in photon counting mode. Therefore Mars-XRD is in fact a combined XRPD/XRF instrument and its design is based on published ideas for an instrument for Mars missions. The combination of XRF and XRD data obtained can be analyzed to:

- identify the minerals present in rocks and soils as well as determine semi-quantitative the proportion of the compounds identified and possible deviations from their ideal compositions (elemental substitutions and solid solutions),
- determine the degree of crystallinity of the mineral(s) present,
- determine the degree of hydration for minerals that contain water within their crystal structure,
- find indications about the presence / abundance of various lattice imperfections from the shape of the line profiles observed.

As many minerals have crystal structures where large lattice spacings occur, the instrument should be able to reveal such large spacings for accurate identification, in particular of clay mineral species (see below). Transmission XRD equipment is not well suited for recording reflections of these large spacings with the required accuracy. Furthermore, strong preferred orientation of the crystallites occurs in natural deposits of layered structures like clay minerals in such a way that the diffracted intensities of these spacings are high when the diffractometer works in reflection geometry, but low when applying in transmission geometry. These are the main reasons why a reflection geometry has been chosen for the Mars-XRD. Moreover, a reflection configuration simplifies the mechanical interfaces with the main sample distribution system of the rover, and may be suitable for contact analysis directly on soils on the Martian surface.

Characteristic numbers for the Mars-XRD

The total mass of the Pasteur payload of the rover will be of the order of 30 kg of which only 8 kg will be available for the scientific instruments, and its electric power will be supplied by solar panels. The Pasteur payload will contain the Mars-XRD as one of the instruments. Because a normal, complete laboratory diffractometer system containing a goniometer, high voltage generator, computer and radiation shielding has a width of ≈1.5 m, a depth of ≈1 m, and a height of ≈2 m; a mass of about 800 kg and an electric power consumption of about 4 kW, it will be clear that the mass and the power consumption and the of the Mars-XRD have to be three orders of magnitude less and that its dimensions have to be two orders of magnitude smaller.

The specifications of the Mars-XRD were defined in May 2004 in the first draft of a specifications document:

- width * height * depth ≈ 220*120*60 mm^3
- mass below 1 kg
- power consumption ~ 2 W
- no moving parts
- precision of angular readings about 0.01 degree under all Martian weather conditions
- continuous registration of the temperature of the specimen to ~1 °C, preferably controlled
- operating temperatures between +40 °C and -150 °C
- the mass required for radiation shielding is included in the "1 kg" mentioned
- automatic alignment and calibration as well as performance monitoring.

In spite of the small mass and power consumption the Mars-XRD should perform almost like his big brothers and be an instrument that has a high angular resolution and precision, that is needed to reveal large spacings for accurate identification of minerals and that delivers well defined and reproducible shapes of the line profiles observed. These specifications require a completely new design of the diffractometer (cf. Fig.1) and that implies the application of components with a low mass such as the X-ray source and the detection system.

It goes without saying that such a system may yield a terrestrial spin-off that forms the start of a real revolution in the X-ray diffraction laboratory practice: a portable XRD system that is just an attachment to your laptop.

The radiation source for XRD will most probably be a radioactive ^{55}Fe source. Apart from the fact that this requires little mass for radiation shielding and no high voltage supply X-ray excitation (high voltages are unwanted in space applications), its main advantage is the long X-ray wavelength that enables the accurate determination of the larger lattice spacings which are usually the most characteristic lattice spacings of a compound. Its main drawback is the high absorption of this wavelength by most minerals which lowers the penetration depth of the X-radiation and thus confines the volume examined.

It is still a matter of debate whether a second X-ray source will be incorporated with a much shorter wavelength (higher X-ray energy) to boost fluorescent radiation from the specimen for efficient XRF analysis. However, being XRF a secondary objective of the MARS-XRD instrument, the higher priority will be given to the optimization of the XRD performances.

The detection system will be a CCD charge coupled device (cf. "Charge coupled devices as X-ray detectors for XRD/XRF" by Nelms, Hutchinson, and Holland below in this issue). It is planned to use a large area device that will

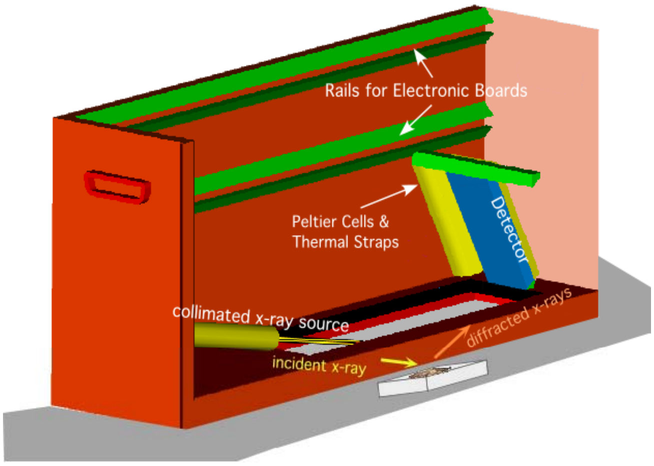


Figure 1. First sketch of the Mars-XRD showing the arrangement of its main components.

be a further development by Leicester University and E2V Ltd (formerly EEV Ltd) of the detector for the XMM-Newton EPIC cameras. It has a novel open-electrode structure and is manufactured using high-resistivity silicon, a combination that gives good quantum efficiency from 0.2 keV to 10 keV - an energy range ideal for XRF/XRD applications.
The detector will be operated in vacuum behind a thin beryllium window and cooled using a thermoelectric cooler. This technique has already been successfully employed as part of the NASA Swift camera developed at Leicester University. The electronics will use a signal processor and a dual-channel amplifier to provide noise reduction in conjunction with cooled operation.

Sampling and specimen preparation for the Mars-XRD

The specimens to be analyzed by the Mars-XRD will be supplied by the specimen preparation device that will be related to the drill of the Mars rover laboratory. This poses a problem, because ideally the specimen should be an unaltered part of Martian material. When using a drill it is difficult to prevent the production of heat or the transfer of another form of energy from the drill to the sampled material. Such an energy transfer often causes well-known effects as phase transformations or changes in the material's "microstructure". It is clear that the use of a drill to obtain a powder destroys much of the microstructure of the material. It is expected that the particles in the specimens will be rather coarse. Then it will be necessary to make use of the spottiness of the diffraction rings - an almost unexplored area in XRPD. However, it is thought that even such powders can be used to identify the compounds present by analyzing the same specimen several times or analyzing various "identical" specimens.

Some complications can occur when drilling into rock material or when dust is transported in the Martian atmosphere: (i) amorphization of entire particles, (ii) development of amorphous surface layers, (iii) transformation of crystalline structures (new formation), (iv) increase of particle and/or crystal size, and (v) introduction of contaminants like fragments of the drill.
Apart from samples prepared by the drill, also the dust that forms the Martian soil will be analyzed. As dust storms are common on Mars, cover large areas and last long, it is expected that no large differences in composition will be found, but they inform about the mechanical-chemical changes caused by collisions of particles during transport by dust storms.

Important factors for specimen preparation: (i) size of the specimen (diameter), (ii) specimen homogeneity, (iii) suitable particle size, (iv) flatness and a low surface-roughness in particular for the observation of the lower diffraction angles, (v) thickness of the specimen, (vi) particle effects, such as the shape of crystallites and preferred orientation, (in the case of clay minerals layered, platy particles may occur and then this effect can be used for the analysis).

Analyses to be performed by the "Mars-XRD"

The information that can be obtained with the "Mars-XRD" is expected to be crucial for the detection and analysis of mineral deposits. In addition, the structural state of some minerals can indicate temperatures and/or pressures that occurred during their formation. Moreover, some minerals may contain water in their crystal structure. In turn the water content may indicate changes in the climate of Mars, or bear signs of life on Mars, as e.g. clay minerals might do.

The determination of the mineral deposits present at as many locations as possible helps elucidating the general geology of that region of Mars and of Mars as a planet. For this purpose it is important to investigate (i) the mineralogy of unaltered basalt, e.g. pyroxene, feldspar, mica, glass, olivine, (ii) the presence and composition of weathering and erosion products, e.g. palagonite, serpentine, nontronite and of hydrothermal products as sulfates and chlorides, (iii) the presence and composition of carbonates and sulfates and (iv) the presence and abundance of ices (water, carbon dioxide) on pristine samples.

Some materials of biological origin are found on earth as minerals and/or structures formed by algae, e.g. Stromatolite, that consists of Ca-carbonates, and Banded Iron Formation (BIF) that consists of alternating layers of Al-Silicates and layers of Fe-oxides + Fe-hydroxides. If comparable minerals will be found on Mars, they may indicate the presence of (past) life.

In what follows some focus will be on clay minerals. Although clay minerals are not very abundant, they are interesting, because they may indicate some weathering and erosion processes, they may contain water - and therefore prove its presence - and they may have trapped simple organic molecules - and therefore indicate the presence of (past) life.
The basic structure of clay minerals consists of silicate containing layers. The distances between the silicate containing layers are the largest lattice spacings for clays minerals, and because these spacings are large in an absolute sense they can host e.g. water and some smaller organic molecules. If clay minerals have taken up water and/or organic molecules, the distance between the silicate containing layers is a measure for the content of water and/or organics of the clay mineral. The large internal silicate layer surfaces are usually charged negatively. For example the layers of the structure of Smectite (montmorillonite) and Vermiculite consist of triple layers of octahedral aluminate between two layers of silicate tetrahedra. If isomorphous substitution of Al by Fe and of Si by Al occurs, then the triple layers become charged. This may enhance selective hosting of some amino acids and bases and at the same time they are protected against external influences for long periods of time.
Therefore clay minerals that expand when taking up water are guide minerals for water and other compounds.

The CCD detector records a two-dimensional diffraction pattern. Such patterns contain much more information than the usual one-dimensional diffraction patterns obtained with common laboratory XRD equipment. In fact a two-dimensional diffraction pattern is a collection of sets of complete and/or incomplete Debije-Scherrer rings. The interpretation of such two-dimensional diffraction patterns is rather complicated and therefore two modes of analysis of the XRD patterns are envisaged: "Quick & Dirty XRPD analyses" and "Detailed XRPD analyses".
In *"Quick & Dirty XRPD analyses"* the two-dimensional diffraction pattern is transformed to a one-dimensional

pattern by adding up all diffracted intensity having the same diffraction angle (i.e. different x, y coordinates along a Debije-Scherrer ring). Obviously some information will be lost in this process and it is expected that this pattern will be somewhat blurred in particular for the lower diffraction angles. In most respects it will be like a common X-ray diffractogram obtained in commercial laboratory XRD equipment and therefore interpretation of one-dimensional patterns may proceed in the same way as for laboratory instruments.

For most minerals the Quick & Dirty technique will show whether their presence is probable or not. For example it will be able to show the occurrence of carbonates and sulfates - which are minerals from brines and evaporites -, basalt related minerals - such as pyroxenes -, and indications for the presence of clay minerals. The clay mineral group can be identified by the observation of its *hk*0 reflections, which are non-specific reflections, as indicated in Fig.2. Moreover, direct indications for water ice (probably type Ih) and carbon dioxide ice can be obtained.

When performing *"Detailed XRPD analyses"* all information of the 2D pattern is used, e.g. effects of preferred orientation of the crystallites, the presence of continuous rings and/or spotty patterns, and -possibly- the 2D intensity profiles of spots and continuous rings.

It is expected that the resolution of the "Detailed XRPD analysis" mode is significantly better than that of the "Quick & Dirty" analysis, and that diffraction data at low(er) diffraction angles can be observed so accurately that identification of the phases they belong to can be conclusive. If e.g. hk0 reflections of clay minerals have been found using "Quick & Dirty" analysis, then identification of the specific clay mineral should become possible by examining the 2D patterns for the 00l diffraction lines (basal spacings) (Fig.2). From these lines the (members of) specific clay mineral groups can be identified such as smectite, vermiculite, mica-illite, talc-pyrophyllite, interstratified clay minerals, chlorite, kaolinite-serpentine and the crypto-crystalline palagonite.

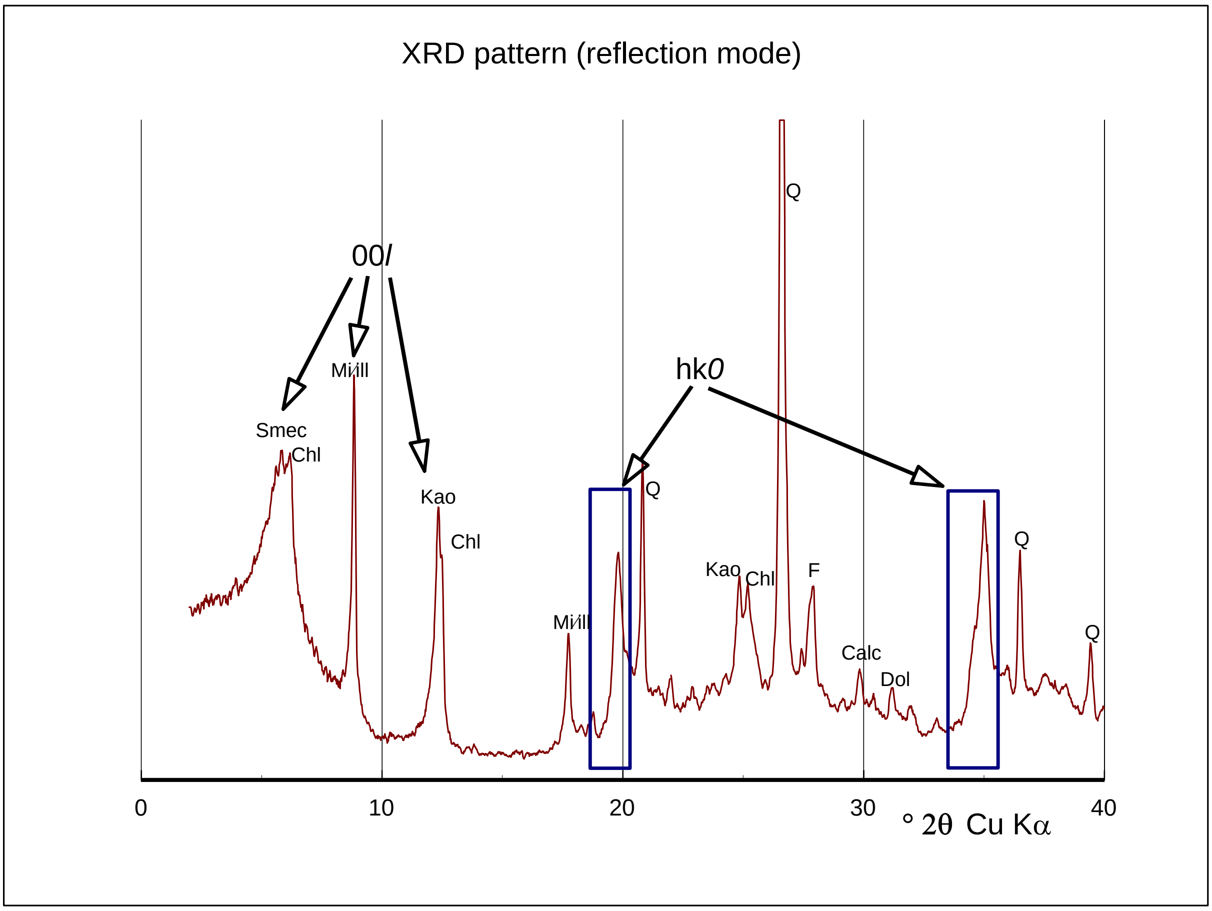


Figure 2: XRPD pattern from a randomly oriented specimen containing Ca-exchanged sediment particles <2 µm (e.s.d.) measured at 50% relative humidity. If the instrument would work in the transmission mode the only reflections observed clearly would be the *hk*0 reflections, representing the clay minerals as a group. In the reflection mode the 00*l* reflections can be observed usually clearly, from which the specific clay mineral groups can be determined. Smec = smectite, Mi/ill= Mica and illite, Kao = kaolinite, Chl = Chlorite.

From the expanding clay minerals, such as smectite and vermiculite, it is expected that the line positions of the raw material can give an indication of the presence of water in the interlayer of these minerals (Fig.3). In collapsed state - i.e. no water in the structure - line positions can indicate the presence of intercalated material. Further, at low angles imogolite-allophane, ferrihydrite and their average particle sizes can be measured. The presence of iron oxides and iron hydroxides, that are found in e.g. banded iron formations (BIF), could then testify the presence of an (extinct) oxidizing environment.

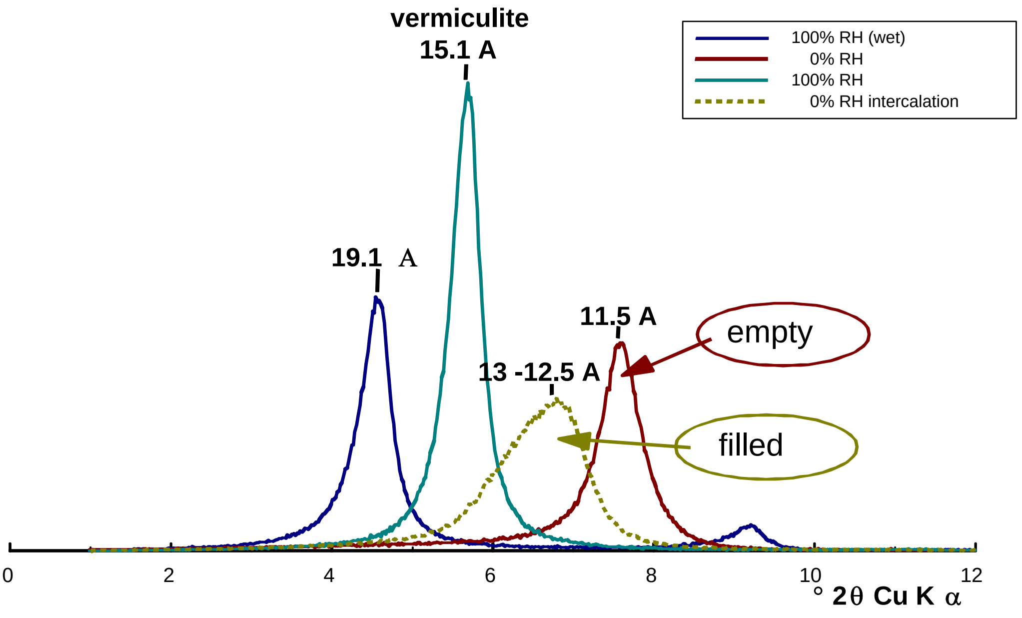


Figure 3: The changes of the (00l) lattice spacings of Smectite (not indexed peaks) and Vermiculite with various % relative humidity (RH) and/or intercalated compounds.

To test the performance of the Mars-XRD on Earth and to analyze observed XRD data quickly as well as reliably it will be almost mandatory to compose libraries of sets of minerals that accompany each other on earth. For these sets of minerals the diffraction patterns for the individual minerals are to be measured using the Mars-XRD or they are to be calculated as if they were collected using the Mars-XRD. From these individual patterns those of mixtures can be composed as an aid for analyzing complex diffraction patterns.

Conclusion

A "proof of principle model" will be constructed for an X-ray diffractometer that can operate on Mars. The information that can be obtained with the "Mars-XRD" is expected to be crucial for the detection and analysis of mineral deposits. From the findings it may be possible to find indications for geological processes that take or took place on Mars, along with indications for past climates and past or present life on Mars.

Charge coupled devices as X-ray detectors for XRD/XRF

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1. Introduction

Certain types of charge-coupled devices (CCDs) are extremely well suited to the detection and characterisation of soft (<10 keV) X-rays. Combined with 2-dimensional position sensitivity this makes them ideal for use as the detector in compact X-ray diffraction/fluorescence instrumentation such as that needed for remote planetary surface investigation. This paper gives an overview of the operation of such devices in the soft X-ray region of the electromagnetic spectrum and their application to X-ray diffraction and X-ray fluorescence.

2. Overview

The history of CCD development from the first production devices at Bell Laboratories in 1970 [1] has been well documented in many references, including [2, 3]. Although not originally developed as such, their use as imaging detectors was realised very early on [4] and application to X-ray detection soon followed [5].

A CCD is a semiconductor photon detector. It comprises an array (either 1- or 2-dimensional) of elements or pixels capable of storing local, photon generated charge. A typical 2-dimensional CCD will have a store section, an image section and a line readout section (figure 1), whilst a 1-dimensional device is essentially just a line readout section.

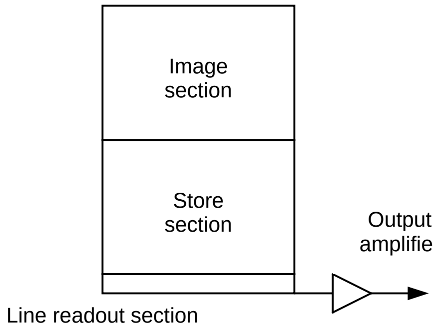

Figure 1. Typical CCD schematic

The charge in the image region can be quickly shifted (frame transfer) into the store section. The stored charge is then shifted one row at a time into the line readout section and each pixel is moved sequentially towards an output node and measured. In this way, a charge-map or image, of the whole CCD can be constructed.

3. Charge generation from X-rays

Absorption of an X-ray photon (<100 keV), in the silicon lattice of a CCD, (after numerous processes) results in the creation of N electron-hole pairs as given by

$$N = \frac{E_x}{\omega}, \qquad 1$$

where E_x is the energy of the interacting photon and ω is the mean ionisation energy (~3.65 eV). Since the creation of electron-hole pairs is not mutually exclusive, the variation is less than that given by purely random statistics. The usual Poissonian variance is modified by an empirical quantity known as the Fano factor, F [45] (~0.15 for silicon [6]) and for N is given by

$$\sigma_N^2 = FN. \qquad 2$$

However, the key factor here is that the number of electrons generated in the silicon structure is directly proportional to the energy of the interacting X-ray.

4. CCD structure and charge storage

The storage elements of a CCD are essentially an array of metal-oxide-semiconductor (MOS) capacitors. The capacitors comprise a conducting electrode deposited onto the silicon substrate with a thin insulating layer of silicon dioxide between. Each pixel actually contains a coupled number of MOS capacitors, commonly three (figure 2). Hence such a CCD is known as a 3-phase device.

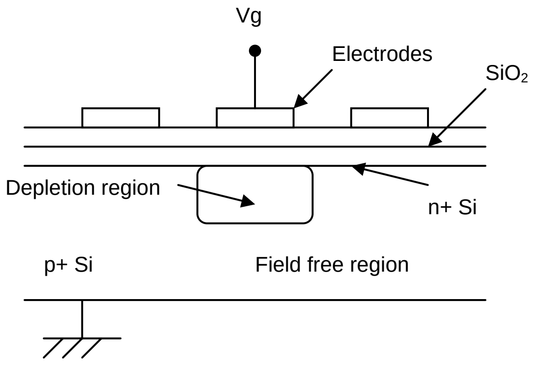

Figure 2. Simplified buried channel CCD pixel structure

Application of a positive voltage to one of the conducting electrodes or gates, will create a depletion region beneath the electrode which is responsible for collecting the charge (electrons) generated by the X-ray. In a 3-phase device the three electrodes are actually common to one whole row of CCD pixels. In the horizontal direction it is the potential applied to the gate of one of the electrodes which holds the charge in position whilst in the vertical direction 'channel stops' are implanted to prevent migration of the electrons (figure 3). The dimensions of the electrode groups and the spacing between the channel stops define the size of a pixel, typically between 10 and 40 μm square. This array of pixels collectively makes up the imaging or storage area of the CCD.

5. Charge transfer and measurement

Charge generation and storage is usually allowed to continue for a certain 'integration' time after which it is desired to measure the charge stored in each pixel. During integration, generated charge is held in the potential well of each pixel by maintaining the voltage on the gate of one electrode. If the voltage on this electrode is reduced to zero and simultaneously the voltage on an adjacent electrode is raised, the potential-well and consequently the charge stored in it is transferred, or coupled, from beneath the first electrode to the second.

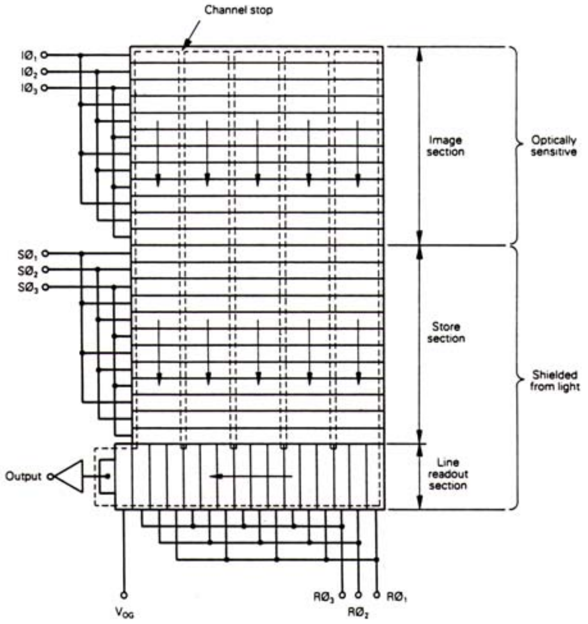

Figure 3. Typical CCD array schematic (*from EEV Imaging III*)

If the groups of three electrodes for each row of CCD pixels are arranged consecutively as in figure 3 with common electrical connections as shown, and the potential of electrode 3 is lowered as electrode 1 is raised the charge is transferred from one CCD row to the next. This procedure can be repeated as many times as is necessary to move the charge to the end of the CCD array, where a series of pixels couple the charge in a perpendicular direction in an area known as the line readout section. Each pixel of the readout register is aligned with a single column of the imaging area and allows a single row of CCD pixel charges to be transferred consecutively towards a charge-sensitive amplifier at the end of the line readout register.

6. CCD read noise

Noise sources in a CCD are either signal related (shot noise, dark current) or device related (charge transfer losses, reset noise, output amplifier noise). For low-energy X-rays relatively small numbers of electrons (of order 100 – 4000) are generated per photon and this signal can easily be swamped by the dominant noise sources – dark current and reset noise. Dark current refers to the thermal generation of electron-hole pairs which can be as high as 20,000 electrons per pixel per second. Since dark current production is temperature dependent, cooling the detector can reduce the thermal charge generation dramatically with a reduction by half for every 7 or 8 °C drop in temperature. Consequently, at typical operating temperatures of -60 °C or less, dark current can be ignored for short integration times. Reset noise is essentially the variation in level to which the CCD output amplifier returns after a reset following the measurement of charge in a pixel. Although this is also thermal in origin, even at -100 °C the fluctuation is still equivalent to ~100 electrons rms, a level that would make any form of X-ray spectroscopy difficult if not impossible. Fortunately this noise source can be effectively cancelled by applying a process to the readout known as correlated double sampling (CDS). This means that the reset level of the amplifier is sampled first, then the pixel charge level is sampled and the two signals are subtracted or correlated. This process is repeated for every pixel that is clocked to the output node.

7. X-ray fluorescence spectroscopy

If the background noise levels are low enough and it is possible to distinguish individual X-ray signals from the dark current signal, the CCD can be operated in “photon counting” mode and it is possible to perform X-ray spectroscopy on the measured photons. When operating in this mode, it is clearly important to match the integration / readout times of the detector system to the X-ray flux from the sample so that the effects of event “pile-up” and image “smear” can be minimised (it is inevitable that, on occasion, more than one X-ray event will be collected in a single pixel during the combined integration and readout time of the detector and that this will result in the loss of spectroscopy information or smearing of the diffraction image). However, as discussed in Section 2 above, some CCD detectors include a store section, so that the X-ray generated charge packets can be shifted into a separate, shielded region of the device while they are transferred to the readout register for sampling. For high flux levels, this approach can significantly reduce the overall number of pixels affected by pile-up of events (typically <<1% of the overall number of CCD pixels depending on the X-ray flux) thereby increasing the overall detection efficiency of the system.

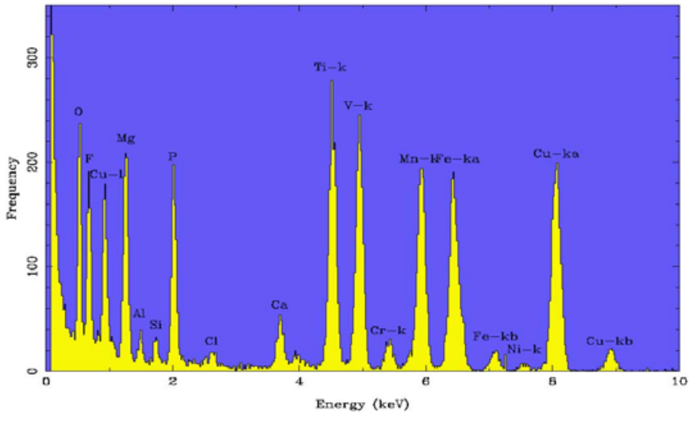

Figure 4. A composite X-ray fluorescence spectrum obtained from a range of elemental samples with a scientific CCD.

An example of an X-ray spectrum obtained with a scientific CCD is given in Figure 4. The figure shows a composite X-ray fluorescence spectrum obtained from a range of samples and clearly demonstrates the ability of the photon counting CCD system to perform XRF on a sample and to identify elements from carbon through to copper. The exact sensitivity and range of elements that can be covered depends on the efficiency of the detector and the type (and strength) of the stimulation source.

8. X-ray measurement performance

The energy resolution of a CCD is dependent upon the noise sources mentioned and described in section 6 and can be expressed as

$$\Delta E(FWHM) = 2.355\omega\left(\frac{FE_x}{\omega} + \sigma_T^2\right)^{\frac{1}{2}}, \qquad 3$$

where the first term in the brackets is the Fano modified signal shot noise and σ_T is the total rms read noise of the CCD in electrons. Ultimate resolution is achieved by minimising the noise terms associated with σ_T and in this case the detector performance is termed Fano limited. For a typical read noise of 5 electrons rms a FWHM of <150 eV can be achieved at ^{55}Fe (5898 eV).

A standard (video) CCD is typically manufactured from low-resistivity, 25 μm epitaxial silicon. When the gate potential is applied to the electrode, a typical depletion depth of 5 μm is achieved with a corresponding field-free region of 20 μm. For an X-ray to be efficiently detected by the CCD it must interact in the epitaxial silicon. X-rays with an energy higher than ~3 keV have characteristic absorption length >5 μm and so the majority of these will interact in the field free region. Consequently a CCD aimed at X-ray detection tends to be manufactured from silicon with higher resitivity and a thicker epitaxial layer. This results in deeper depletion, sometimes as much as 40 μm and such CCDs are generally known as deep-depletion or high-resitivity devices. It is easy to see that this will result in many more X-rays and those at higher energies, interacting in the depletion layer. In fact detection efficiencies can be as high as 90% at 6 keV and 40% at 8 keV.

9. CCDs for X-ray Diffraction Measurements

With good detection efficiency in the 0.2-10 keV energy range, good energy resolution at temperatures easily achievable with a thermoelectric cooler (i.e. Peltier cooler), reasonably good spatial resolution (~10-40 μm) and relatively large area coverage (CCDs are available in a number of two and three side buttable formats that allow them to be readily mosaiced together), CCDs are a good choice of detector for use in compact X-ray diffraction / fluorescence instrumentation. In fact, as mentioned above, if the detectors are constructed from high-resistivity silicon, detection efficiencies in the region of 60-90% can be achieved at energies of around 6 keV (compared to efficiencies of around 20% at 6 keV for devices constructed from the standard low-resistivity silicon) and energy resolutions are essentially fano limited at -60°C. Examples of the variation of detection efficiency with energy are shown for various different types of CCD in Figure 5 and energy resolution is shown as a function of energy in Figure 6 for various system noise values.

In addition to the properties described above, CCDs also offer the advantages of photon counting operation. As well as providing the obvious capability for performing simultaneous x-ray diffraction and x-ray fluorescence analysis, photon counting mode also provides:

- the ability to remove fluorescence events (through post-processing of the event energies) thereby producing a cleaner diffraction profile. This approach avoids the need for a blocking filter which also attenuates the useful X-ray signal
- the ability to distinguish between the k-alpha and k-beta X-ray diffraction peaks, which provides further useful information in data-starved and time-critical applications.

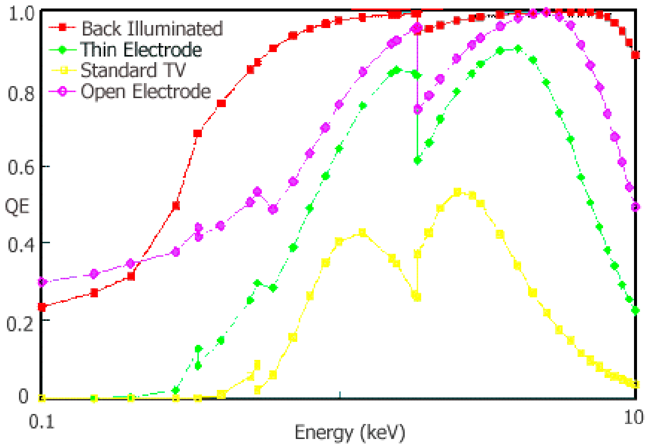

Figure 5. Detection efficiencies as a function of energy for various types of CCD.

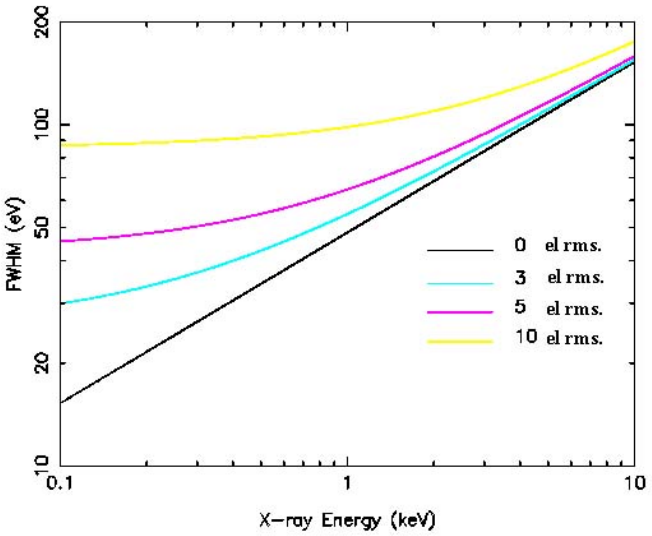

Figure 6. Spectral resolution (expressed as FWHM) as a function of X-ray energy for a range of system noise values.

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Coupling the PDF-4/Organics Relational Database to SIeve+, a Hanawalt and Fink Search Indexing Plug-In

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Introduction

The International Centre for Diffraction Data (ICDD) has been the reference source for X-ray Powder Diffraction (XRPD) data for over 50 years. The primary information in the PDF is the collection of d-I data pairs, where the d-spacing (d) is determined from the Bragg angle of diffraction, and the peak intensity (I) is obtained experimentally under the best possible conditions for a phase-pure material. These data provide data mining [1-2] capability as well as “fingerprint” identification of the compound because the d-spacings are fixed by the geometry of the crystal and the intensities are dependent on the contents of the unit cell. Hence, d-I data may be used for identification of unknown materials by locating matching d-I data in the PDF with the d-I pairs obtained from an unknown specimen.

The PDF has exhibited recent dramatic growth in entry population over the past 5 years and the new PDF-4/Organics results from a collaboration with the Cambridge Crystallographic data centre (CCDC). An illustration of organic entry growth for the PDF-4/Organics RDB is given in Table 1.

Identification is the most common use of the PDF, but the presence of considerable supporting information for each entry in the PDF allows further characterization of the specimen. In addition, we wish to demonstrate the use of the PDF-4 relational database as a filter for search-indexing. In this case, we will use a new plug-in for PDF-4 databases, SIeve+, to illustrate search results using Hanawalt and Fink methods.

Category	PDF-4/ Full File 2003	PDF-4/ Organic 2003	PDF-4/ Organic 2004
Organic Compounds	**25,609**	**147,201**	**217,077**
Inorganic Compounds	**133,370**		**3,048**
Both Organic and Inorganic	**1,931**	**1,776**	**1,931**
Only Inorganic	**131,439**		**1,117**
Calc. patterns from CSD		**122,816**	**191,468**
Drug Activity		**4,508**	**6,343**
Pharmaceuticals	**2,039**	**1,192**	**2,039**
Excipients	**801**	**184**	**1114**
Forensic Materials	**3,767**	**2,015**	**2,113**
Pigments	**342**	**284**	**296**
I/Ic	**73,087**	**125,342**	**195,316**
Total Entries	**157,048**	**147,201**	**218,194**

Table 1. *Selected entry counts for PDF-4 databases. Please note that because entries can be listed in both the inorganic and organic collection, the total number of distinct entries is obtained from the organic and only inorganic rows in the table.*

PDF-4/Organics

The PDF-4 database contains interplanar spacings (d) and relative intensities (I). However, other useful data such as synthesis, physical properties and crystallographic data are also stored in the database. With this new format, we will provide a broader range of analyses, for example, improved quantitative analyses, full pattern display, bibliographic cross referencing, etc. The PDF-4 uses relational database technology that provides pliable access to the database to carry out data mining studies and enhances the pursuit of conventional materials characterization using diffraction techniques (see Faber et al. [2]).
Example searchable fields are illustrated in Table 2.

Property	Entry Population
Drug Activity	**6,343**
Pharmaceuticals	**2,352**
Excipients	**1,114**
Merck	**1,554**
Pigments	**296**
Color	**214,501**
Density	**201,084**
Melting Point	**64,733**
Organic Functional Group Designations	**41,552**
Empirical Formula	**All**
# of Elements	**All**
Periodic Table	**All**
# Searchable Fields	**>30**

Table 2. *Example searchable fields in the PDF-4/Organics 2004 that can be used as pre-filters for Search-Indexing, using the RDB plug-in, SIeve+.*

In addition to better access to some of the RDB fields, users can also build search criteria by combining individual search conditions using Boolean operators. The availability of logical operators for combining search criteria is very useful for retrieval of relevant information from the database.

Search-Indexing using the Plug-in, SIeve+ in the PDF-4/Organics 2004

Manual techniques were first discussed by Hanawalt and these persist for a variety of reasons. The search-indexing plug-in, SIeve+, discussed here follows a traditional path to act as a replacement for paper search manuals published by the ICDD. An advantage to this approach is that Hanawalt [3,4] and Fink [5] methods can be followed in great detail as search-indexing proceeds. Educational benefits accrue following this approach. A more detailed report concerning PCSIWIN, the predecessor of SIeve+ has been given [6].

The Hanawalt search method has been implemented for many years at the ICDD. The method involves sorting the patterns in the PDF according to the d-spacing value of the strongest line. This list is partitioned into discrete d-space intervals defined as Hanawalt groups. A small overlap in d-intervals is employed to reduce the probability of missing powder pattern entries due to uncertainty in the d-space accuracy. Each Hanawalt group is sorted in order of decreasing d-spacing of the second most intense diffraction line. Subsequent lines are listed in order of decreasing intensity. The analysis rests on the three most intense lines. All reference lines must then be compared to the unknown. The Fink method was designed as an index based on the eight strongest d-spaces in the experimental pattern, but these are ordered in decreasing d-spacing. In short, the Fink method considers the 8 longest of the strongest diffraction lines. To help account for preferred orientation effects, the lines need to be permuted to remove limiting intensity criteria. This permutation process is easily computerized (in contrast to paper manual searches).

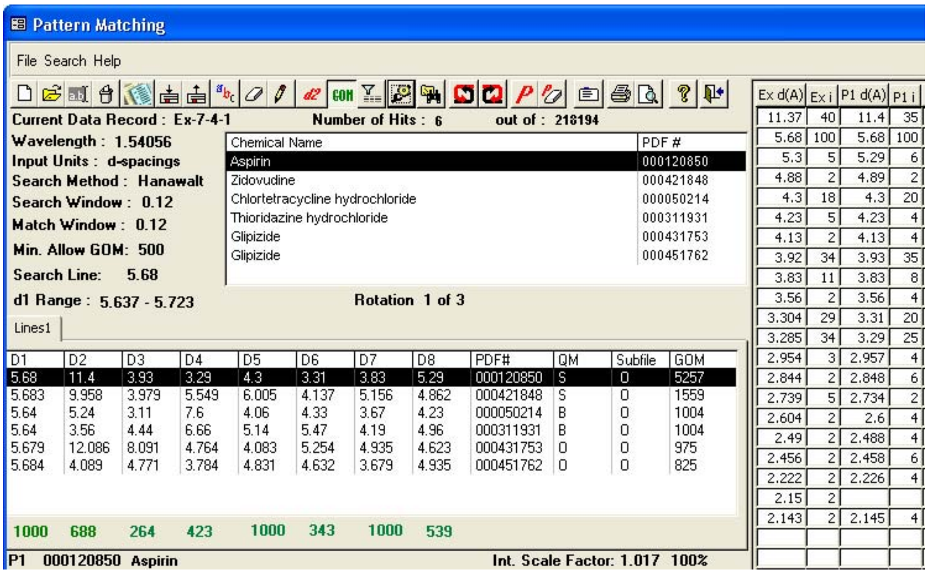
Filtering criteria need to be "remembered" while carrying out the search/indexing process. We have developed a "plug-in" for the PDF-4 databases that implements the Hanawalt/Fink strategy, including chemistry, subfile, quality-mark filters and any of the searchable properties in the database (see Table 2).

SIeve+

The basic idea of the plug-in is to provide d,I pairs as input to the program. The d-spaces are in Å and the I's are peak intensity values from the x-ray powder diffraction experiment. The principal input is from an ASCII file that contains the d,I pairs. However, the plug-in can also accommodate 2θ, I-pairs if the first ascii record also contains the wavelength. The uncertainty in d, Δd, can be obtained by taking the derivative of Bragg's Law:

$$\Delta d = d \cdot \cot\theta \cdot \Delta\theta \ . \qquad \text{Eq. 1}$$

In the case of the Hanawalt method, the search window, $SW = \Delta(2\theta_{SW})$ defines the Hanawalt group; the match window, $MW = \Delta(2\theta_{MW})$ defines the criteria used to judge matches for individual lines for each member of the group. The angular dependence of the search window and match window are defined by Eq. 1. The SIeve+ results illustrated in Figures 1 and 2 show that aspirin is the unknown phase.



Current Data Record : Ex-7-4-1
Number of Hits : 6
out of : 218194
Wavelength : 1.54056
Input Units : d-spacings
Search Method : Hanawalt
Search Window : 0.12
Match Window : 0.12
Min. Allow GOM: 500
Search Line: 5.68
d1 Range : 5.637 - 5.723
Rotation 1 of 3
Lines1

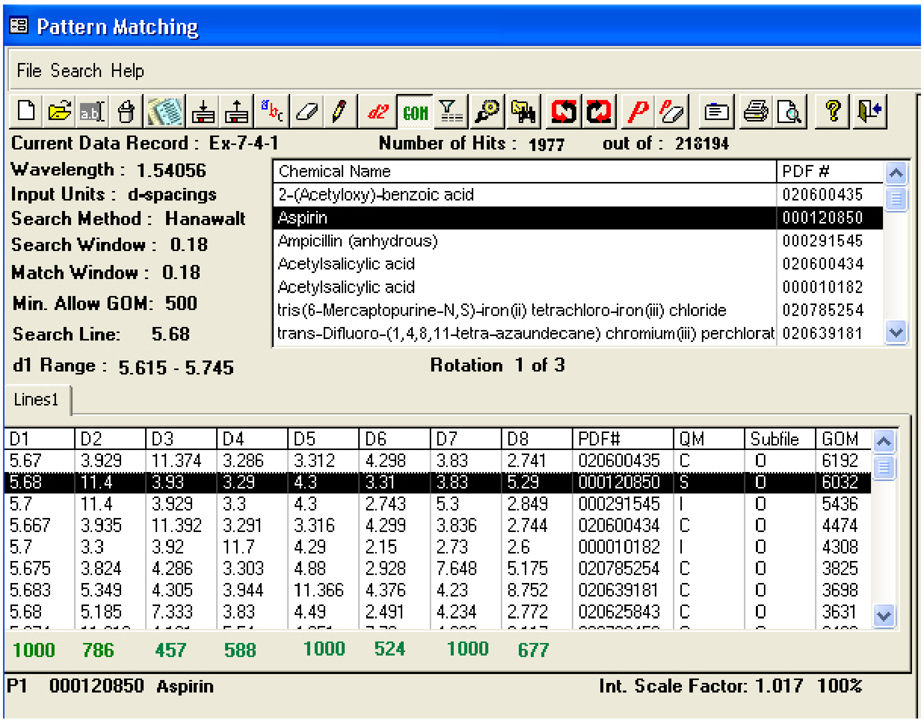
Chemical Name	PDF #
Aspirin	000120850
Zidovudine	000421848
Chlortetracycline hydrochloride	000050214
Thioridazine hydrochloride	000311931
Glipizide	000431753
Glipizide	000451762

D1	D2	D3	D4	D5	D6	D7	D8	PDF#	QM	Subfile	GOM
5.68	11.4	3.93	3.29	4.3	3.31	3.83	5.29	000120850	S	0	5257
5.683	9.958	3.979	5.549	6.005	4.137	5.156	4.862	000421848	S	0	1559
5.64	5.24	3.11	7.6	4.06	4.33	3.67	4.23	000050214	B	0	1004
5.64	3.56	4.44	6.66	5.14	5.47	4.19	4.96	000311931	B	0	1004
5.679	12.086	8.091	4.764	4.083	5.254	4.935	4.623	000431753	O	0	975
5.684	4.089	4.771	3.784	4.831	4.632	3.679	4.935	000451762	O	0	825
1000	688	264	423	1000	343	1000	539				

P1 000120850 Aspirin
Int. Scale Factor: 1.017 100%

Ex d(A)	Ex i	P1 d(A)	P1 i
11.37	40	11.4	35
5.68	100	5.68	100
5.3	5	5.29	6
4.88	2	4.89	2
4.3	18	4.3	20
4.23	5	4.23	4
4.13	2	4.13	4
3.92	34	3.93	35
3.83	11	3.83	8
3.56	2	3.56	4
3.304	29	3.31	20
3.285	34	3.29	25
2.954	3	2.957	4
2.844	2	2.848	6
2.739	5	2.734	2
2.604	2	2.6	4
2.49	2	2.488	4
2.456	2	2.458	6
2.222	2	2.226	4
2.15	2		
2.143	2	2.145	4

Figure 1. *Hanawalt method applied to an over-the-counter medication. The drug is aspirin. The tablets were ground and standard XRD experiments were performed. A peak-listing program was used to define d-spaces and peak intensities for all Bragg lines detected. A wide search window and match window were employed for this analysis.*



Current Data Record : Ex-7-4-1
Number of Hits : 1977
out of : 218194
Wavelength : 1.54056
Input Units : d-spacings
Search Method : Hanawalt
Search Window : 0.18
Match Window : 0.18
Min. Allow GOM: 500
Search Line: 5.68
d1 Range : 5.615 - 5.745
Rotation 1 of 3
Lines1

Chemical Name	PDF #
2-(Acetyloxy)-benzoic acid	020600435
Aspirin	000120850
Ampicillin (anhydrous)	000291545
Acetylsalicylic acid	020600434
Acetylsalicylic acid	000010182
tris(6-Mercaptopurine-N,S)-iron(ii) tetrachloro-iron(iii) chloride	020785254
trans-Difluoro-(1,4,8,11-tetra-azaundecane) chromium(iii) perchlorat	020639181

D1	D2	D3	D4	D5	D6	D7	D8	PDF#	QM	Subfile	GOM
5.67	3.929	11.374	3.286	3.312	4.298	3.83	2.741	020600435	C	0	6192
5.68	11.4	3.93	3.29	4.3	3.31	3.83	5.29	000120850	S	0	6032
5.7	11.4	3.929	3.3	4.3	2.743	5.3	2.849	000291545	I	0	5436
5.667	3.935	11.392	3.291	3.316	4.299	3.836	2.744	020600434	C	0	4474
5.7	3.3	3.92	11.7	4.29	2.15	2.73	2.6	000010182	I	0	4308
5.675	3.824	4.286	3.303	4.88	2.928	7.648	5.175	020785254	C	0	3825
5.683	5.349	4.305	3.944	11.366	4.376	4.23	8.752	020639181	C	0	3698
5.68	5.185	7.333	3.83	4.49	2.491	4.234	2.772	020625843	C	0	3631
1000	786	457	588	1000	524	1000	677				

P1 000120850 Aspirin
Int. Scale Factor: 1.017 100%

Figure 2. *Hanawalt method applied after pre-filtering using the PDF-4/Organics 2004 RDB. Notice that the Hanawalt group has been reduced to just 6 candidate reference materials.*

In Figure 1, wide search and match windows were chosen and the result is a Hanawalt group that contains 1,977 entries. Each of these reference patterns are then compared line by line against the "unknown".

In contrast, Figure 2 shows the results of coupling the PDF-4/Organics RDB as a pre-filter to the search indexing functions in SIeve+. Only 6 reference patterns need be compared to the unknown phase. It important to recognize that the Pharmaceutical subfile search in the PDF-4 was executed and the search results were conveniently transmitted to SIeve+.

Summary

We have outlined how the PDF-4/Organics can be used as a pre-filter to search-indexing using classical Hanawalt and Fink methods. The advantage of pre-filtering centers on the ability to use *any* combination of the searchable properties in the RDB. These can be applied to search-indexing using SIeve+. There were no filtering protocols available with older search-index paper manuals. In contrast for the plug-in, SIeve+, the effort required to examine large numbers of entries in the Hanawalt or Fink group is minimized and relevant solutions to search-indexing are illustrated. This streamlines the search-indexing process.

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FORMULATION ANALYSES OF OFF-THE-SHELF PHARMACEUTICALS

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INTRODUCTION

Several common high sales volume pharmaceutical tablets were examined for phase identification by X-ray powder diffraction. The purpose of the analysis was to see whether common, yet complex multi-ingredient formulations, could easily be analyzed using a new database, PDF-4 / Organics, and associated software designed for pharmaceutical analysis.

The PDF-4/Organics database is an ongoing annually updated collaboration between the International Centre for Diffraction Data (ICDD) and the Cambridge Crystallographic Data Centre (CCDC). This database combines data taken from both powder diffraction experiments and data collected from single crystal crystallographic determinations that can be calculated into a reference powder pattern. The database also contains bibliographic references for sample preparation, data collection, and associated physical property measurements. In total the database contain 218,194 entry sets with 416,554 references citations from 931 journals. Data from all sources are standardized, statistically analyzed, and extensively reviewed and edited prior to publication. In the 2004 release, several inorganic salts and excipients were also added to the database to aid those doing formulation analysis in law enforcement and pharmaceutical analyses. The inorganic additions included data from collaborations between the ICDD, FIZ-Karlsruhe and the National Institute of Standards and Technology (NIST). Therefore the database represents select data from multiple sources all combined for the purpose of unknown identification.

The conversion of the data from multiple global sources into a common relational database, PDF-4/Organics, was a multi-year development effort by the ICDD. The analyses described in this paper are one of the first large scale tests to see if the database and associated software performed for its intended use in organic and organometallic material identification.

SAMPLE PREPARATION

Samples were chosen from contributions by the authors and coworkers. The selection was haphazard with the exception that all samples received were analyzed and the study focused on as-received tablets taken directly from commercial packaging. The formulated tablets investigated are shown in Table 1.

Samples were analyzed on two different powder diffractometers. The authors are grateful to Bernie Squires of Rigaku-MSC, Inc., who ran several samples on a Rigaku MiniFlex desktop X-ray Diffractometer, during instructional classes at the annual ICDD X-ray Diffraction Clinic. A second set of samples were run on a PANalytical X'Pert Pro MPD with an X'Celerator Detector during an evaluation trial at Oak Ridge National Laboratory. In both cases the authors had unique and temporary access to the equipment, therefore each sample was analyzed a single time.

Tablet	Manufacturer
Alka-Selzer Plus®	Bayer
Tums® EX (Extra Strength)	GlaxoSmithKline
Pepcid® AC	Johnson&Johnson-Merck & Co
Promethazine Hydrochloride	Paddock Laboratories, Inc.
Benadryl®	Warner – Lambert Company
Kroger Decongestant	The Kroger Company
CVS Decongestant Antihistamine	CVS/Pharmacy®
Alavert™	Wyeth Consumer Healthcare
Robitussin® Cough Drops Honey Lemon	A. H. Robbins
Claritin	Schering-Plough
Celebrex™ Capsules	G. D. Searle & Co
Donnatal	Wyeth Pharmacueticals
Effexor®	Wyeth Consumer Healthcare

Table 1. *Tablets and manufacturer or commercial source.*

Tablets were ground in a mortar and pestle and then one of two sample preparation methods were used depending on the instrument available for analysis. Both diffractometers used a Seeman-Bohlin focusing reflection geometry.

Method A – Cavity mounts were backfilled with powdered tablets. The samples were then run on the Riguku MiniFlex, using Cu radiation and variable slits, a 0.05 step size with scans from 5 to 65 degrees two theta. Total data collection time was approximately 2 hours using a scintillation counter.

Method B – Samples from powdered tablets were lightly dusted onto a Vaseline® coated zero background holder. Ni filtered Cu radiation was used with a 15 minute total data collection time. The area from 5 to 80 degrees two theta was scanned using a 0.01 degree step size.

DATA REDUCTION AND ANALYSIS

In both cases the data was received in electronic format. Once received data was displayed using the program POWDERX [1]. Then the background was stripped using the Sonneveld algorithm and a 2nd derivative peak finding program was used to generate a text file of d-spacing and intensities. The authors intentionally avoided using sophisticated integrated software packages that are available with most modern diffractometers in order to more fully test the capabilities of the database.

As mentioned above the data in the PDF-4 database comes from multiple sources and editors review the data for accuracy and self consistency and a complex series of indexes are prepared that allow the database with interface to automated data collection processes and rapid search and identification algorithms [2,3]. In Release 2004, a prototype version of the program SIeve+ was used for searching. SIeve+ (Search, Index, Sieve) is a new program [4] developed by the ICDD® to replace the historical PCSIWIN program and the functional operation of paper products such as the Hanawalt Search Manual, Alphabetic and Organic Indexes. In this way the database can be used to identify materials through conventional Hanawalt, Alphabetical and Fink searches. SIeve offers the advantage over paper products in that these searches are rapidly performed by using a 32-bit code and can handle the large size and entry populations of modern databases. The PDF-4/Organics database is housed in a 7 CD-ROM set. SIeve introduces a new text importer that can automatically read a wide variety of input files containing d-spacings and intensity information. The program also includes Fink and Long 8 search algorithms [5]. The former uses the strongest and longest eight d-spacings and the latter uses the 8 longest d-spacings. These searches have historical precedent and have demonstrated success in identifying low symmetry complex compounds which have larger unit cells and characteristic d-spacings in the high d, low angle region of the diffraction pattern. These searches have lost favor in the last 20 years since the permutation of the 8 lines for an active index resulted in enormous size which slowed computer searches or made a paper index too cumbersome (multiple volume) whenever one searched a large entry population. Fast processors and large storage in modern PC's enable these search techniques.

In the analyses text files produced during data reduction were imported into SIeve+ using the file importer. All three search algorithms, Hanawalt, Fink, and Long 8, were used to identify phases. A goodness of fit between the observed d-spacing and the reference d-spacing is calculated for each of the top 8 d-spacings and a cumulative score is used to rank the candidates [5]. The program is integrated with the database so that the database subfiles can be examined and many parameters can be interactively changed in the search programs.

RESULTS

13 Different tablet formulations were analyzed by the methods described above. The major crystalline phase was identified in each tablet for all formulations. Common excipients such as sucrose, mannitol, cellulose, and alpha lactose monohydrate were frequently identified in the tablet formulations. In fact, cellulose was a major ingredient in five formulations and alpha lactose monohydrate in four formulations. The importance of adding excipients to the database is demonstrated in the analysis of Benadryl, shown in Figure 1. Benadryl® contains an inorganic excipient, calcium hydrogen phosphate hydrate and an or ganic excipient, cellulose. The PDF-4/Organics database has the ability to simulate digitized patterns. The pattern for cellulose shown in Figure 1 was simulated from PDF 00-050-2241, a sample of bleached Egyptian cotton, by applying a pseudo-Voigt peak shape and optimizing the

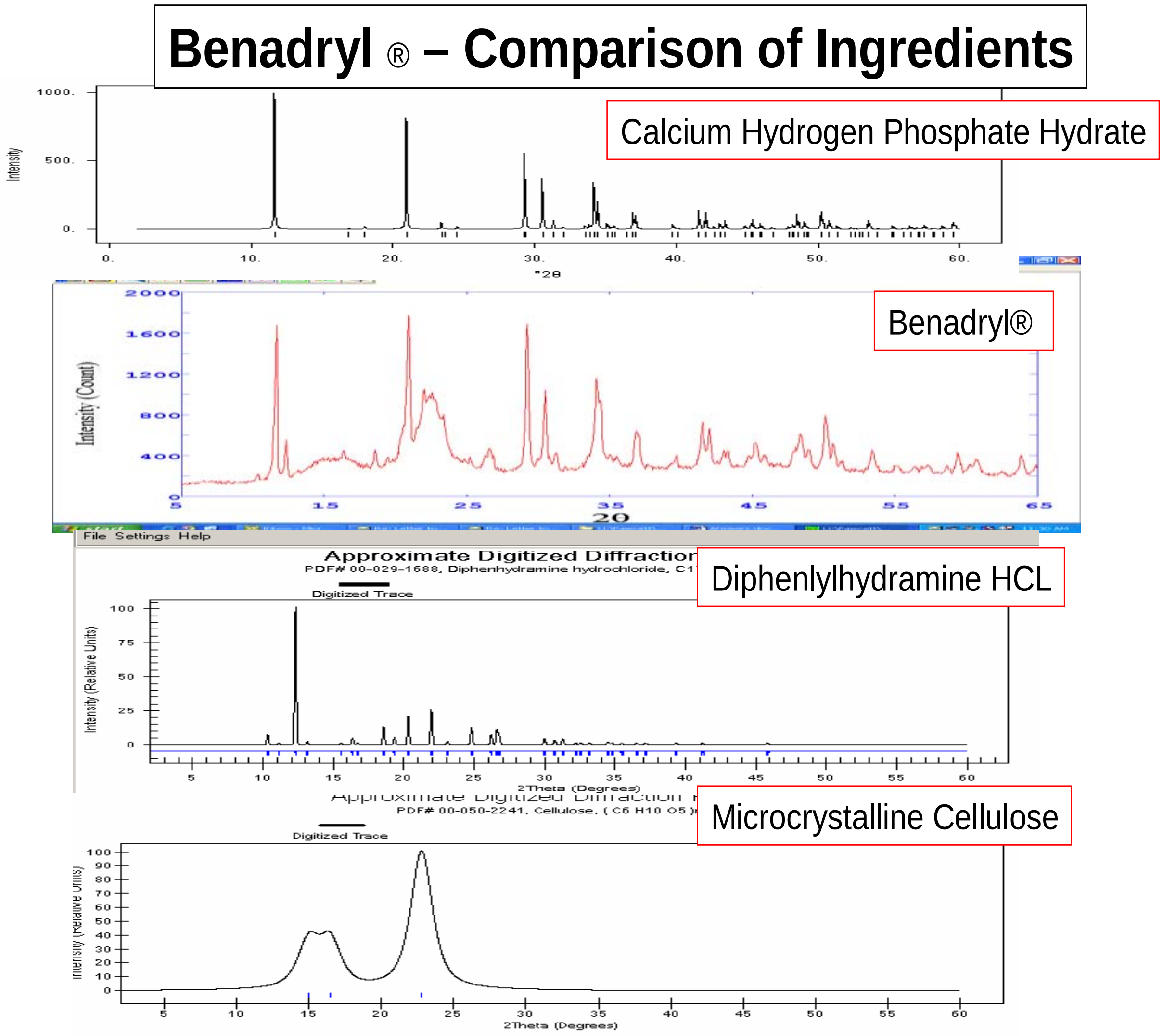
Benadryl ® – Comparison of Ingredients

Figure 1. *Comparison of the raw X-ray diffraction data for a tablet of Benadryl® compared to the digitized reference patterns of calcium hydrogen phosphate hydrate, diphenylhydramine HCl (active ingredient) and microcrystalline cellulose.*

peak width to the sample. Using this method, all five tablets containing micronized cellulose could be identified with a simulated pattern analysis. Inorganic excipients were frequently found in the various tablets. These included titanium dioxide, silicon dioxide, iron oxides used as colorants and fillers, calcium carbonate and sodium bicarbonate used in antacids, and talc used as a processing aid.

The program SIeve+ after identification of the major crystalline excipients eliminates peaks due to the phase match and then searches and matches the residual pattern. Using this procedure additional phases and active ingredients were identified. In the 13 tablets there were 15 active ingredients, 13 of which were identified. Alka-Selzer Plus® had two active ingredients, the antacid sodium bicarbonate and aspirin. In the Promethazine hydrochloride tablet analysis two polymorphs of promethazine hydrochloride were identified. The active ingredient not identified in this analysis was loratidine. Loratidine is the active ingredient in both Alavert™ and Claritin. Two excipient phases were identified in each of these tablets and, as one would expect, the unidentified residuals closely resemble each other. The structure of loratidine has been elucidated, published, and is contained in the Cambridge Structural Database (CSD). However, the structure is significantly disordered which prevented the calculation of a high quality reference pattern for inclusion in the Powder Diffraction File. This drug will be targeted for analysis by ICDD's grant-in-aid process, where materials of industrial importance are targeted for characterization by qualified laboratories for inclusion in the Powder Diffraction File. The grant program has characterized hundred of commercial drugs. Overall the analyses identified 87 % of the actives by number and 92% by chemistry.

The identification process accounted for 48 phases in the 13 tablets. Besides the aforementioned difficulty in analyzing loratidine, there was also large residuals in the analyses of Pepcid AC®, CVS decongestant and the Robitussen® cough drop. Three phases or more were identified in each of these latter samples but several unidentified peaks remained. Several difficulties arise in analyzing the residual patterns that includes issues with both experimental measurements and the data reduction algorithms. The data reduction process did not correct for specimen orientation and did not correct for close overlapping peaks in the residual analysis. The latter reduces the effectiveness of the match process as the number of phases and peaks are identified. There were also many low intensity peaks (<5) that may have been easier to resolve and identify by using longer count times, smaller step sizes, and better counting statistics. The authors did not pursue this study since this was not the intent of this analysis, but anticipate that several additional phases could be identified by taking the steps outlined above.

The course of the investigation yielded several unanticipated results. For example, four formulations contained alpha lactose monohydrate, but they matched three different PDF reference files. The PDF files include a stereo specific lactose whose pattern was calculated from a single crystal analysis and two unindexed experimental powder patterns. We hypothesize that the three files may represent three degrees of molecular orientation since the patterns differ primarily in relative intensity. The fourth sample, Effexor®, was so severely oriented that automated phase identification was unable to find a solution. However given a clue from the prior analyses it was noticed that the typically weak 040 and 060 peaks were the strongest two peaks in the pattern. These peak intensities were manually corrected which resulted in rapid identification. Overall, the thin film sample preparation technique (Method B) resulted in highly accurate d-spacings but some specimen orientation. In most cases, Effexor® being the exception, the d-spacing accuracy facilitated the identification due high goodness of merit (GOM) fits used to sort and list candidate identification.

Through trial and error we found that using a mixed search strategy was more effective than using any of the search algorithms independently. The results are interpreted as follows. In most tablets the strongest phase was an excipient that was readily identified using a Hanawalt Search. Once this phase was removed we were frequently trying to identify low symmetry organic compounds that are effectively identified using Fink or Long 8 searches. In the PDF-4/Organics database patterns calculated from crystallographic analyses are only calculated out to thirty degrees two theta (Cu radiation). This was a practical tradeoff between content and size of the database since each 5 degrees two theta would effectively double the database size. However, as a consequence, residual patterns may have artificially large peaks above 30 degrees which can interfere with a Hanawalt search that is based on the longest and strongest lines. An alternative approach would be to record experimental data to 30 degrees. We do not recommend this approach with pharmaceutical tablets since many of the high symmetry excipients need the wider angular range to experimentally measure enough d-spacings to achieve a high GOM match. The mixed algorithm search strategy was effective in identifying phases where experimental data collection encompassed a broad two theta range. Finally we should note that many formulations contained micronized, microcrystalline or amorphous content. This includes materials such as cellulose, cellulose derivatives, lactose and starch. This can present a challenge to many data reduction programs resulting in false peak assignments or poor intensities if these materials are not adequately separated from the background.

CONCLUSION

Several common high sales volume pharmaceutical tablets were examined for phase identification by X-ray powder diffraction. Using the PDF-4/Organics database and associated search software the major crystalline phase was identified in each of the 13 tablet formulations tested. An average of 3.5 phases were analyzed per tablet and the active ingredient, usually a minor phase, was identified in 87 % of the formulations. All analyses were performed on ground tablets without any physical or chemical treatments to separate or concentrate the phases.

The results emphasized the effectiveness of using a combined source database, such as PDF-4/Organics for analyzing pharmaceutical formulations. Active ingredients were identified by reference to both single crystal derived powder patterns and experimental powder patterns. In this particular series of experiments significantly more phases were identified by comparison to the experimental powder diffraction data than by the reference patterns calculated from single crystal studies despite the 7/1 ratio of calculated to experimental patterns in the database. We attribute this result to the multi year focus on obtaining experimental patterns on commercially relevant materials in the ICDD's grant program and the prevalence of inorganic excipients in the samples.

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(1) POWDERX is a program written by Dr. Cheng Dong, (Institute of Physics, Chinese Academy of Sciences, P.O.Box 603, Beijing 100080, P.R. China. E-mail: chengdon@aphy.iphy.ac.cn) Powder X is a Graphical Powder Diffraction Analysis program which includes; specimen displacement, aberration correction, background stripping, alpha-2 stripping, smoothing, peak offset determination, peak find. It is available upon request for non-commercial use.

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(3) J. Faber and F. L. Needham, "The New Organic Powder Diffraction File: Applications for Polymorphism and Search Indexing, American Pharmaceutical Review, (2002), 5, Issue 2, 70-75.

(4) SIeve+ is a new program designed to work as an interactive plug-in with PDF-4/Organics. This program is an upgrade of the program PCSIWIN and has additional features tailored for pharmaceutical analysis. More details can be found at www.icdd.com

(5) J. Faber, C. A. Weth and J. Bridge, "A plug-in program to perform Hanawalt or Fink search-indexing using organics entries in the ICDD PDF-4/Organics 2003 database", Powder Diffraction 19 (1), March 2004.

Crystal structure of guaifenesin, 3-(2-methoxyphenoxy)-1,2-propanediol

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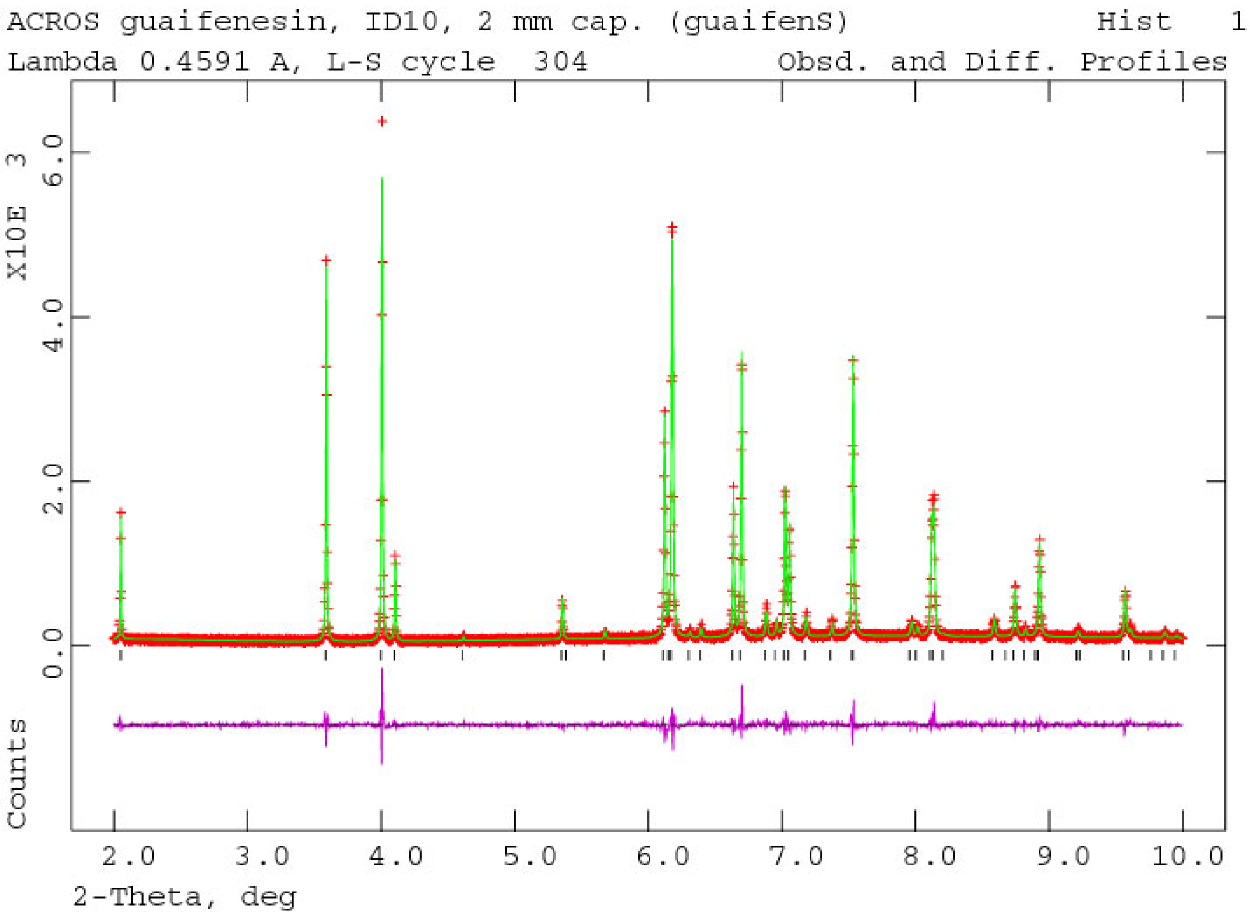
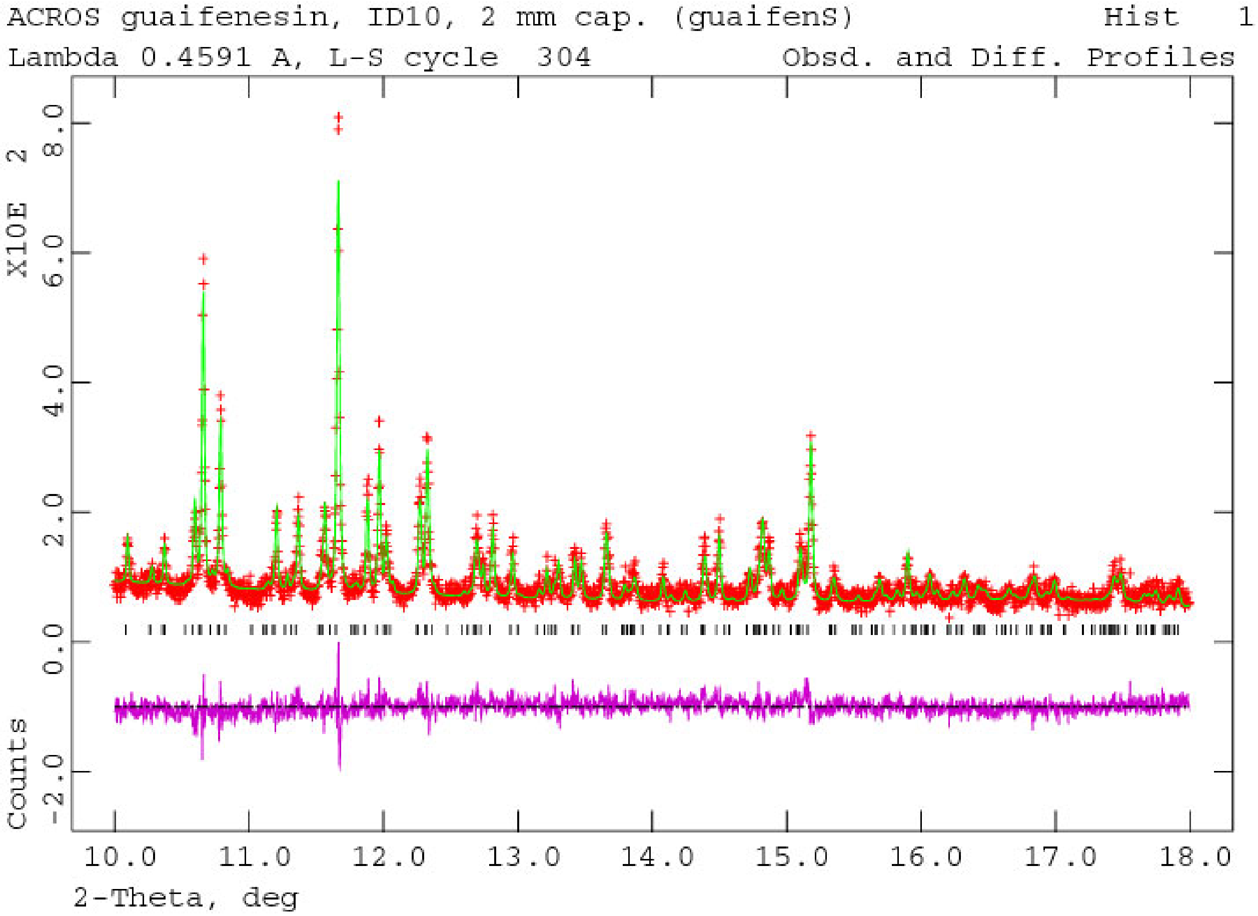
Guaifenesin, 3-(2-methoxyphenoxy)-1,2-propanediol ($C_{10}H_{14}O_4$, CAS registry number 93-14-1) was first synthesized in the 1940's, and is used as an effective expectorant (mucus thinner) in many prescription and over-the-counter cough remedies and decongestants (Shervington and Shervington, 1998). My most recent encounter with guaifenesin was in the form of Duratuss GP 120-1200 extended release tablets (UCB Pharma). These tablets consist of guaifenesin and (+)-pseudoephedrine hydrochloride (Blanchard, 1990). Although a calculated pattern 02-063-6701 for (+)-pseudoephedrine hydrochloride is included in the PDF-4 Organics 2004 (Mathew and Palenik, 1977), no such pattern exists for guaifenesin, as its crystal structure has apparently never been determined. To carry out a quantitative phase analysis of the Duratuss tablets, the crystal structure of guaifenesin was determined using synchrotron powder diffraction data, because single crystals have proven impossible to grow.

Commercial guaifenesin reagent (Fisher ACROS) was ground in a mortar and pestle, and packed into a 2 mm glass capillary. The powder pattern (1.600-18.000 $^{\circ}2\theta$, 0.002 $^{\circ}2\theta$ steps, 0.5 sec/step) was measured from this rapidly-rotated capillary on the MR-CAT ID10 beamline at the Advanced Photon Source at Argonne National Laboratory, using a wavelength of 0.459141 Å (27.0 keV). The pattern could be indexed (Boultif and Louër, 1991) on a primitive orthorhombic unit cell having a = 7.65705(7), b = 25.67020(24), c = 4.97966(4) Å, and V = 978.793(15) Å^3 (M(24) = 135.7, F(24) = 1074.0(0.0007,33). The systematic absences unambiguously determined the space group as $P2_12_12_1$ (#19), a common space group for chiral molecules. Although guaifenesin occurs in both *(R)* and *(S)* enantiomers, all commercial guaifenesin is racemic. Presumably the powder consists of separate crystallites of *(R)* and *(S)* molecules. The *(R)* enantiomer was selected for structure solution. The structure was solved using Monte Carlo simulated annealing techniques as implemented in the Reflex Powder Solve module of Materials Studio 2.2 (Accelrys, 2003). The center of mass, three orientation angles, and five torsion angles (a total of 11 parameters) were allowed to vary, with default parameters and convergence criteria. Several annealing runs (each of which yielded an apparently chemically-plausible model) were required before a refinable model was obtained. This refinement yielded the residuals wRp = 0.1808, Rp = 0.1344, χ^2 = 4.674, and $R(F^2)$ = 0.3119. Although the fit to the observed pattern was plausible, the quality of the fit and the magnitudes of the residuals did not reflect the quality of the raw data, and the torsion angles were unreasonable.

To help understand the nature of the errors, a quantum chemical geometry optimization of the *(R)* enantiomer (fixed lattice parameters) was carried out using density functional plane wave pseudopotential techniques as implemented in CASTEP (Segall *et al.*, 2002). The optimized structure yielded the expected hydrogen bond network. The differences between the refined and optimized structures caused me to ask whether the *(S)* enantiomer could be incorporated into this structure with a different conformation. With the benzene ring fixed, the *(R)* enantiomer was converted manually into the *(S)* enantiomer using Cerius^2 (Accelrys, 2001), and the propyl torsion angles adjusted manually to bring the oxygens of the hydroxyl groups into positions similar to those in the optimized *(R)* structure. The crystal structure of this conformation of the *(S)* enantiomer was also optimized using CASTEP. The refined structure was similar to the average of the two optimized structures, suggesting a possibility of co-crystallization of the enantiomers.

The optimized coordinates of the (R) and (S) enantiomers were used to carry out a refinement of the racemate in $P2_12_12_1$. When the occupancies of the two enantiomers were refined, the (R)/(S) ratio was 0.13/0.87(1). The final and best refinement was obtained using only the (S) enantiomer. Guaifenesin does indeed contain (R) and (S) crystallites, but the molecule has a very different conformation than that obtained from the original structure solution.

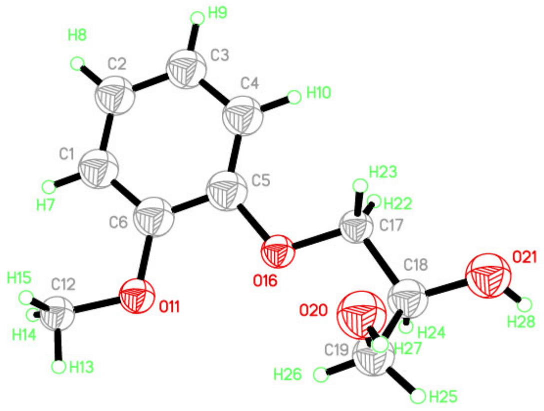


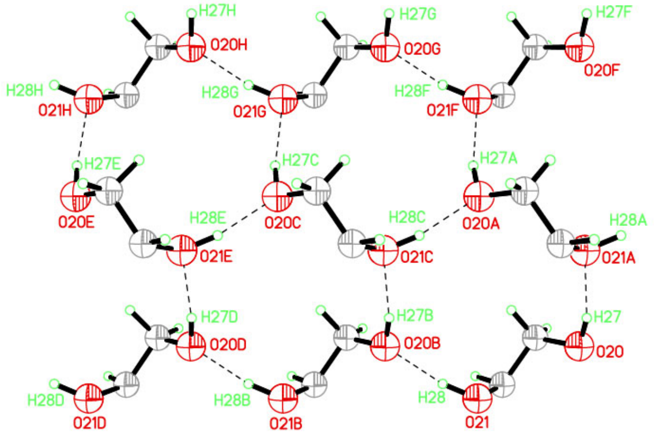


All data processing was carried out using GSAS (Larson and Von Dreele, 2000). The C_6H_4 benzene ring was refined as a rigid body. Soft constraints were applied to bond distances and bond angles; the torsion angles were unconstrained. All atoms were refined isotropically. The hydrogen U_{iso} were constrained to be 1.3× the displacement coefficient of the atom to which they are attached.

The hydrogen positions in the side chains were fixed at the locations determined by the quantum calculation.

The final refinement of 56 variables using 8213 observations yielded the residuals *wRp* = 0.1092, *Rp* = 0.0856, χ^2 = 1.643, $R(F^2)$ = 0.1179, and *R(F)* = 0.0931. The soft constraints contributed 1.5% to the final reduced χ^2. The largest peak in the difference Fourier map was +0.25 *e*, and the deepest hole was -0.23 *e*. Several of the hydrogens could be located in a difference Fourier map calculated without the hydrogens. The agreement of the observed and calculated patterns is excellent.





There are no surprises in the geometry of the molecule; all bond distances and angles fall within the normal ranges. In particular, the torsion angles are close to the expected values from the statistical analysis of the Cambridge Structural Database. The conformation of the molecule is different than that expected for an isolated molecule, and is determined by the formation of two hydrogen bonds. These hydrogen bonds lie roughly along the *a*- and *c*-axes, forming a 2-dimensional network parallel to the long *b*-axis. These hydrogen-bonded layers dominate the crystal structure. The phenyl-phenyl and methyl-methyl interactions are normal.

The excellent agreement between the optimized and refined structures (the root-mean-square difference in C and O atom positions is only 0.052 Å) means that we can use the quantum calculation to understand the energetics of this crystal structure. By the normal geometrical criteria (Jeffrey, 1997) the two hydrogen bonds would be considered strong. The Mulliken overlap populations in the hydrogen bonds (0.13 *e*) are exceptionally large, and correspond to hydrogen bond energies of 50 kcal/mole (Kaduk, 2002). Since each molecule participates in four hydrogen bonds (two as a donor and two as an acceptor), formation of the hydrogen bond network lowers the energy by 100 kcal/molecule. The local minimum energy of the observed conformation (Hartree-Fock calculation using a 6-31G** basis set in Spartan'04 (Wavefunction, 2003)) is 3.8 kcal/mole higher than the global minimum energy conformation. This energy is probably an underestimate, for in an isolated molecule the hydroxyl groups rotate from their positions in the solid state to "try" to form intramolecular hydrogen bonds. Paying a small conformational energy penalty to gain a large amount of energy by the formation of the hydrogen bonds explains the formation of the crystal structure.

With this crystal structure of guaifenesin and the known structure of (+)-pseudoephedrine hydrochloride (Mathew and Palenik, 1977), we can carry out a quantitative phase analysis of Duratuss GP 120-1200. The tablets are supposed to contain 120 mg of (+)-pseudoephedrine hydrochloride and 1200 mg guaifenesin, so we would expect 90.9 wt% guaifenesin and 9.1 wt% pseudoephedrine. A Rietveld refinement of the pattern of the ground tablets yielded concentrations of 91.62(2) and 8.38(15) wt% – close to the expected values. However, the tablets weigh 1540 mg, not 1320 mg. To understand the nature of the "extra" mass, a portion of the ground tablets was blended with a quartz internal standard, and the analysis repeated. The Rietveld refinement yielded 90.4(4) wt% guaifenesin and 7.7(4) wt% pseudoephedrine, and 1.9% other phases. A weak low-angle peak in the pattern indicates the presence of a trace of an additional crystalline phase, probably a stearate or laurate. No significant concentration of amorphous binder or microcrystalline cellulose was detected. Dividing the expected 120 mg pseudoephedrine by the 1540 mg tablet weight yields a pseudoephedrine concentration of 7.8 wt%. The tablets do indeed contain the stated dose, with almost of all of the balance of the tablet being composed of guaifenesin.

Acknowledgement

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Results of the second Reynolds Cup contest in quantitative mineral analysis

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Introduction

Phase identification and quantification is a frequent task in materials science as well as in geosciences. Although a wide range of methods have been established, serious errors may occur when unknown compositions have to be analyzed in practice. This is especially true for complicated mixtures containing clay minerals [1]. One way to get a realistic picture on the ability of the scientific community in analyzing real samples is to organize a “round robin”. To obtain reliable results, such a test has to be performed on known samples of realistic compositions and should reach a broad and representative field of laboratories. The first Reynolds Cup was initiated by colleagues from ChevronTexaco and the U.S. Geological Survey [2]. They decided to provide 3 mineral mixtures representing different types of sedimentary rocks for qualitative and quantitative phase analysis. In contrast to the previous IUCr round robin [3, 4], the task included the qualitative phase analysis to evaluate the complete analytic procedure as necessary in daily analysis. Additionally, the use of supporting methods and combinations was explicitly allowed to get an overview of the methods used in common practice. Only the participants delivering the most accurate results were named. The name “Reynolds Cup” was chosen to honor Robert C. Reynolds Jr., a pioneer in clay science and phase analysis.

After the results of the first contest have been published at the 2002 Clay Minerals Society meeting in Boulder (Colorado), an “ad hoc” committee decided to continue with a second contest in 2004 in a similar manner. The author was commissioned with the organization. The contest was announced at several conferences attended by mineralogists and crystallographers as well as at the DTTG homepage and the CMS, MSA and IUCr Rietveld list servers in December 2003.

Sample Preparation

The mixtures were prepared from pure mineral samples obtained mainly from the collections of the TU Bergakademie Freiberg, Germany. Pure minerals (Table 1) were hand-picked from crushed single crystals or separated by chemical treatment and size fractionation in the case of clay minerals.

Table 1: Reference minerals

Name	**Variety/description**	**Origin**
quartz	optical grade clear crystals, some cm	Brazil
K-spar	adularia, monoclinic, clear crystals, some cm	Rhone glacier/Switzerland
albite	white crystals, some cm	Striegowa/Poland
oligoclase	white crystals, lamellae (antiperthite?)	Arendal/Norway
calcite	island-spar, optical grade crystals, some cm	unknown locality
dolomite	white crystal, some cm	unknown locality
magnesite	white dense masses	Wald/Austria
anhydrite	clear crystals, 3-5 mm	Wathlingen/Germany
halite	single crystal	artifical
pyrite	crystals, 3-10 mm	Peru
hematite	red-black crystals	Cumberland/GB
rutile	chemical grade, synthetic pigment, powder	artifical
anatase	chemical grade, powder	artifical
kaolinite	Hinckley index 0.54, <20 µm fraction	Capim/Brazil
dickite	white masses	Altenberg/Saxony
muscovite 2M1	clear platy crystals, some cm	Custer/CO
illite 1Mt	sample RM 30 *, < 6.3 µm fraction	Silverton caldera/CO
I/S mixed layer	R3 ordering, ca. 85-90 % illite, < 2 µm	Füzeradvany/Hungary
montmorillonite	IBECO Ca, white variety, < 0.2 µm	Morocco
chlorite	Mg-rich, IIb polytype	Bernstein/Austria

However, some minor impurities (maximum 1-3 %) were accepted for some of the 20 minerals. An estimation of the amount of these admixtures was performed by Rietveld refinement. The nominal composition of the mixtures (Table 2) was corrected accordingly. Additionally, a rough estimation of the uncertainties of the nominal compositions of the mixtures was done on the basis of the estimated detection limit of the impurities. The sum of uncertainties was between 1-1.5 % for the three samples, re

Table 2: Nominal composition of the mixtures

Mineral	**RC2/1(wt.%)**	**RC2/2(wt.%)**	**RC2/3(wt.%)**
Quartz	**24.8**	**45.7**	**14.7**
K-Feldspar	**8.5**	**9.2**	**2.1**
Albite	6.5	4.0	
Oligoclase		6.7	2.9
Plagioclase	**6.5**	**10.7**	**2.9**
Calcite	**5.0**		**18.6**
DOLOMITE	**2.0**		**6.0**
Magnesite			**4.9**
Halite			**1.5**
Anhydrite			**14.6**
Pyrite	**2.5**		
Hematite		**2.5**	
Anatase	**0.1**	**1.5**	
Rutile		**1.5**	
Kaolinite	16.0	9.9	
Dickite		5.5	
Kaolinite group	**16.0**	**15.4**	
Illite 1Mt	10.5	5.5	
I/S mixed layer	10.1		
Montmorillonite	9.5		8.0
Muscovite 2M1		5.0	17.1
Total dioct 2:1	**30.1**	**10.5**	**25.1**
Chlorite	**4.5**	**3.0**	**9.6**
Total	*100.0*	*100.0*	*100.0*

tainties was between 1-1.5 % for the three samples, resulting in a total sum of about 4 %. All materials were broken to < 0.4 mm size for main components and to < 0.2 mm or < 0.1 mm for minor components of the planned mixtures. The air-dried material was weighted in for a total mass of 256 g of each mixture.

These samples were homogenized by 24 h overhead tumbling in 800 ml glass bottles together with mixing balls. Then, the mixtures were split into 8 parts in a rotary sample splitter and recombined 5 times. After a further splitting run, the 8 splits were split again into 8 parts (now 4 g) using a micro-rotary splitter.

In this way 64 4-g-units of each mixture were obtained. In order to check the homogeneity of the splits, 2 sample sets were taken randomly from these 64 units. No significant differences could be seen in the XRD patterns and between the XRF results.

Data Evaluation

In order to avoid nomenclature problems during reporting and judging of the results, some grouping of minerals was done. For example, all dioctahedral 2:1 layer silicates like muscovite, illite, smectite(di) and I/S mixed layers have been considered to be in one group, as well as all minerals belonging to the kaolin group. We used the sum of deviations from actual wt-% ("bias") as a criterion for the accuracy of the analyses. All together, 29 minerals (or groups) had to be analyzed in the 3 samples. The winner would be the person who reports data that have the lowest sum of bias for all three mixtures. Misidentified minerals were not counted as additional bias because the concentration reported for these phases are obviously lacking for others due to the closure of the data.

Results

About 4 days after sending the start signal to the list servers, 60 laboratories worldwide have expressed interest in the available sets, each containing 3 mineral mixtures. This indicates the great interest of the community in improving the analytical methods and to take part in a round robin. The samples have been sent out to these 60 laboratories in 18 countries of 5 continents in late December 2003. The only information given to the participants was that the compositions were designed to represent three different types of sedimentary rocks (mudstone, sandstone/siltstone, saliniferous rock) and that the amorphous content could be assumed to be insignificantly low. 35 participants from 11 countries returned results until May 1st. No delay was accepted. This standing is large enough to give an insight in the state-of-the-art in mineral analysis. The participants applied a range of different methods for phase identification and quantification. Techniques for sample preparation were also reported because they form an important part of the analytical procedure. In Table 3, the methods used primarily for quantification are indicated by **X**, and the supporting methods by +. The best results are at the top, highest bias at the end of the table.

One participant only reported qualitative data (last line). Not surprisingly, nearly all participants used X-ray powder diffraction as the principal method of quantification. Although different clay minerals were present, the majority of the contestants used Rietveld methods or other full pattern fitting techniques. There is a clear tendency that users of single line methods are concentrated in the lower half of the standing. On the other hand, the expertise of the operator seems to play an important role: Contestants using the same method/program or similar combinations are sometimes placed at the opposite ends of the standing.

Table 3: Analytical methods applied

XRD single line	XRD pattern summation	XRD Rietveld	XRD oriented samples	grainsize separation	chemical analysis	IR spectroscopy	SEM-EDX	TG-DTA-DSC	BET specific surface	water absorption	cation exchange capacity	carbonate analysis	Raman microprobe
	X	X	+	X	X								
	X		+	+	+	+	+	+			+		
		X	+			+			+	+			
	X		+										
		X	X	X	X								
		X											
		X	+	+			+						
	X		+										
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+			+		X		X				X	X	
X			+					+					
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The results clearly show that qualitative analysis is still a serious problem. Many contestants failed to detect the minor phases. Others misinterpreted their data and reported phases that were not present. For example, 4 people discovered palygorskite instead of the ordered I/S mixed layer mineral in sample 2/1. In many cases, trioctahedral smectites were mistaken for the montmorillonite, as wellas any trioctahedral micas for muscovite/illite. Some participants trusted automatic search-match routines and re ported long lists of exotic minerals in low concentrations. The clay mineral assemblage in sample 2/1 was complicated because of the presence of an ordered I/S mixed layer together with discrete montmorillonite and illite. Only nine participants reported the presence of a mixed-layer mineral.

On the other hand, nearly half of the contestants delivered reliable results, 9 of them better than 50 % bias (Fig. 1). The top 4 reached sums of bias below 29 %.

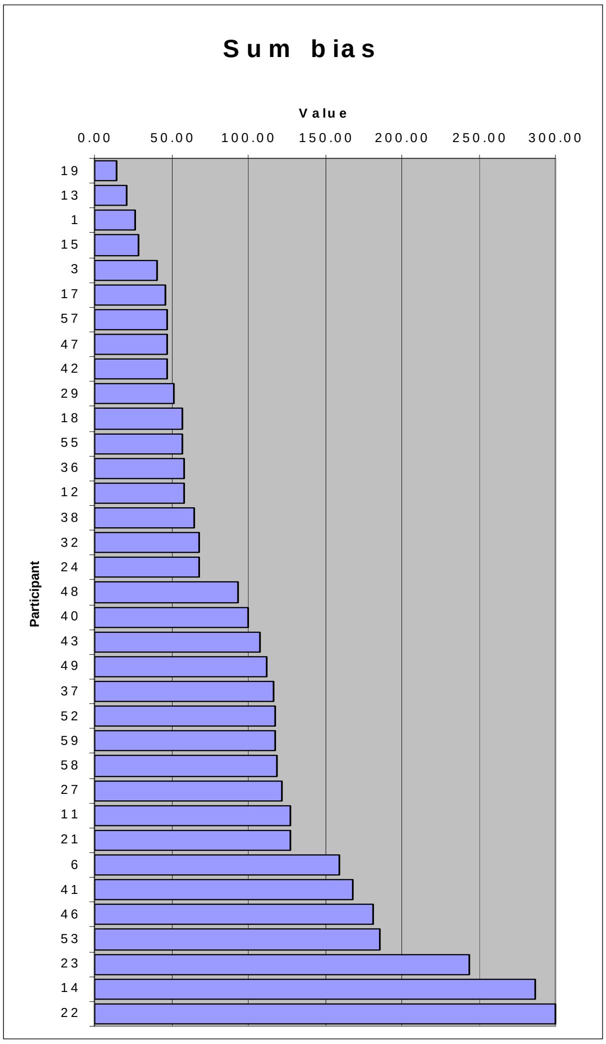

Figure 1: Cumulative bias, all participants

The third place was a share between Michael Ploetze from ETH Zuerich/Switzerland and Steve Hillier from Macaulay Institute in Aberdeen/Scotland. They reached biases of 26.3 and 28.7 %, respectively. Michael used Rietveld analysis (BGMN/AUTOQUAN) of the bulk samples, supported by water absorption experiments. Steve applied a self-developed pattern summation program (X-LS MINERAL) with an internal standard to texture-free (spray-dried) powder patterns. The second place goes to the team of ChevronTexaco in Houston/USA around Dougal McCarty and Jan Srodon. This group used the self-developed pattern fitting program QUANTA with internal standard, based on a genetic algorithm. The winner was Oladipo Omotoso from CANMET Energy Technology in Devon/Canada. He carried out a phase separation into fractions </>2µm and analyzed both by a combination of Rietveld refinement (TOPAS for coarse fraction, SIROQUANT for clay-bearing fine fraction) and NEWMOD simulation of the clay patterns, supported by chemical analysis of the dissolved matter. He reached the unbelievable low bias of 14 %. Dewey Moore, the president of the Clay Minerals Society, presented the awards at the society's meeting in Richland/WA. Congratulations to our champions in mineral analysis!

Figure 2: Left to right: Jan Srodon and Dougal McCarty, the Reynolds Cup, Oladipo Omotoso and Michael Ploetze

Thanks to all contestants for their efforts in improve the quality of phase analysis and especially for their fairness and constructive hints. We hope to have a third Reynolds Cup in two years.

Acknowledgements

The German Research Foundation, the IUCr Commission on Powder Diffraction, the Clay Minerals Society and the German-Swiss-Austrian Clay Group (DTTG) generously supported the second Reynolds Cup.

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SUPER SPEED

One day Size/Strain and Quantitative Phase Analysis Software Workshop 02.09.04, part of the European Powder Diffraction Conference (EPDIC-9), Prague, Czech Republic.

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The Workshop, organised by Lachlan Cranswick, had the aim of showing what is practical with the latest powder diffraction software by using 20-minute 'live' presentation sessions. Session speakers could tackle complex problems as introductory remarks were kept to a minimum as participants had had the opportunity to read up on the software via published weblinks prior to the workshop. Several speakers had also introduced their work during the preceding Size/Strain IV satellite workshop sessions. Recognition should be given to all speakers for their ability to present a coherent oral presentation while simultaneously running software demonstrations.

A. Vermeulen, PANalytical, Almelo started the morning **'Size/Strain Analysis using Powder Diffraction Data'** session with *"New user-friendly possibilities for size-strain analysis with X'Pert HighScore Plus"*. It was demonstrated using the automatic mode of the Reitveld refinement part of the software how easy it is to obtain crystallite size and microstrain details. These details would be appreciated particularly for novice users who have little knowledge of the Rietveld approach. Using a more sophisticated approach the next contribution was from G. Ribarik and T. Ungar, Budapest, with *"Convolutional Multiple Whole Profile (CMWP)-fit for size/strain analysis: size-distribution, dislocation structures and stacking faults"*. Freely available at http://www.reyni.hu/cmwp/ CMWP is a program developed for the determination of microstructural parameters from diffraction profiles of materials with cubic or hexagonal crystal lattices. The whole measured powder diffraction pattern is fitted by the sum of a background function and ab-initio theoretical functions for size and strain broadening. It is assumed that the crystallites have lognormal size distribution and the strain is caused by dislocations. Strain and size anisotropy is taken into account by the dislocation contrast factors and the ellipticity of crystallites. The fitting procedure gives as output the median and variance of the size distribution, the ellipticity of crystallites, and the density and arrangement of dislocations. The demonstration showed that this information could be readily derived from ASCII input files. M. Leoni, Trento, with *"PM2000 - a Whole Powder Pattern Modelling (WPPM) approach to structure / microstructure refinement"*, described their modelling approach that is accomplished without *a priori* fixed analytical profile functions. WPPM assumes that the line profile produced by a crystallite size distribution and various defects are convoluted together with the instrumental component and then the pattern is directly synthesised through fast Fourier transformation. After describing parameters (defects, instrumental broadening, size broadening models, models for faulting) and a brief description of the structure of the program, (user customisable through the use of macros, libraries written as plug-ins) data for ceria was shown as an example. CPD round robin CeO_2 data was successfully modelled to high accuracy using this approach. Specific aspects of this wide-ranging Fullprof program were demonstrated by its author, J. Rodriguez-Carvajal - (CEA-CNRS) within his session: *"Size/Strain analysis of complex materials using Fullprof"*. Many microstructural effects can be studied assuming the Voigt model for instrumental and intrinsic diffraction peak shape. Anisotropic size effects were studied by linear combinations of spherical harmonics to model the Lorenzian part of peak broadening. An 'apparent shape' of crystallite coherence domains can be derived. During *"Size/Strain analysis using the BGMN Fundamental Parameters Rietveld software"* by J. Bergmann, Dresden, it was stressed and demonstrated that there is no necessity for a refinement strategy influenced by the user. Much is accomplished through automatic refinement. Crystallite size and microstrain broadening can be readily refined anisotropically An example was given for Si_3N_4 modelling of bimodal size distribution and strain. L. Lutterotti, Trento presented *"Size/Strain analysis using the MAUD for Java Rietveld software"*. MAUD (Materials Analysis Using Diffraction) is a general-purpose program for diffraction spectra fitting. The interface is written in Java^{TM} to provide a common program for any platform supporting this standard. The interface can be used over the network. Examples with Fe_3O_4 were presented along with crystallite size distributions. The MudMaster program, available at ftp://brrcrftp.cr.usgs.gov/pub/ddeberl/, is written in Microsoft Excel macro language. Its author, D. Eberl USGS, Boulder, Colorado with "*MudMaster: A program for crystallite size and strain analysis of clays using the Bertaut-Warren-Averbach method"* outlined it capabilities. The program, written for mineral analysis requires Lorentz-polarisation factor, (Lp), and layer scattering intensity, (G^2), values. MudMaster analysis of the 001 reflection for the clay mineral illlite was demonstrated. Some thoughts on crystal growth theory that give rise to various distributions were explained. Recent data on Alaska river bourn samples were analysed using MudMaster. The rate of migration of various mineral samples downriver was tracked by their respective characteristic size distributions. The final contribution in the session was by A. Kern, Bruker-AXS, Karlsruhe *"Size-Strain analysis by convolution based profile fitting using Topas"*. The direct convolution approach for direct fitting of profile shape functions by Topas was introduced. Again modelling of CDP CeO_2 round robin data was utilised to illustrate the functionality and accuracy of Topas. Flexibility of the program was illustrated by the ability to incorporate "do it yourself" functions e.g. anisotropic line broadening spherical harmonic functionality within Topas.

The afternoon session on **'Quantitative Phase Analysis using Powder Diffraction Data'** was started with J Bergmann, Dresden, with *"Quantitative Phase Analysis using the BGMN Fundamental Parameters Rietveld software"* showing the power of Fundamental Parameters to handle both routine and complex materials. This was followed by J. Rodriguez-Carvajal - (CEA-CNRS) with *"Quantitative Phase Analysis using Fullprof"*. An enhancement to one of the most widely used Rietveld packages GSAS was presented by A. Gualtieri, of the U. of Modena & Reggio Emilia with *"Quantitative phase analysis using GSAS Rietveld software with EXPGUI interface"*. Developed at NIST, EXPGUI is a user-friendly graphical user interface (GUI) editor for GSAS experiment (.EXP) files and shell, which allows all the other GSAS programs to be executed with a GUI. EXPGUI is written in scripting language, so it is largely platform independent. Diverse examples that included preferred orientation corrected with a March-Dollase model or spherical harmonics, and structure disorder of clay minerals using DiFFaX to obtain approximate or working structural models to be used in the QPA were discussed. Further talks were given by L. Lutterotti, University of Trento, with *"Quantitative Phase analysis using the MAUD for Java Rietveld software"* and D. Eberl, USGS, Boulder, Colorado, with *"RockJock: A program for XRD quantitative analysis of complex mineral assemblages using an internal standard and whole and partial pattern fitting"*. The final contribution was from A. Kern, Bruker-AXS, Karlsruhe *"Quantitative analysis by convolution based profile fitting using Topas"* He demonstrated that the use of instrument function constraints ("Fundamental Parameters Approach") drastically extends the capabilities and application areas of quantitative Rietveld analysis, including complex cement materials. Further data from the CPD Round Robin QPA were also used as illustration.

Computer Corner

Updates on Freely Available Crystallographic and Powder Diffraction Software

Suggestions, corrections, comments and articles on new or updated software are appreciated; especially if you know of new program features, program updates and announcements that should be mentioned here.

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Abstract The edition's computer corner features a number of articles including information on new releases of structure drawing software, all of which also can include the display of polyhedra.

New Powder3D multi-pattern data reduction and graphical presentation software by B. Hinrichsen, R. E. Dinnebier and M. Jansen

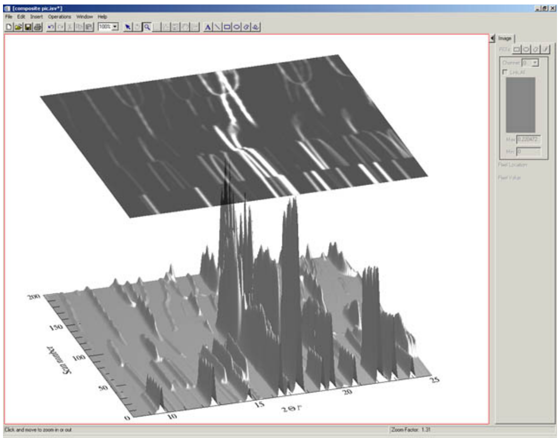
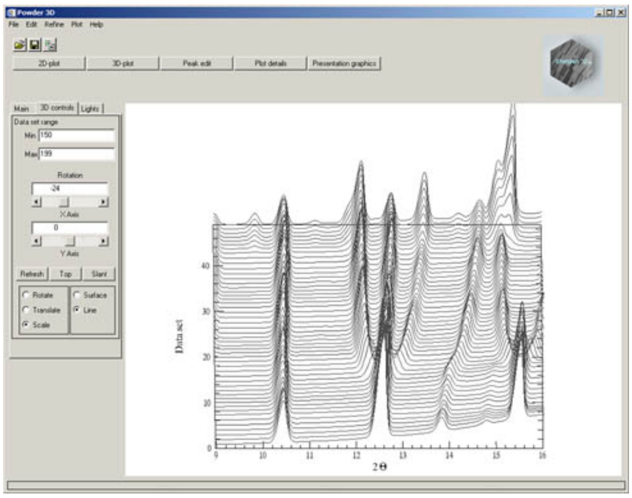


Fig 1: *Example of multiple data display in Powder 3D.*

A program for viewing and initial analysis of masses of data is the Powder3D software freely available at http://www.fkf.mpg.de/xray/ Based around the IDL engine, it can view single or a series of diffraction patterns, peak hunting, peak fitting, K-alpha1/2-stripping, optimised smoothing, background determination and cropping of data.



Min 150
Max 199
Rotation -24
0

Fig 2: *Waterfall / Series plot generated by Powder 3D.*

Rietveld Software Updates (as of mid October 2004):

Hugo Rietveld website:
http://home.wxs.nl/~rietv025/
BGMN (18th Sep 2004)
http://www.bgmn.de/
BRASS (13th Sep 2004)
http://www.brass.uni-bremen.de/

DBWS (22nd February 2000)
http://www.physics.gatech.edu/downloads/young/download_dbws.html
Debvin (25th May 2001)
http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/debvin/DEBVIN/
GSAS (27th Sep 2004)
http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/
EXPGUI (2nd October 2004)
http://www.ncnr.nist.gov/programs/crystallography/
Jana (26th June 2004)
http://www-xray.fzu.cz/jana/jana.html
LHPM-Rietica (27th November 2001)
ftp://ftp.ansto.gov.au/pub/physics/neutron/rietveld/Rietica_LHPM95/
MAUD for Java (GPL'd) (26th Feb 2004)
http://www.ing.unitn.it/~luttero/maud/
Prodd (19th August 2002)
http://www.ccp14.ac.uk/ccp/web-mirrors/prodd/~jpw22/
Profil (24th May 2001)
ftp://img.cryst.bbk.ac.uk/pdpl/ (if Profil FTP site is unavailable, use the CCP14 Mirrors)
Rietan 2000 (GPL'd) (1st July 2004)
http://homepage.mac.com/fujioizumi/rietan/angle_dispersive/angle_dispersive.html
Winplotr/Fullprof (15th October 2003) (if Fullprof FTP site is unavailable, use the CCP14 Mirrors)
http://www-llb.cea.fr/winplotr/winplotr.htm
ftp://charybde.saclay.cea.fr/pub/divers/fullprof.2k/ (if Fullprof FTP site is unavailable, use the CCP14 Mirrors)
Winmprof (21st June 2001)
http://lpec.univ-lemans.fr/WinMProf/
XND (30th March 2004)
http://www-cristallo.polycnrs-gre.fr/xnd/xnd.html
ftp://ftp.grenoble.cnrs.fr/xnd/ (if XND FTP site is unavailable, use the CCP14 Mirrors)

All the above Rietveld programs are also available via the CCP14 based mirrors in UK, USA, Australia and Canada (http://www.ccp14.ac.uk/mirror/).

Summary lists of some software available via the EPSRC funded CCP14 website:

"What do you want to do?" (lists of software by single crystal and powder methods)
http://www.ccp14.ac.uk/mirror/want_to_do.html

Anharmonic Thermal Refinement Software
http://www.ccp14.ac.uk/solution/anharmonic/
Data Conversion for Powder Diffraction
http://www.ccp14.ac.uk/solution/powderdataconv/
Image Plate Software
http://www.ccp14.ac.uk/solution/image-plate/
Incommensurate Structure Software
http://www.ccp14.ac.uk/solution/incomm.htm
Indexing Software for Powders
http://www.ccp14.ac.uk/solution/indexing/
LeBail Method for Intensity Extraction
http://www.ccp14.ac.uk/solution/lebail/
Pawley Method for Intensity Extraction
http://www.ccp14.ac.uk/solution/pawley/
PDF, High Q Powder diffraction Analysis Software
http://www.ccp14.ac.uk/solution/high_q_pdf/
Peak Find/Profiling Software for Powder Diffraction
http://www.ccp14.ac.uk/solution/peakprofiling/
Pole Figure and Texture Analysis Software
http://www.ccp14.ac.uk/solution/pole_figure/
Powder Diffraction Data Visualisation
http://www.ccp14.ac.uk/solution/powder_data_visual/
Rietveld Software
http://www.ccp14.ac.uk/solution/rietveld_software/
Search-Match Phase Identification Software
http://www.ccp14.ac.uk/solution/search-match.htm
Single Crystal Structure Solution Software relevant to Chemical Crystallography
http://www.ccp14.ac.uk/solution/xtalsolution/
Single Crystal Structure Refinement Software relevant to Chemical Crystallography
http://www.ccp14.ac.uk/solution/xtalrefine/
Single Crystal Suites linking to multiple programs relevant to Chemical Crystallography
http://www.ccp14.ac.uk/solution/xtalsuites/
Spacegroup and Symmetry operator determination software and source code
http://www.ccp14.ac.uk/recomm/sym_operators_to_spacegroups.html
http://www.ccp14.ac.uk/recomm/spacegroups_to_sym_operators.html
Spacegroup and Structure Transformation Software
http://www.ccp14.ac.uk/solution/transform/
Structure Conversion and Transformation
http://www.ccp14.ac.uk/solution/structconv/
Structure Drawing and Visualisation
http://www.ccp14.ac.uk/solution/structuredrawing/
Unit Cell Refinement of Powder Diffraction Data
http://www.ccp14.ac.uk/solution/unitcellrefine/

Nano: a software for quantitative analysis of nanoparticles by X-ray diffraction powder data.

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INTRODUCTION

Since 1989 [1], when IBM researchers demonstrated their ability in constructing a 35-atom depiction of the company's logo, the possibility to manipulate individual atoms has spawned a tidal wave of research and development at the nanoscale. Nanomaterials have been showing unique chemical, physical and electrical properties which can explain the ever flourishing interest of the scientific and industrial communities. Four generations of nanotechnology have been identified [2]: passive nanostructures, active nanostructures, 3D nanosystems and heterogenous molecular nanosystems. We are still in the phase of passive nanostructures - nanoparticles (NPs) designed to perform one task.

In order to tailor their properties and relative expected performances, NPs have to be studied and characterized in detail. The most important parameters to be controlled are size, strain, shape, internal domain structure homogeneity, surface structure. Such a complex characterization poses severe problems because all traditional methods, even the most popular and widespread for the structural characterization of micromaterials as x-ray powder diffraction (XRPD), cannot be straightforwardly applied at this nanoscale. Indeed, relevant basic differences distinguish a nanomaterial from a typical polycrystalline micrometric material.

A nanocrystalline powder is generally well described by an assembly of nanoparticles with nanometric size having a certain spread (size distribution). In the reduced domain size of nanocrystalline materials, a major role is played by the surface atoms which, for extremely small nanoparticles, can even exceed the number of bulk atoms. Surface energies generate changes in the length of the interatomic bonds determining important strain contributions and/or surface atoms lattice reconstruction [3]. This already justifies the introduction of a size-related lattice parameter in the Bragg equation [4], which cannot be anymore routinely applied as for conventional micrometric polycrystalline powders. In addition, there is extensive documentation in literature of the occurrence of non crystallographic crystalline phases for some specific noble metal nanoparticles of few nanometers in diameter [5]. This further condition prevents from describing the structure of these materials with a crystallographic approach and suggests the use of the Debye function [6], which does not require lattice periodicity, to calculate the diffracted intensity.

The software here presented is devoted to the characterization of nanoparticles in terms of size, strain and structure by using XRPD data. Presently, the software allows to treat multiple datasets collected on noble metal monoatomic nanoparticles with face cubic centered (f.c.c.) derived structure. This class of materials needs of a dedicated theoretical approach [7] due to the presence of non crystallographic phases (icosahedral and decahedral), aside to the expected cuboctahedral phase (undistorted portion of the f.c.c. parent lattice), which represents a further level of complexity to account for.

PROGRAM DESCRIPTION

The theoretical approach implemented in the program is based on a full-Newton least-squares whole-powder-pattern method. It allows to deal with powder diffraction data of randomly oriented nanocrystals (without texture effects) which are treated as a mixture of crystallographic and non crystallographic phases. It make use of the Debye function to calculate the diffracted intensity of all crystalline phases. The major theoretical features are: nanoparticles are described by a concentric shell model with fixed shape; a log-normal size distribution and an arctangent-like size-strain dependence are computed for each crystalline phase; strain is approximated as a uniform and isotropic surface-led radial deformation inside each single nanoparticle; static random disorder is represented in the Debye-Waller factor; an amorphous-metal scattering contribution is included in the background to be considered as a surface-related effect. Adimensional interatomic distances are calculated for each cluster of the three structure types for a maximum NP diameter of 50 nm and stored into a database which may be used independently of the specific material. To save computer time each distance is convoluted in direct space with a gaussian function and all these gaussians are then summed up to obtain a continuous pair distribution function (PDF) which is finally sampled onto a fixed grid with a suitable step.

The flow chart showed in Fig. 1 describes the way the program works.

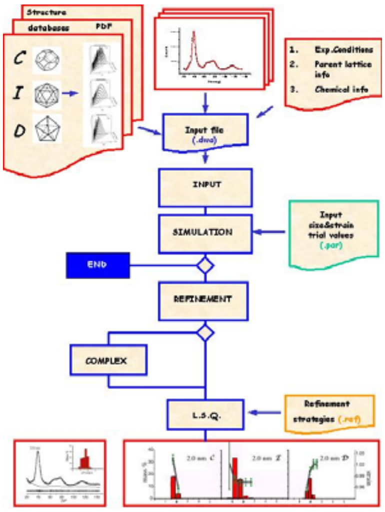


Fig. 1: *Flow Chart of NANO*

The main input *.dwa file is organized in three consecutive sections: I) the datasets section, II) the structure model section , III) the refinement and output section. In Section I the program reads all information about the data (filename, format, experimental conditions); in Section II all information about the distances database are given together with chemical and crystallographic information on the parent lattice and the parameter initialisation files (*.par), one for each structure phase; in Section III two possible jobs (simulation or refinement) can be executed. For both jobs, the parameters files (*.par) which contain size&strain trial values have to exist. After a simulation the program can be stopped. If running a refinement job, an optional refinement level using the COMPLEX algorithm [8] can be chosen to explore the phase space and provide less rough size&strain values to the final least-squares refinement. A strategy refinement file (*.ref) can be supplied.

The program allows the creation of prototype files both for the *.par and for the *.ref files.

The output files written by the program are: experimentally observed and best fit profiles (including single structure type contributions) in the *.cal file, one for each dataset, and one file (*.inf) containing size and strain refined parameters for each structure type, mass and numerical fractions (giving the relative abundance of each structure type in the mixture) and statistical parameters (goodness of fit GoF, profile agreement index etc). Optionally, a multi-page graphical output in Encapsulated PostScript format can be produced.

FIRST APPLICATIONS

Thiol-passivated gold NPs with mean diameters of 2.0, 3.2 and 4.1 nm (±1 nm) were investigated by XRPD at the Brazilian Synchrotron Light Laboratory (LNLS) [9]. The XRPD patterns were processed with the NANO program [10]. The pattern best fits and corresponding cumulative size distributions are showed in Fig.2. In Fig.3 final size-strain distributions *vs*. the domain diameter are given for the three structure types. Table I summarizes the final refined values for % mass fraction (W), mean domains diameter (<D>) and isotropic thermal factors (B) together with the final GoF. An amorphous phase was detected as previously evidenced by HRTEM [9]. In addition, the derived strain profiles allowed an easy assessment of the nearest neighbour distances deformations which well agreed with EXAFS studies [10].

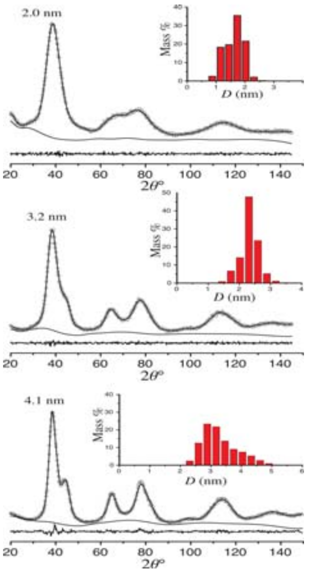


Fig. 2: *Pattern of the best fits*

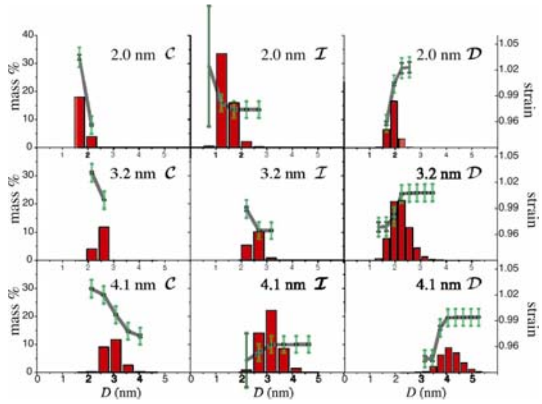
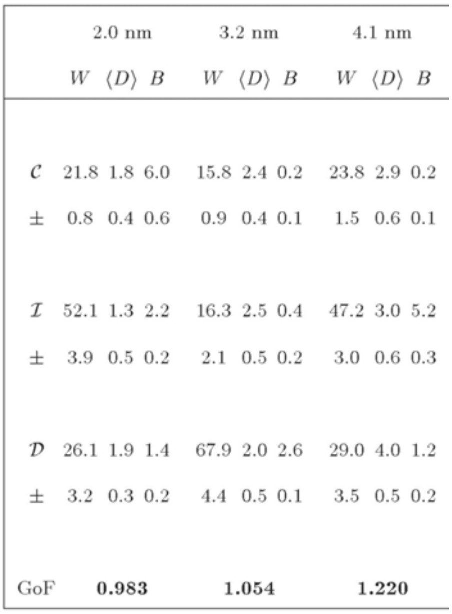


Fig. 3: *final size&strain distribution*



	2.0 nm			3.2 nm			4.1 nm		
	W	$\langle D\rangle$	B	W	$\langle D\rangle$	B	W	$\langle D\rangle$	B
$\mathcal{C}$	21.8	1.8	6.0	15.8	2.4	0.2	23.8	2.9	0.2
±	0.8	0.4	0.6	0.9	0.4	0.1	1.5	0.6	0.1
$\mathcal{I}$	52.1	1.3	2.2	16.3	2.5	0.4	47.2	3.0	5.2
±	3.9	0.5	0.2	2.1	0.5	0.2	3.0	0.6	0.3
$\mathcal{D}$	26.1	1.9	1.4	67.9	2.0	2.6	29.0	4.0	1.2
±	3.2	0.3	0.2	4.4	0.5	0.1	3.5	0.5	0.2
GoF	**0.983**			**1.054**			**1.220**		

Table 1: *Table of results produced by Nano*

Work is in progress to extend the present theoretical approach to process XRPD data collected on polyatomic NPs with different shapes (rods, disks etc).

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PowDLL: a reusable .NET component for interconverting powder diffraction data.

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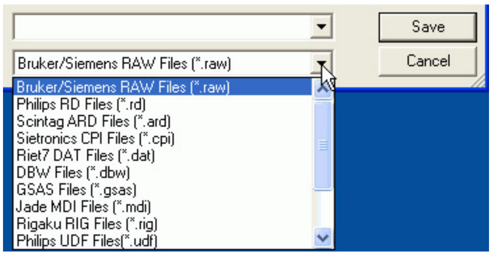
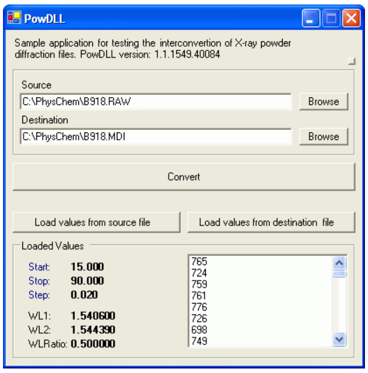
PowDLL is a .NET assembly used for the interconversion procedure between variable formats of powder diffraction files. Although there are computer programs dealing with data conversion, this is the first application which can be used in two ways: i) as a standalone utility combined with the executable client provided by the author ii) as a reusable dynamic link library imported in any .NET language using the “PowDLL.PowderFileTypes” statement which is the fully qualified type name of the assembly. Upon declaration of an appropriate object, three boolean public methods are exposed which return *True* when no exception is raised. These methods which are: DoFileConversion(Input, Output, ShowError), LoadDataFromFile(Input, FileType, ShowError) and WriteDataToFile(Output, FileType, ShowError) can be accessed by any external module that references the library. If an error occurs, the System.Exception object takes control and shows an appropriate message keeping the process alive. The library is capable of handling fourteen popular file formats either ASCII or binary. Each format has its own private structure in accordance with the encapsulation concept of the object oriented programming. Available import/export formats include: .raw (v1-v3), .rd, .ard, .cpi, .dat, .dbw, .gsas, .mdi, .rig, .udf, .uxd, .xda, .xdd, .xy and pdCIF (import only).



PowDLL is written in Visual Basic.NET and was compiled and debugged using Visual Studio.NET. It consists of about 1800 lines of source code and requires the .NET Framework 1.1. The client .exe file must be present in the same directory.



Sample application for testing the interconvertion of X-ray powder diffraction files. PowDLL version: 1.1.1549.40084

Source: C:\PhysChem\B918.RAW

Destination: C:\PhysChem\B918.MDI

Start: 15.000
Stop: 90.000
Step: 0.020

WL1: 1.540600
WL2: 1.544390
WLRatio: 0.500000

765
724
759
761
776
726
698
749

The library as well as the executable (including source code) are freely distributed for use and redistribution and can be downloaded from: http://users.uoi.gr/nkourkou/

New Versions of DRAWxtl
a Program for Crystal Structure Display

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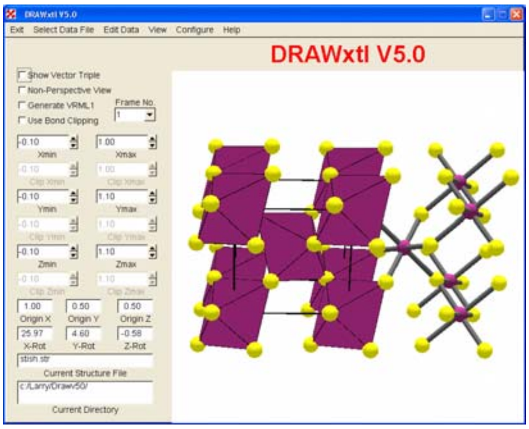
The computer program DRAWxtl, recently described in CPD Newsletter 31 (http://www.fkf.mpg.de/cpd/cpd31.pdf), has been substantially modified in the past few months, with the introduction of V5.0 and V4.1. Both new versions have the same rendering capabilities, but V5.0 has a full-featured graphical-user interface (GUI), while V4.1 is leaner, does not require C++ or any sophisticated graphical library, and can be run in the background just like V3.x. If desired, V4.1 can also display a real-time representation of the structure. As in earlier versions, the program is designed to display crystal structure elements on ordinary computers with minimal user input and maximal flexibility. It reads the basic description of a crystal structure, including unit-cell parameters, space group, atomic coordinates and thermal parameters, combines them with parameters that define the view, and outputs a geometry object that contains arrows, polyhedra, planes, lone-pair cones, spheres or ellipsoids, bonds, and unit-cell boundary lines. The program renders the structure object immediately using a series of OpenGL calls through the glut interface. Scene descriptions for the popular Persistence of Vision (POV) ray-tracing program, or Virtual Reality Modeling Language (VRML) are written to disk. The POV scene file can be used ‘as is’ to produce high-quality hard-copy diagrams, but it can also be edited to make use of the more sophisticated features of POV such as transparency, backgrounds and/or light effects. The VRML version is suitable for use with WWW browsers such as Netscape, FireFox, Mozilla, or Internet Explorer, and can be used to make displays suitable for interactive examination over the Internet.

In the new versions, we have removed the restriction that forced a given atom to have only a single role in the drawing. Formerly, an atom could be the center or vertex of a polyhedron, or be rendered as a sphere or ellipsoid. Now any atom can have any role. We have also added a number of new commands to draw the following entities: (1) arrows representing magnetic-spin vectors, (2) a general parallelepiped distinct from the unit cell, and (3) dashed-bonds. We also added commands that generate POV surface finishes, and the frame command has been modified to create drawings with separate parts of the diagram having different contents, or even different space groups.

As shown below, V5.0 implements a full-featured GUI that uses the Fast Light Tool Kit (FLTK). Not only is the structure drawing rendered as in V4.1, but also parameters of the structure and the diagram can be modified and the changes viewed in real time. In this multi-frame diagram of stishovite, one of the new capabilities of the frame command is demonstrated by composing the left-hand unit cell with SiO_6 octahedra; whereas the right-hand portion is drawn with balls and sticks. The main screen includes widgets to set the overall limits of the diagram and a few other parameters; whereas the pull-down menus are used to access structural elements such as polyhedra, bonds, etc. Complete on-line help is also available.

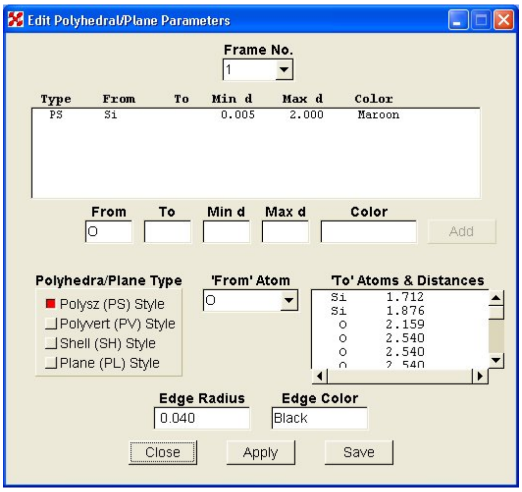


☐ Show Vector Triple
☐ Non-Perspective View
☐ Generate VRML1
☐ Use Bond Clipping

Frame No. 1

Xmin -0.10
Xmax 1.00
Clip Xmin -0.10
Clip Xmax 1.00
Ymin -0.10
Ymax 1.10
Clip Ymin -0.10
Clip Ymax 1.10
Zmin -0.10
Zmax 1.10
Clip Zmin -0.10
Clip Zmax 1.10
Origin X 1.00
Origin Y 0.50
Origin Z 0.50
X-Rot 25.97
Y-Rot 4.60
Z-Rot -0.58
Current Structure File stish.str
Current Directory c:/Larry/Draw50/

Below, is a representative of the edit windows, is a screen shot of the window used to edit polyhedra and planes. To help in setting the minimum and maximum distances for the polyhedron, the "To" interatomic distances are shown in the combo box. Whenever a particular line in that box is highlighted, the appropriate data are transferred to boxes 'From', 'To', etc. Once all these items are non-blank, the program activates the 'Add' button. When this button is pressed, the data are transferred into the upper window. Alternatively, the data in the window can be edited directly. Once the data have been adjusted as desired, either the 'Apply' or 'Save' is pressed. At that time, the changes are shown in the main-screen display. The 'Frame No' combo box is shown and active whenever the data file contains more than one frame.



Frame No. 1

Type	From	To	Min d	Max d	Color
PS	Si		0.005	2.000	Maroon

From O

Polyhedra/Plane Type
■ Polysz (PS) Style
☐ Polyvert (PV) Style
☐ Shell (SH) Style
☐ Plane (PL) Style

'From' Atom O

'To' Atoms & Distances

Si	1.712
Si	1.876
O	2.159
O	2.540
O	2.540
O	2.540

Edge Radius 0.040

Edge Color Black

Obtaining the Program

As before, the new versions of DRAWxtl run under Linux, other Unix derivatives, and Windows (9X, Me, XP, NT, and 2000). In addition, a port of the programs to Mac OS X is in progress at the time of this writing. The source code, executable programs for Windows (and OS X?), sample data sets, and the manual are available from http://www.lwfinger.net/drawxtl. DRAWxtl is open-source software, and is free to anyone. We hold copyright on the code, and like any other piece of intellectual property, we ask that you respect our rights.

XtalDraw for Windows

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The XtalDraw suite of crystallographic software for Windows is freely available from the website http://www.geo.arizona.edu/AMS/amcsd.php. The program reads crystal structure data and produces interactive images of the structure rendered as ball and stick, polyhedral or displacement ellipsoids. When initially drawn, the crystal structure is oriented with **c*** coming out of the screen and the **b**-axis horizontal, just like the International Tables. The images can be rotated with the arrow keys, or oriented in specific crystallographic directions through a dialog box interface. The image can be resized by hitting the +/- keys or by specifying a certain image width.

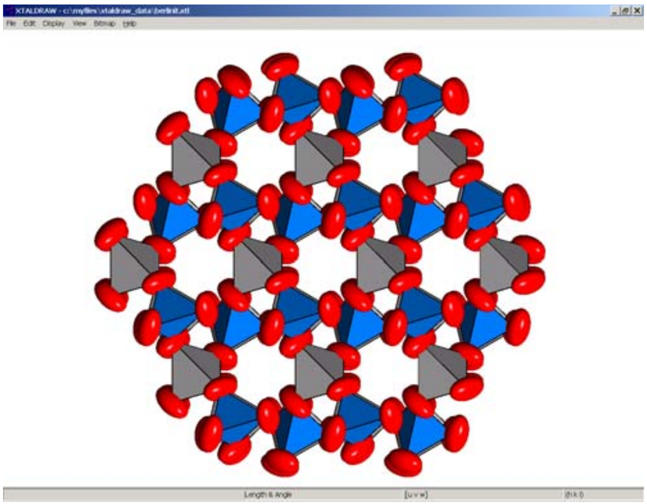

Fig. 1: *Structure of Berlinite (Aluminium Phosphate) as generated by Xtal Draw.*

Default atom colors are chosen to match Lipson and Cochran (1957) and sphere radii are scaled to Shannon and

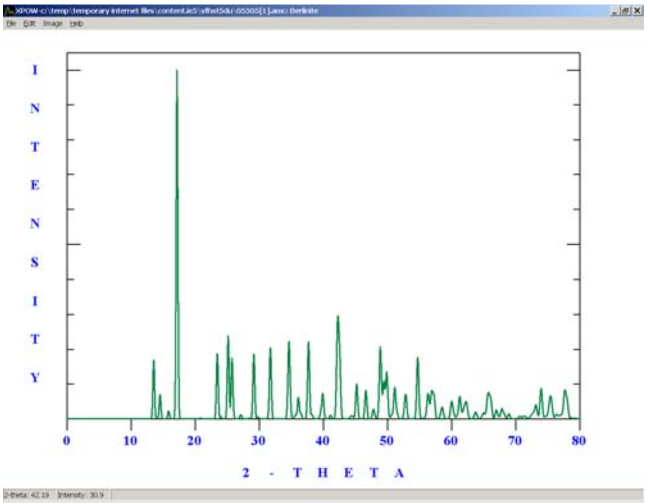

Fig. 1: *Powder diffraction pattern of generated by Xtal Draw.*

Prewitt (1969). The user can easily alter these and new defaults can be established. If the data permits, then displacement ellipsoids can be drawn. The user can alter the probabilities associated with the ellipsoids and thus change their sizes. Initially, a complete unit cell of the crystal is drawn. The extent of the drawing can be altered in several interactive ways.

A useful feature of the software is the ability to make animations of the images created with the program. This feature permits the study of crystal structure behavior as a function of some arbitrary parameter of interest, such as temperature, pressure, dehydration, and so on. The images can be easily ported into gif89 freeware, such as Gamani Movie Gear, to create animations for the Internet or for PowerPoint presentations.

The software also computes several important crystallographic parameters that are presented in ASCII files, such as bond lengths, angles, polyhedral volumes, distortions, displacement ellipsoid and thermal motion TLS rigid body analysis. Furthermore, powder diffraction profiles can also be computed from the crystal structure data in an interactive fashion, with user defined radiation sources, limits and peak widths.

Perhaps one of the important aspects of the software that separates it from others is that it is intimately linked to a free online database, The American Mineralogist Crystal Structure Database at http://www.geo.arizona.edu/AMS/. This database currently contains the crystal structure data for every crystal structure published in the American Mineralogist, The Canadian Mineralogist, the European Journal of Mineralogy and Physics and Chemistry of Minerals, and the process of adding structures from Acta Cryst has just been initiated. The database has ~7000 datasets right now. It is jointly maintained by the American, Canadian, German and European mineralogical societies. After the XtalDraw software has been installed from the Database website, then searches on the website produce hyperlinks that automatically download the dataset by ftp and open it directly into XtalDraw for the users pleasure.

STRUPLO 2004:
A new version of the structure drawing program

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WWW: http://www.brass.uni-bremen.de/

The crystal structure drawing program *STRUPLO*, initially programmed in FORTRAN [1] is completely rewritten in Delphi and redesigned with extensive modifications and new options. It is part of the *BRASS* (The Bremen Rietveld Analysis and Structure Suite) program package [2,3]. The main features are:

- Bitmap graphics
- Bonds can be drawn as cylinders, atoms as spheres
- Atoms are drawn with their predefined ionic radius. The size of cations and anions can be scaled separately or individually.
- Polyhedra are identified within a sphere of given radius between the central atom and the ligands
- Fast online rotation
- Online identification of any element (atom, bond, polyhedron)
- Each of the elements can be deleted and undeleted at any time
- Online distance and angle calculation, complete table of distances and angles
- Attributes (e.g. color, transparency, atom size etc.) can be assigned to all items, to chemical elements, to single atoms in the asymmetric unit, or to any single atom or item.
- Symmetry operators are generated from space group symbol (routine [4] translated to Delphi) with origin shift for nonstandard space groups.
- The void space, i.e., the empty space not occupied by atoms, is calculated according to the procedure described in [5]. This is especially useful to determine diffusion paths, e.g., in porous materials like zeolites.

The following figures show a screen print of a typical page in the user interface (Fig. 1) and several examples of projections of zeolite A [6] in various representations.

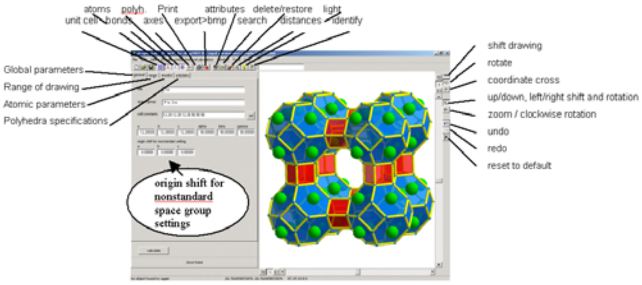

Fig. 1: *Page of the STRUPLO user interface within the BRASS program package*

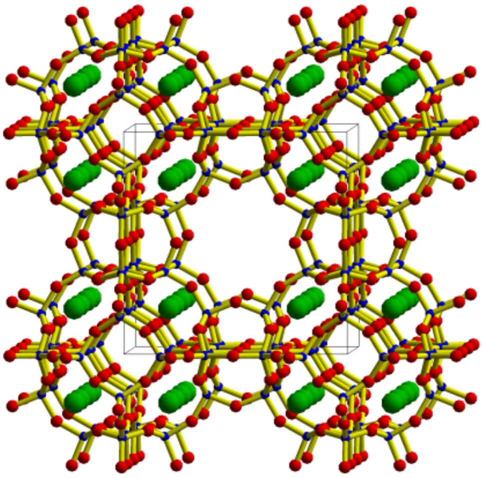

Fig. 2: *Zeolite A: ball and stick model. blue: Si/Al, red: O, green: Na*

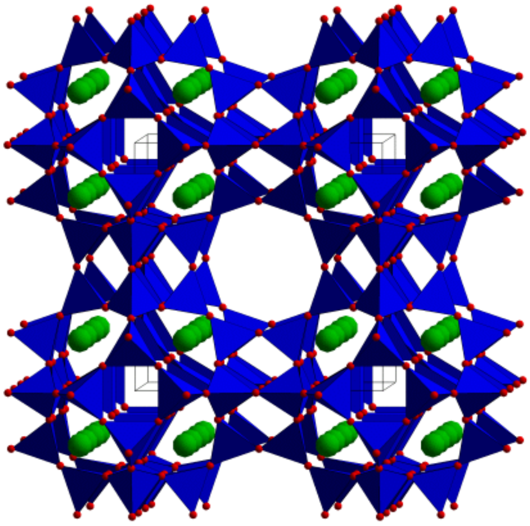

Fig. 3: *Zeolite A: polyhedral representation with Na shown as spheres*

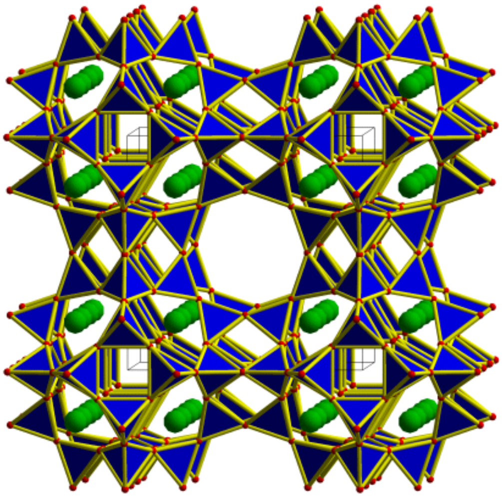

Fig. 4: *Zeolite A: polyhedral outlines shown as cylinders*

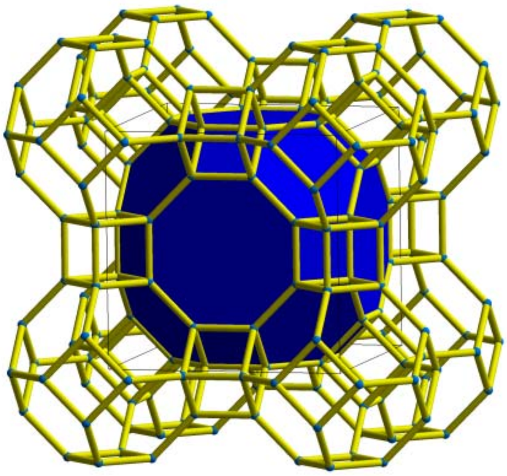

Fig. 5: *Zeolite A: ball and stick model. blue: Si/Al, red: O, green: Na*

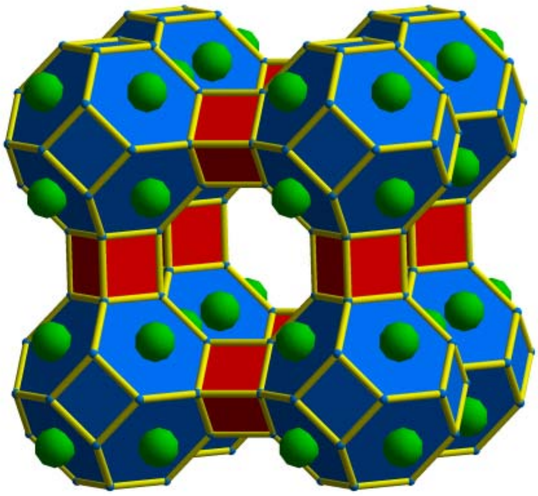

Fig. 6: *Zeolite A: ball and stick model. blue: Si/Al, red: O, green: Na*

BRASS containing the STRUPLO program can be downloaded from the *BRASS* homepage (http://www.brass.uni-bremen.de/) of the Central Laboratory for Crystallography and Applied Material Sciences (ZEKAM) at the university of Bremen. After download, an install routine will guide through the installation procedure.

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PDFgetX2: a user-friendly program to obtain the pair distribution function from X-ray powder diffraction data

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1. Overview

The program PDFgetX2 [1] processes X-ray powder diffraction data to obtain the pair distribution function (PDF). The PDF method directly measures the inter-atomic distances in the intuitive real space [2]. For a long time, this has been the method of choice for studying the structure of amorphous materials and liquids [3]. Recent advances in the PDF technique have shown it to be a powerful local structure probe of nano-crystalline and highly crystalline materials [4]. One key to a proper PDF analysis is to quantitatively extract both Bragg peaks (if any) and the diffuse scattering intensities containing the average and local structural information, respectively. PDFgetX2 aims to facilitate the user interaction with data from laboratory or synchrotron X-ray measurements during this otherwise arduous and intensive process. This program has the following features. i) User-friendly interface. All user inputs are through series of self-explanatory graphic user interfaces (GUI). User inputs are also kept to the minimum with built-in commonly used settings and atomic X-ray scattering data look-up tables. ii) Flexible data corrections. A rather large number of corrections are available, and each of them can be turned on/off independently using the GUI. iii) Easy problem diagnosis. Instead of being a black box, PDFgetX2 makes every intermediate correction term and its effect on the data accessible by a simple button click. iv) Complete history file for time saving and reproducibility. All data processing parameters are saved together with the data, and can be reloaded back to fully reproduce an earlier analysis. v) Efficient use and documentation. A simple parameter optimization algorithm is available to fine tune the PDF quality. The program executable and a user's guide are downloadable from PDFgetX2 web page at http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/ and from the CCP14 website. A short tutorial with example data sets can be found in the user's guide.

2. Program Description

The program PDFgetX2 is written in IDL[1]. It runs on the freely downloadable IDL Virtual Machine (IDL^{VM}) (available at http://www.rsinc.com/download/), which is supported on Linux/UNIX, WINDOWS, and MACINTOSH platforms.

Key implemented corrections in PDFgetX2 are based on the formula of the measured scattering intensity I_{raw} (each term is described below):

$$I_{raw} = NMAP(I_{coh} + I_{comp}) + I_{bkg} \tag{1}$$

The goal is to recover the coherent intensity I_{coh}, as the only term conveying atomic structure information. The PDF, $G(r)$, is obtained by the sine Fourier transform,

$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)dQ, \tag{2}$$

where $S(Q) = \frac{I_{coh} - < f^2 >}{< f >^2} + 1$ and Q is the magnitude of the momentum transfer. The commonly applied corrections, described in detail in [2], are:

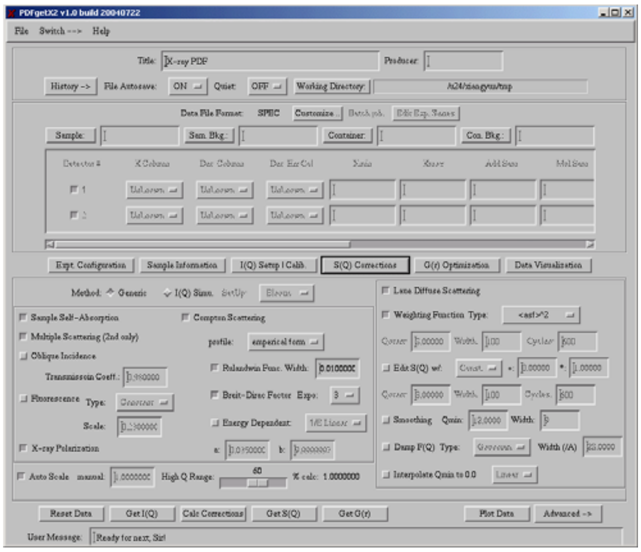
1. Background scattering I_{bkg} subtraction. The I_{bkg} should be measured under the sample experimental condition without the sample.
2. X-ray polarization correction *P*. The X-ray polarization factor is the only parameter.
3. Sample self-absorption correction *A*. Parameters used here are the measured sample absorption coefficient and the sample geometry (transmission, reflection, etc.).
4. Multiple scattering correction *M*. This term is only significant in the case of strongly absorbing samples.
5. Compton intensity I_{comp} subtraction. The sample composition is needed to compute the theoretical Compton scattering profile. If the Compton contributed at high *Q* is removed by energy discrimination, a window function can be applied [5].
6. Normalization factor *N*. The high *Q* method is used for automatic normalization. Theoretical elastic scattering intensities are computed given the sample composition.

Additional corrections may be necessitated depending on specific experimental setups. Particularly, for the recent RA-PDF development that makes use of 2D detectors [6], oblique incident angle correction [7] and empirical energy dependence of the detection efficiency [8] are available in the program. An optional constant fluorescence intensity subtraction is also implemented.

Standard uncertainties due to finite counting statistics are estimated (if not present in the input data) and propagated in all steps. The final *S(Q)* and *G(r)* data files (automatically saved by default) are multiple-column ASCII files with the processing parameters in the header. The *S(Q)* data also contain the Faber-Ziman coefficients for all partial structure factors as additional columns. The *G(r)* file format is compatible with the PDF modeling programs PDFFIT [9] and DISCUS [10].

3. A Quick Example

To get some practical sense about the use of PDFgetX2, we will quickly go through one RA-PDF data processing example from a new binary antimonide, Ti_2Sb (see Ref. [11] for more detailed information). The goal of this PDF study was to resolve the local Ti square net distortions hinted by crystallographic analysis. The powder sample (around 0.5 g in flat plate transmission geometry) was measured at the high energy station 6-ID-D at the Advance Photon Source (APS) at Argonne National Laboratory. A short data collection time of 40 seconds was achieved with the RA-PDF method employing an image plate area detector. The raw 2D data were first integrated using the program FIT2D [12] to get the two column data $Q/2\theta$ vs. I. Then we are ready to fire up PDFgetX2 to obtain the PDF. Fig. 1 gives a glimpse of the program GUI.



PDFgetX2 v1.0 build 20040722

Title: X-ray PDF

File Autosave: ON

Quiet: OFF

Working Directory: /u24/xiangyun/tmp

Data File Format: SPEC

Method: Generic

Weighting Function Type: <asf>^2

profile: emperical form

Ruland-win Func. Width: 0.0100000

Breit-Dirac Factor Expo: 3

% calc: 1.0000000

User Message: Ready for next, Sir!

Figure 1: *A glimpse of the program PDFgetX2 GUI.*

The first phase of data analysis is to tell the program about the experiment (all with GUIs). This can be divided into four categories (the parameter values for this example will be shown in following parentheses). i) The scattering intensity profiles. Here we select the sample and background data files by clicking on the corresponding buttons. Additional information, such as the data file format (CHI) and the type of the data X column (2θ) should also be specified. ii) The X-ray properties. This includes the X-ray wavelength used (0.1266 Å) and the polarization factor (1.0). iii) Sample information. Elements are selected from the periodic table graph; atomic fractions are typed into the corresponding fields (Ti:2, Sb:1). The sample geometry (flat plate IP transmission) and the measured sample absorption coefficient (0.50) are also required. iv) The set of corrections to apply and some additional correction specific parameters if necessary. In addition to the default corrections, this RA-PDF setup requires at least the sample absorption, oblique incidence, and Compton scattering corrections. We shall start with these selections.

The second phase is to crunch the data and improve the PDF quality. Fortunately, only category (iv) needs to be adjusted during the second phase (maybe except when the range of data used is to be changed). The starting point is the scattering intensity $I_{raw}(Q)$ as shown in Fig. 2(a). It is generally straightforward to obtain a high quality PDF when the required processing parameters are determined experimentally. However, we would find the above settings result in a rather poor quality PDF, e.g., as shown in Fig. 2(b). This is because the RA-PDF method imposes further implications due to the lack of energy resolution of the image plate detector. There are two main issues: the fluorescence intensity and the energy dependence of the detection efficiency. So we switch these two corrections on. However, these two corrections are not convenient to determine experimentally. Here we can either choose to employ the trial-error approach or take advantage of the optimization feature of the program to find the optimal parameter values. In either case, a high quality PDF as shown in Fig. 2(c) (blue solid circle) results.

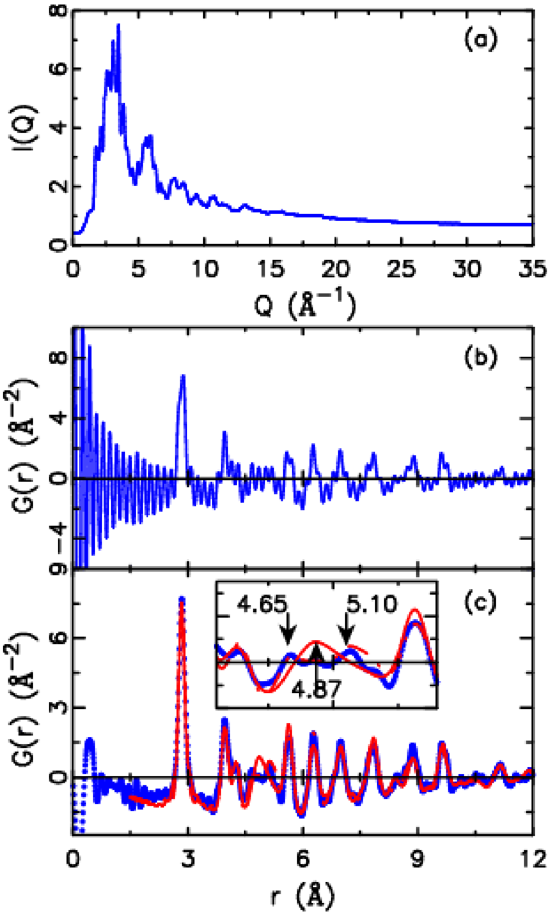


Figure 2: *(a) The scattering intensity I_{raw} of Ti_2Sb vs. Q. (b) One poor quality PDF resulting from insufficient corrections. (c) The experimental PDF after proper corrections (blue solid circle), the simulated PDF from the distorted structure model (red dashed line), and the simulated PDF from the undistorted model (red solid line). Inset zooms in the 4-5 Å region.*

Shown also in Fig. 2(c) are the model PDFs calculated from the undistorted Ti_2Sb crystal structure (red solid line) and the distorted structure (red dashed line). The most pronounced evidence of the superiority of the distorted model appears in the 4-5 Å region. The single peak (4.87 Å) in the undistorted model splits into a doublet (4.65 and 5.10 Å) which is clearly in the data and also the distorted model. The experimental PDF provides direct proof of the existence of local Ti structure distortions.

Finally, the program PDFgetX2 can work without the GUIs through manual function calls. This requires knowledge of IDL and internal PDFgetX2 structure to some level. This makes it possible for PDFgetX2 to batch process multiple data sets and interface with other programs.

Acknowledgments

We would like to acknowledge financial support from the U.S. Department of Energy (DOE) through grant DE-FG02-97ER45651 and NSF through NIRT grant DMR-0304391. APS and 6ID-D are funded by DOE through grants W-31-109-Eng-38 and W-7405-Eng-8, respectively.

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BRASS,
the Bremen Rietveld Analysis and Structure Suite

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BRASS [1,2] is a common platform for a suite of programs covering the display and Rietveld analysis of powder diffraction data and closely related tasks such as Fourier and grid search calculations and the drawing and crystal chemical evaluation of structure models.

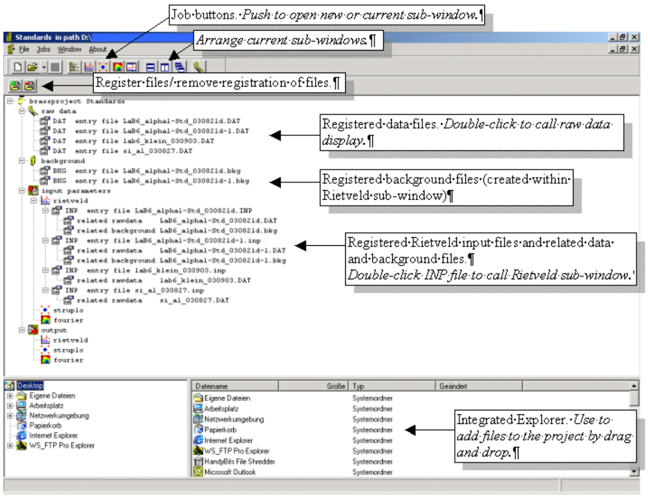
Currently accepted powder diffraction data formats are (contact us for further types to be incorporated):

- DAT = PC-Rietveld+ format
- RAW = Siemens binary data
- RD = Philips binary data
- UDF = Philips ASCII data
- XRDML = PANalytical html-type ASCII data

The general organization of BRASS:

- Main window contains all different types of jobs (Rietveld, Struplo, Fourier, Pattern display) as sub-windows
- Project manager sub-window (see below) provides access to registration and unregistering of files by drag and drop (or add/ remove buttons) and to the call of the different jobs (Rietveld, Struplo, Fourier, Pattern display) by double click.
- Job sub-windows may be opened in parallel.

Each job type runs separately but information is easily exchanged by dedicated buttons.



Job buttons. *Push to open new or current sub-window.*

Arrange current sub-windows.

Register files/remove registration of files.

Registered data files. *Double-click to call raw data display.*

Registered background files (created within Rietveld sub-window)

Registered Rietveld input files and related data and background files.
Double-click INP file to call Rietveld sub-window.

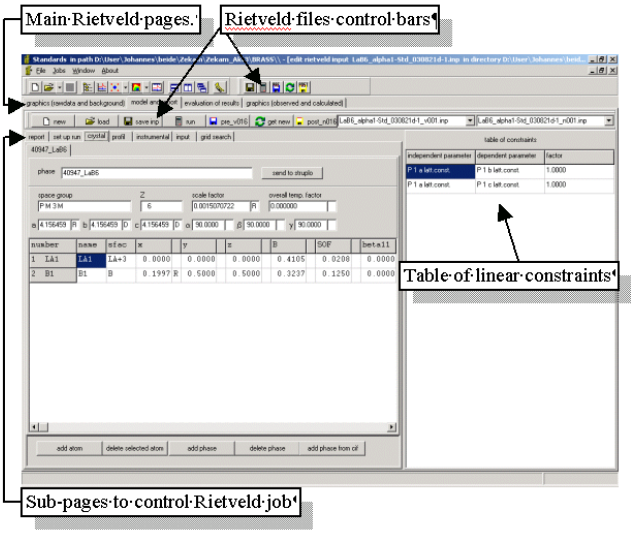
Integrated Explorer. *Use to add files to the project by drag and drop.*

```
brassproject Standards
  raw data
    DAT   entry file LaB6_alphal-Std_030821d.DAT
    DAT   entry file LaB6_alphal-Std_030821d-1.DAT
    DAT   entry file lab6_klein_030903.DAT
    DAT   entry file si_al_030827.DAT
  background
    BKG   entry file LaB6_alphal-Std_030821d.bkg
    BKG   entry file LaB6_alphal-Std_030821d-1.bkg
  input parameters
    rietveld
      INP   entry file LaB6_alphal-Std_030821d.INP
        related rawdata    LaB6_alphal-Std_030821d.DAT
        related background LaB6_alphal-Std_030821d.bkg
      INP   entry file LaB6_alphal-Std_030821d-1.inp
        related rawdata    LaB6_alphal-Std_030821d-1.DAT
        related background LaB6_alphal-Std_030821d-1.bkg
      INP   entry file lab6_klein_030903.inp
        related rawdata    lab6_klein_030903.DAT
      INP   entry file si_al_030827.inp
        related rawdata    si_al_030827.DAT
    struplo
    fourier
  output
    rietveld
    struplo
    fourier
```

Rietveld features:

- Comprehensive graphical user interface.
- The background may be defined by a polynomial function or graphically by set points for linear interpolation
- Separation of instrumental and sample effects based on the reformulation of the Pseudo Voigt function according to [2, 3]

- Handles peak broadening due to anisotropic strain [4], as modified in [5], and anisotropic shape of small crystals [2]
- By a single button push, *BRASS* creates numbered backups of any intermediate state of the Rietveld input and the main output files for later re-use and study
- Automatically keeps track of the main actions on the input files (Rewriting of input files by push button, Rietveld run or backup) in a report window
- Drag-and-drop type setting of linear constraints
- Handles intensity loss due to beam overflow for rectangular [6] and circular sample area [7]
- Online graphics present the evolution of residuals and convergence in the subsequent cycles of a refinement
- Display of Rietveld plot, quantitative phase composition, grid search and fourier diagrams and full ASCII output of the last Rietveld run
- Rietveld kernel roots: Wiles and Young [8], as extensively modified by Hill and Howard [9], and Fischer et al. [10,11]



LaB6_alpha1-Std_030821d-1_v001.inp

LaB6_alpha1-Std_030821d-1_n001.inp

40947_LaB6

phase 40947_LaB6

space group PM3M

Z 6

scale factor 0.0015070722 R

overall temp. factor 0.000000

a 4.156459 R

b 4.156459 D

c 4.156459 D

α 90.0000

β 90.0000

γ 90.0000

number	name	sfac	x		y		z		B		SOF		beta11
1 LA1	LA1	LA+3	0.0000		0.0000		0.0000		0.4105		0.0208		0.0000
2 B1	B1	B	0.1997	R	0.5000		0.5000		0.3237		0.1250		0.0000

table of constraints

independent parameter	dependent parameter	factor
P 1 a latt.const.	P 1 b latt.const.	1.0000
P 1 a latt.const.	P 1 c latt.const.	1.0000

For STRUPLO features: see separate document and [2].

BRASS can be downloaded from the BRASS homepage (http://www.brass.uni-bremen.de/) of the Central Laboratory for Crystallography and Applied Material Sciences (ZEKAM) at the university of Bremen. After download, an install routine will guide through the installation procedure. All published use should cite ref. [1].

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News from the
International Centre for Diffraction Data (ICDD)

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Phone: +610.325.9814
Fax: +610.325.9823

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www.dxcicdd.com
E-mail: info@icdd.com

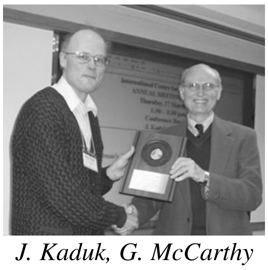
Announcements & Awards

The Annual Meeting of Members presented a venue for recognizing several members' service and contributions to the Powder Diffraction File (PDF), the ICDD, and the scientific community as a whole.

- Julian Messick was honored for his leadership in guiding and mentoring the ICDD as Treasurer from 1996 to 2005. His resignation was reluctantly accepted as the directors and members offered well wishes in his future, more leisurely, endeavors. During the presentation by Chairman of the Board, Jim Kaduk, Julian was also acknowledged for his nearly 30 years of service as an ICDD employee. Hired in 1966, Julian was employed as the PDF Production Manager, served as Deputy General Manager & Secretary of the Corporation from 1980 to 1983; Secretary/General Manager from 1983 to 1994; and Interim Executive Director in 2001. We thank Julian for generously sharing his time and talents with the organization during his tenure.


J. Messick, J. Kaduk

- Dr. Gregory McCarthy, North Dakota University, Fargo, ND, was awarded the 2005 Distinguished Fellow Award. The leadership and vision displayed in Greg's historical efforts were instrumental in structuring the foundation of the modern ICDD organization, and contributed to the success that ICDD experiences today in serving as the world's center for diffraction data. Congratulations to Greg! Through this award, the ICDD recognizes Greg's volunteer efforts and extends its deep appreciation.


J. Kaduk, G. McCarthy

New Treasurer Announced

Congratulations to Dave Taylor of the United Kingdom who was recently named as the new ICDD Treasurer by the Board of Directors. Dave has been actively involved with the ICDD since 1999, and has served the organization in many capacities: Regional Co-chair for the United Kingdom, Director-at-Large, Member of the Finance and Bylaws Committees, and Board liaison to the Education Subcommittee. Dave, along with his wife Ann, often represents ICDD at international meetings by attending the ICDD exhibit booth. As an active member, former Industrial Group Chairman, and Council member of the British Crystallographic Association (BCA), Dave also brings to the ICDD his five years of experience as the BCA treasurer.


D. Taylor

X-ray Clinics

Recently, our clinics on Practical XRF, Fundamentals and Advanced Methods of XRD were held at headquarters. The focus on practical applications, hands-on experience, and intense personal instruction, differentiates the ICDD clinics from other venues. Don't just take our word for it, please read a testimonial from one of our attendees:

"I attended the ICDD X-ray clinic in June 2005. As a USGS X-ray technician, I was hoping to obtain a deeper understanding of the science of X-radiation. And did I ever! From Plank's Constant to noise curves to coherent scatter and attenuation coefficients, the able instructors covered all of it in a friendly, comprehensible fashion. The science lectures were great!

The labs also provided new and useful information. Of particular value was the sample preparation lab wherein we learned that it is possible to minimize preferred orientation. A simple mounting technique, with which I was unfamiliar, improves random distribution of mica and other minerals, producing a better X-ray profile. Again, just great!

The adjective that best describes the week of the clinic is 'polished.' The instructors, the lectures and labs, the accommodations, transportation to and from ICDD headquarters, the included snacks and lunches, and the evening discussions were perfect. It was money well spent. I'm a smarter X-ray tech for having attended."

Sincerely,
Rhonda Driscoll, US Geological Survey

For more information regarding the ICDD X-ray Clinics, including next year's dates, please visit

www.icdd.com/education/clinics.htm

Denver X-ray Conference (DXC)

2005 Conference

"X-ray Imaging" was the focus of this year's DXC. Covered in the plenary as well as a special session, this topic attracted many attendees, all of whom were enlightened and entertained by the broad-range, energizing talks. During the week of 1–5 August, Colorado Springs provided the setting for DXC attendees to experience workshops and sessions focusing on cutting-edge training, applications, techniques, and instrumentation, as related to X-ray materials analysis. Please visit **www.dxcicdd.com** for more information.

PPXRD-5

The ICDD is proud to present the 5th Pharmaceutical Powder X-ray Diffraction Symposium. Designed to create a forum for the exchange of knowledge and cutting-edge ideas among those interested in XRD and the pharmaceutical industry, PPXRD-5 will be held 14–16 February 2006 in Somerset, New Jersey. Abstracts are being solicited for this event; the deadline is 15 October 2005. You can also save 25% by registering by 1 November 2005.

For even more valuable pharmaceutical XRD training, don't miss the optional hands-on workshop—Characterization of Pharmaceutical Solids: Crystal Studies and XRD Applications, being held on 13 February 2006.

Learn more at **http://www.icdd.com/ppxrd/**.

Scholarships

The Ludo Frevel Crystallography Scholarship deadline is fast approaching; all applications must be received by 31 October 2005. Winners will be announced in January 2006. See complete application details at

http://www.icdd.com/resources/awards/frevel.htm

ICDD Members Meet in Florence

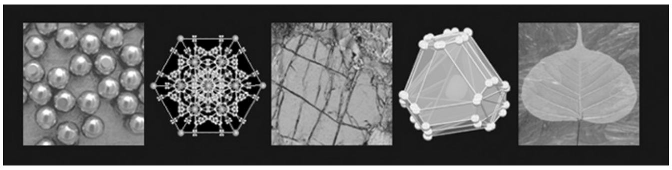
The IUCr Congress provided a venue for an informal meeting of regional ICDD members. On 22 August, the rooftop terrace of the Tornabuoni Beacci Hotel in Florence, Italy, provided a picturesque setting, where approximately 50 members and their families gathered to enjoy fine cuisine and meet the ICDD Board of Directors. It was indeed a pleasure to meet so many of our members, many of whom have never had the opportunity to travel to ICDD headquarters in Newtown Square.

The Louërs, the Goebels, & the Snyders

Bernd Hinrichsen, M. Delgado & W.Wong-Ng

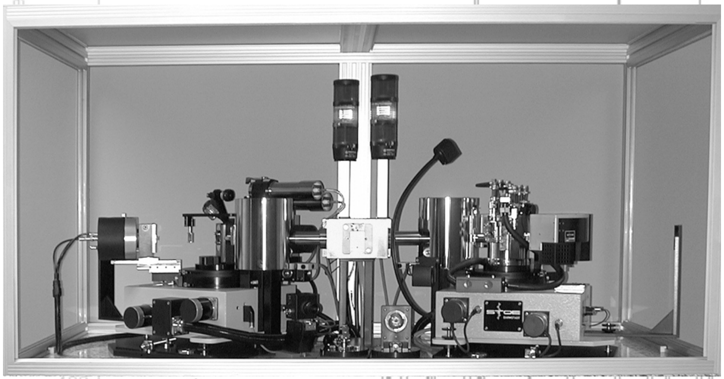
Product News: PDF-4+

The ICDD is pleased to announce our first database release with a new collaborative partner, Material Phases Data System (MPDS). This collaboration incorporates structural data from the Linus Pauling File into the PDF creating a new product PDF-4+. PDF-4+ is the successor to PDF-4/Full File and now contains 240,050 material data sets standardized and reviewed from data contained in the ICDD, Pauling File, Inorganic Crystal Structure Database (ICSD) and National Institute of Standards and Technology (NIST) databases. The Pauling File addition brings new data and new capabilities to PDF-4+ with the addition of atomic parameters and an inorganic structural prototyping system. This system uses atomic environment, cell parameters, Wyckoff notation and space groups to organize inorganic materials into common families. This enables research scientists to identify materials, even those without a reference pattern, by polytype analysis. The addition of atomic parameters also enables molecular graphics and the calculation of variable wavelength X-ray, electron, and neutron diffraction patterns based on fundamental principles and software developed by ICDD members, scientists and collaboration partners.



Further Information

To learn more about the ICDD, its products and services, please visit our web sites: **www.icdd.com** and **www.dxcicdd.com**.



What's On

19-21 September 2005
SES-III - Synchrotron Environmental Science III. Upton, NY, USA
http://www.cems.stonybrook.edu/ses-iii/index.html

22-24 September 2005
7th International Meeting on Single Nucleotide Polymorphism and Complex Genome Analysis , Hinckley, Leicestershire, UK
http://snp2005.nci.nih.gov

3-7 October 2005
4th NCCR Practical Course - Synchrotron Data Acquisition Techniques in Macromolecular Crystallography. Swiss Light Source, Villigen, Switzerland
http://www.structuralbiology.unizh.ch/course05.asp

6-7 October 2005
Watching the Action: Powder Diffraction at non-ambient conditions. Max-Planck-Institute for Solid State Research, Stuttgart, Germany
http://www.fkf.mpg.de/xray

10-14 October 2005
Autumn School - Application of Neutron and Synchrotron Radiation in Engineering Materials Science. Hamburg, Germany
http://www.tu-berlin.de/~pnam

17-19 October 2005
3rd MECA SENS Conference on Stress Evaluation by Neutron and Synchrotron X-Ray Radiation. Bishop's Lodge Resort, Santa Fe, New Mexico, USA
http://www.lansce.lanl.gov/mecasens2005

25-27 October 2005
MM4MX Molecular Modelling for Macromolecular Crystallographers - a MAXINF2 sponsored workshop. Diamond Light Source, Oxfordshire, UK
http://www.diamond.ac.uk/News/LatestEvents/mx_workshop_2005.htm

30 October 2005
Recent Advances in Phasing Methods for High-Throughput Protein Structure Determination an International Workshop. Peking University, Beijing, China..
http://www.ccs.pku.edu.cn/wp2005

3-5 November 2005
Pittsburgh Diffraction Conference '05 - The 63rd edition. Argonne National Laboratory, Argonne, IL, USA
http://www.pittdifsoc.org/63rd_PDS_announce.htm

27 November - 2 December 2005
International Conference on Neutron Scattering 2005, Sydney, Australia.
http://www.sct.gu.edu.au/icns2005

5-6 December 2005
WINS2005 - Workshop on Inelastic Neutron Spectrometers 2005. Cairns, Australia..
http://www.iucr.org/cww-top/mtg.wins2005.html

9-13 January 2006
Crystal Growth and Characterisation of Advanced Materials - an international Workshop. Crystal Growth Centre, Anna University, Chennai, India
http://www.iucr.org/cww-top/mtg.chennai.jpg

14-16 February 2006
PPXRD-5 - The 5th Pharmaceutical Powder X-ray Diffraction Symposium. Somerset, New Jersey, USA
http://www.icdd.com/ppxrd

20-23 February 2006
RX 2006 - 6th Colloquium on X-Rays and Matter. Limoges, France
http://www.iucr.org/cww-top/mtg.rx2006.pdf

28 May - 3 June 2006
SRI2006 - Ninth International Conference on Synchrotron Radiation Instrumentation. Daegu, Exco, Korea
http://sri2006.postech.ac.kr/

9-13 July 2006
SAS2006 - The XIII-th International Conference on Small-Angle Scattering. Kyoto, Japan
http://www2.scphys.kyoto-u.ac.jp/sas2006/index.html

22-27 July 2006
ACA 2006 - The American Crystallographic Association Annual Meeting. Honolulu, Hawaii, USA
http://www.hwi.buffalo.edu/aca/

28 August - 2 September 2006
Analyse structurale par diffraction des rayons X, cristallographie sous perturbation Summer School - Ecole thematique. Nancy, France
http://www.lcm3b.uhp-nancy.fr/nancy2006/

1-4 September 2006
EPDIC-10 - European Powder Diffraction Conference, University of Geneva, Geneva, Switzerland.
http://www.sgk-sscr.ch/EPDIC10/EPDIC10.html

13-15 September 2006
ECRS 7 - The 7th European Conference on Residual Stresses. Berlin, Germany
http://www.ecrs7.de/

17 November 2006
Protein crystallization: Present and future - Crystallisation Workshop . EMBL Hamburg Outstation, Hamburg, Germany
http://www.embl-hamburg.de/workshops/2005/htx/

18-19 November 2006
Theoretical Crystallography and Materials Science - Satellite Conference of the AsCA'06 / CrSJ meeting. Tsukuba, Japan
http://www.lcm3b.uhp-nancy.fr/mathcryst/asca2006.htm

7-17 June 2007
Engineering of Crystalline Materials Properties: State-of-the-Art in Modelling, Design, and Applications, the 39th crystallographic course at the Ettore Majorana Centre, Erice
http://www.crystalerice.org/futuremeet.htm

How to receive the IUCr CPD Newsletter

The best and fastest way to receive the CPD Newsletter is to download it in electronic format, as a .pdf file, from the CPD web-site.

If you wish to be added to the mailing list for the Newsletter of the IUCr Commission on Powder Diffraction or have changed address, please contact the Chairman:
Robert Dinnebier (r.dinnebier@fkf.mpg.de).

Call for contributions to the next CPD Newsletter (No 32)

The next issue of the CPD Newsletter will be edited by Robert Dinnebier, to appear in December 2005. Robert will greatly appreciate contributions from readers on matters of interest to the powder diffraction community, e.g. meeting reports, future meetings, developments in instruments, techniques, and news of general interest. Please contact him for sending articles and suggestions. Software developments can be directly addressed to Lachlan Cranswick or to the Editor of Newsletter No 32.

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