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Powder Diffraction in Mining and Minerals

(Lachlan Cranswick and Gert Kruger, Editors)

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CPD Chairman’s Message

The main topic of the CPD Newsletter No 27 is of a rather general interest: applications of Powder Diffraction in the mining industry and to the study of mineral phases. Actually, this is just a paradigm to show the versatility of PD, through a selection of working examples, and an up-to-date review of methodologies that find many further applications beyond the specific field of mineralogy. Besides the usual contributions, including the ‘Computer Corner’, conference and school reports, news from the ICDD and the ‘What’s on’ pages, this issue provides a free offprint of a recent paper by *N.V.Y. Scarlett*, *I.C. Madsen* and co-workers (J. Appl. Cryst. 35 (2002) 383-400). The article is the second part of the extensive report on the ‘Quantitative Phase Analysis’ Round Robin. The CPD Newsletter is intended as a Forum, for an open discussion of new methodologies, applications and current opinions on PD: readers are therefore invited to send contributions and comments on the articles, on the Newsletter as a whole, and on all the CPD activities.

The XIX IUCr Congress and General Assembly, held in Geneva last August, marked the end of a triennium for the various IUCr Commissions. The report on the CPD activity (1999-2002), presented at the IUCr assembly (to be published in Acta Crystallographica), is available on the CPD web-site (http://www.iucr.org/iucr-top/comm/cpd/). Following an unwritten rule, several CPD members decided to quit even if the formal IUCr bylaws would allow them a longer term. It is a widely shared opinion among the CPD that a frequent turnover is a favourable condition for an active membership and to properly consider the many different methodologies and applications of PD. The necessary continuity in the CPD action is assured by the presence of a few members serving a second term and by appointing Consultants, among which, as a tradition, the past Chairman.

Before concluding this short message and introduction to Newsletter No 27, I wish to remember three colleagues who passed away recently. Even if the CPD Newsletter does not regularly reports obituaries it would be impossible not to remember here *D.K. Smith*, *R.W. Cheary* and *R. Jenkins*. Their names will be at least familiar to readers, as they appear in many of the most significant studies and activities related to PD in the last thirty and more years. Beyond their unquestionable scientific stature, for those of us who had the pleasure to know them and to appreciate their kindness, competence and advise, and to be involved by their enthusiasm in PD research, they will certainly be a lasting memory.

Paolo Scardi

CPD projects

QUANTITATIVE PHASE ANALYSIS ROUND ROBIN

Readers can refer to the enclosed offprint for an exhaustive discussion on the outcomes of the QPA Round Robin for samples 2,3 and 4 (synthetic bauxite, natural granodiorite and pharmaceuticals). The first part of the study was reported in a previous publication by I.C. Madsen *et al.* (J. Appl. Cryst. 34 (2001) 409-426), distributed as a free offprint together with the CPD Newsletter No 25.

First and second (enclosed) parts can be freely downloaded from the CPD web-site (http://www.iucr.org/iucr-top/comm/cpd/), where additional information and original data files can be found. We wish to thank again the IUCr Editorial Office for giving us permission to include the reprint from the Journal of Applied Crystallography (JAC) as an annex to the present issue.

SIZE-STRAIN ROUND ROBIN

The preliminary report and analysis of results are still available at http://www.boulder.nist.gov/div853/balzar, CPD and CCP14 Web-sites. A paper has been recently submitted for publication on the Journal of Applied Crystallography, and a reoprt should appear in one of the forthcoming issues of the CPD Newsletter.

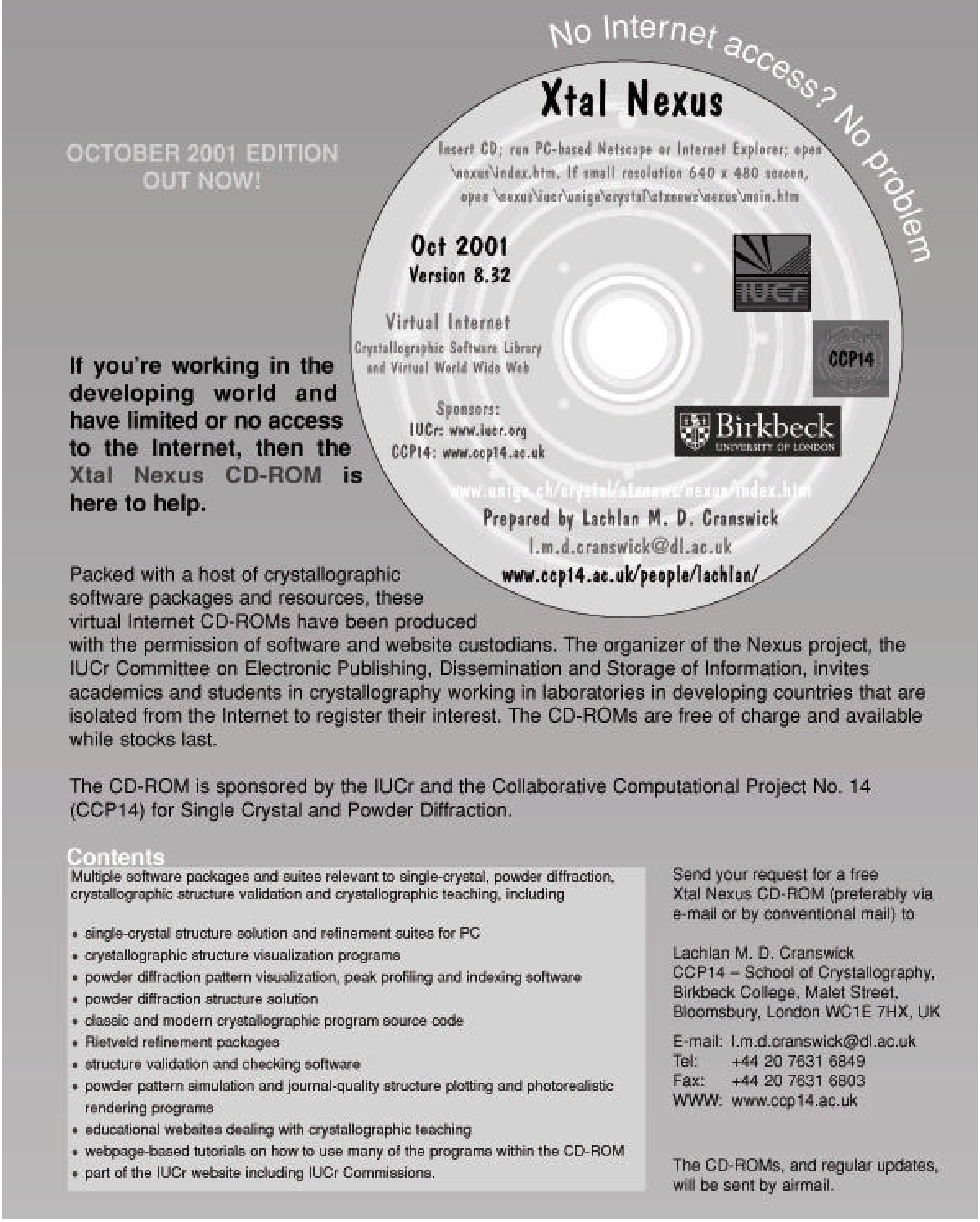
From the Editors of Newsletter 27

X-ray powder diffraction has had a long association with mineralogy. It has always been one of the major techniques for the analysis of minerals, used for phase identification, the calculation of phase abundance and crystal structure determination. Suppliers of X-ray analytical equipment in mineral-rich parts of the world, such as Southern Africa, for many years sold more diffraction equipment than XRF spectrometers, contrary to their experience in the rest of the world. This reflects of course on the relative importance of mining and exploration in those countries. It illustrates, however, the historical importance of powder XRD in the area of mining and mineralogy.

When X-ray diffraction reached its maturity as an analytical technique the situation changed somewhat, with other analytical techniques (mostly for rapid elemental analysis) becoming more important. Developments in instrumentation and computing capabilities for powder diffraction reversed this trend in recent years. It was therefore decided to devote this issue of the newsletter to a random walk through powder diffraction in mining and mineralogy, with glimpses at the past, current practice and ideas about the future. This not supposed to be a comprehensive review on the theme and lack of space also prevent extensive coverage; however it should readers an idea of the present and past variety of ideas and applications in the field.

It remains necessary to emphasize that the mining and other mineralogical industries require trained, qualified and motivated people using "appropriate" methods. The results obtained in a number of previous and present Round Robins (organised by the CPD and others) that focused on quantification, structure refinement, size-strain measurements and search-match capabilities, showed that “dodgy”, inaccurate and wrong results can routinely occur, even in well-known laboratories. It is only by continuous training, testing and publication of results that we can be sure of the quality of our results. We trust that the CPD newsletter is a timely and appropriate resource for people who wish to know what is out there and what methods they should be investigating to ensure they get the most appropriate results for the problems on hand.

Gert Kruger and Lachlan Cranswick



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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 Large Scale Facilities (LSF) 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*:* http://www.pulverdiffraktometrie.de

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

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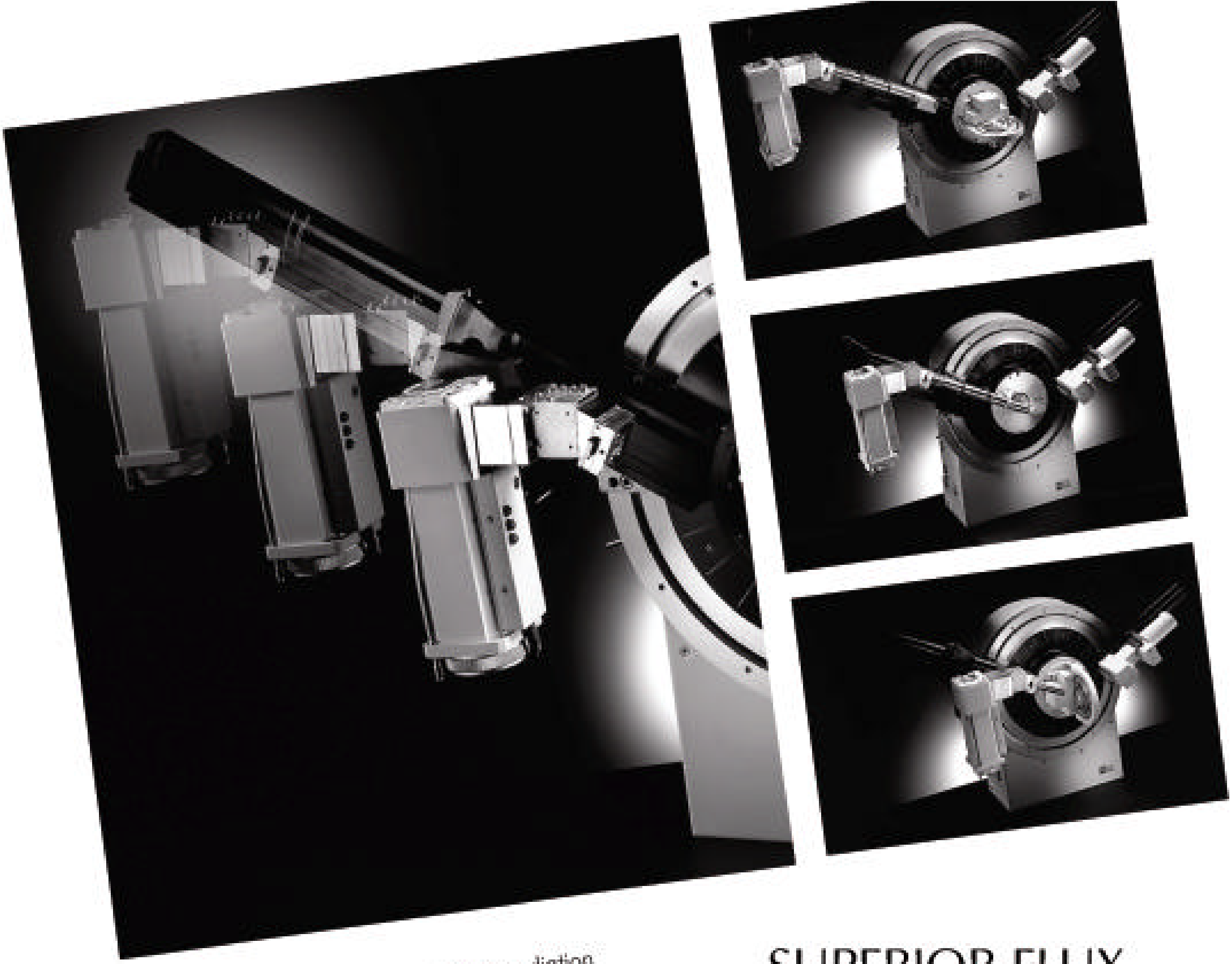

Spray Drying for X-ray Powder Diffraction Specimen Preparation

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Introduction

One only has to look in the literature at the number of publications and variety of methods and techniques of preparing a random powder for analysis by X-ray powder diffraction (XRPD) to realize that eliminating preferred orientation (texture) is a difficult task [1,2]. The effort expended is also an indication of just how important the elusive random powder is for many applications. Making a random powder is difficult because most minerals have anisotropic shapes. The clay minerals, with which I am most familiar, tend to be platy and the slightest amount of pressure applied during the loading and mounting of the sample induces a preferred orientation. Diffraction from some planes is then over-represented whilst for others it is diminished. Many other groups of minerals are also prone to preferred orientation, particularly those with good cleavage. The feldspars and carbonates are noteworthy because they are such common constituents of many mineral samples.

Of the various methods used to prepare random powder samples the most common are probably various forms of back or side loading of a standard cavity mount. Undoubtedly this is simply because such procedures are relatively straightforward and quick to perform but even the most careful packing of a powder sample into a standard cavity holder will doubtless result in some degree of preferred orientation. This may not present a problem if reproducibility rather than truly random orientation is the key issue. If, however, a methodology, including preparing and loading of samples, is to be used by more than one person, perhaps over a long period of time when expertise in the laboratory will come and go, then guarantees of reproducibility are unlikely.

One alternative to back and side loading is a method known as spray drying. This method consists of spraying a sample, usually as an aqueous suspension, into a heated chamber where it dries in the form of the spherical spray droplets. The resulting dry product consists of thousands of tiny spherical granules of the sample components (Figure 1).

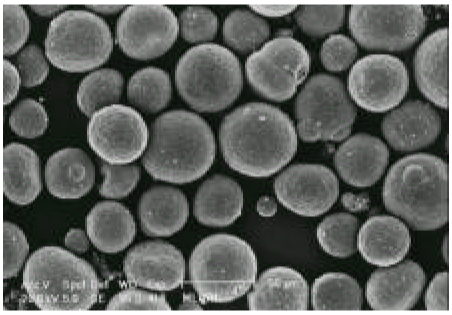

Figure 1: *Example of the spray dried clay mineral kaolinite.*

Purposely breaking open the granules or sectioning them (Figure 2) shows that the granules are by and large solid agglomerates of the individual mineral particles.

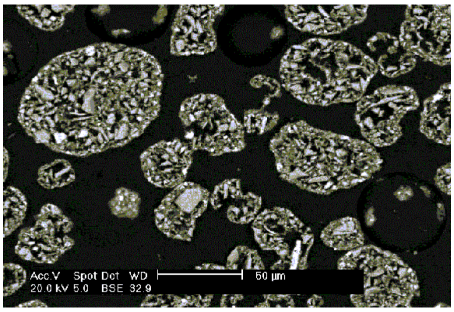

Figure 2: *Backscattered electron image of polished section through granules of a sample of sandstone prepared by spray drying.*

Typically, the average diameter of the granules is about 50 microns. Both the arrangement of any component within the spherical granules and the random way in which spherical granules pack together ensure that preferred orientation is eliminated. Spray drying is therefore a method capable of producing truly random powder samples for XRPD. In fact, spray drying is a well-known and widely used industrial process. Indeed, there have been several attempts to use it for XRPD sample preparation [3,4,5,6] but previously it has not been widely adopted. This appears to be largely due to problems of sample recovery. A method and equipment has been developed at the Macaulay Institute [7,8] that overcomes this difficulty and allows spray drying to be used as a routine method of sample preparation for mineral samples including rocks, soils, sediments or similar materials. The method is essentially a modification of that of Smith et al. [6] in that the spray is generated by a pneumatic method of atomization, but using an artists air-brush instead of a less controllable two nozzle system. Additionally, the sample is collected on a sheet of paper allowing it to be recovered easily from the drying chamber. This equipment is now in use in a number of different laboratories worldwide.

Advantages and applications of spray-drying

One of the main advantages of spray drying is that as a consequence of eliminating preferred orientation, the XRPD patterns from spray-dried samples are extremely reproducible. By way of example, Figure 3 and 4 illustrate XRPD patterns obtained by three different operators who emptied and loaded two portions of the same sample six times each. One portion was spray dried and the other freeze-dried. For the freeze-dried portion (Figure 3) no two runs were the same. Additionally, the extent of preferred orientation for each phase, as indicated by enhanced intensity, is inconsistent between phases. In contrast, the diffraction pattern from the spray-dried portion (Figure 4) is reproducible by, and between, all three operators.

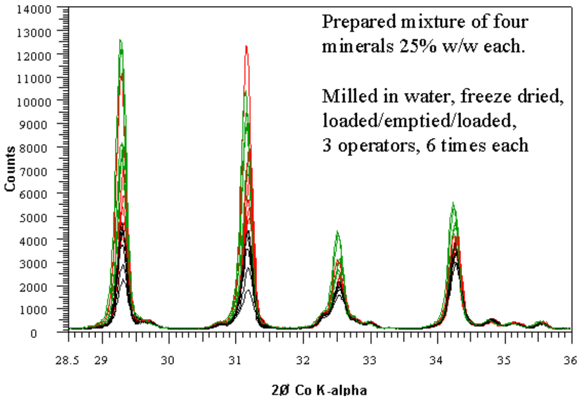

Figure 3: *XRPD patterns of a synthetic mixture of 25% chlorite, 25% muscovite, 25% albite and 25% calcite, all minerals which frequently exhibit preferred orientation. XRPD patterns from 18 separate loadings of a freeze-dried portion of the mixture by 3different operators (red, green, blue, 6 patterns each).*

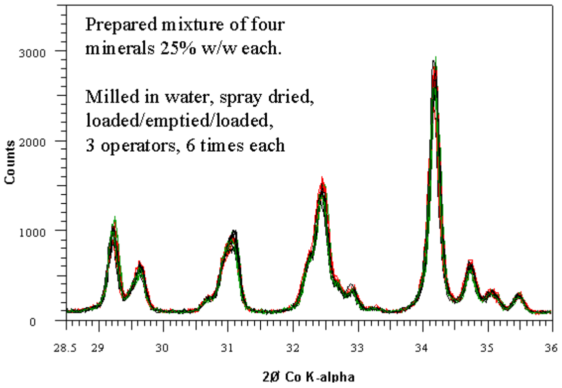

Figure 4: *XRPD patterns of a synthetic mixture of 25% chlorite, 25% muscovite, 25% albite and 25% calcite, all minerals which frequently exhibit preferred orientation. XRPD patterns from 18 different loadings of a spray-dried portion of the mixture by 3 different operators (red, green, blue, 6 patterns each).*

There can be little doubt that the problem posed by preferred orientation has been one of the biggest obstacles to the development of reliable methods of quantitative analysis of powder samples [9]. Elimination of preferred orientation by spray drying and the consequent reproducibility of diffraction data means that spray drying is an excellent starting point for quantitative phase analysis. This is especially the case if peak based reference intensity ratio (RIR) methods are used, but also means that Rietveld based procedures do not need to incorporate steps to refine preferred orientation. The practical importance of this is emphasized for example by the studies of Hill et al. [10] and Mumme et al. [11]. These authors demonstrate the wonderful potential of the Rietveld method of quantitative phase analysis for complex geological samples, but they were not successful in applying corrections to account for severe problems with preferred orientation in normal back-loaded or side drifted cavity mounts. Instead they resorted to dealing with preferred orientation by using small samples mounted in rotating capillary tubes, but with the result that each XRPD pattern took on average about 45 hours to collect. Had a means of preparing their samples by spray drying been available to these authors they could have recorded their diffraction data in much less time from normal cavity mounts.

A further practical advantage of spray drying is that in combination with wet grinding (which is preferable over dry grinding to reduce particle size) samples may be spray-dried directly from the mill in which they are ground. This is simply a matter of experience in loading the right proportions of sample to water into the mill in order to obtain a suspension of appropriate consistency to spray. Spray-dried powders are also much easier to load and handle than most other forms of powder since they can simply be poured into the cavity in excess, this is then tapped vigorously from side to side to obtain good packing, and surplus material removed.

Results of an informal Round Robin organized by Steve Norval (ICI) and presented at the British Crystallographic Association Meeting at Heriot Watt University, Edinburgh [12] showed that spray drying was the best method of preparing a random powder. The sample supplied to participants was a mixture of hydromagnesite and huntite. Figure 5 shows the sample run as received and Figure 6 the sample run after spray drying. In both figures the powder patterns are compared to reference patterns from the PDF file. The very much better correspondence of intensity data from the spray-dried sample to the reference patterns is obvious.

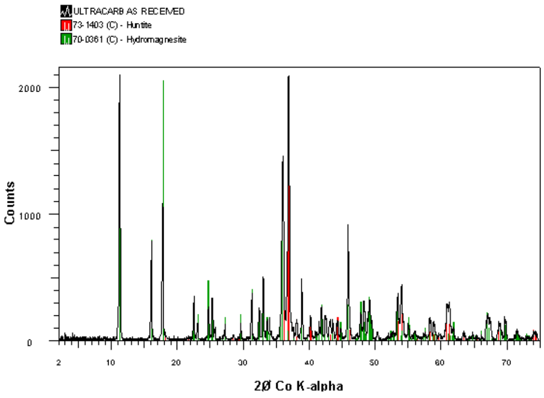

Figure 5: *Sample consisting mainly of huntite and hydromagnesite run as received. Note obvious and common discrepancies of measured intensity and intensity as indicated by PDF files (calculated patterns) for these minerals.*

Additionally, this sample also revealed another potential advantage, namely the more reliable use of intensity data for search match procedures. Since the intensity data of the spray dried sample is not affected by preferred orientation it became obvious that the sample also contains minor/trace amounts of magnesite and calcite. This conclusion is not at all obvious for the non-spray dried sample because one cannot easily separate discrepancies in intensity data that arise from preferred orientation from those that have other causes.

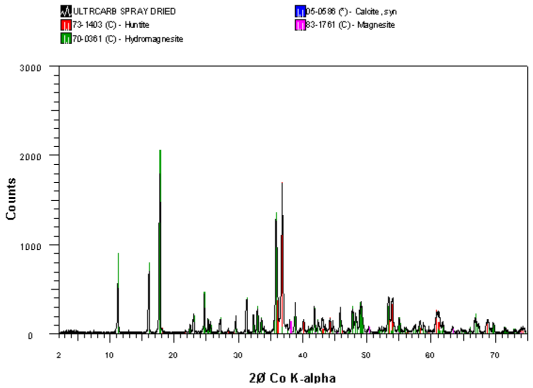

Figure 6: *Sample consisting mainly of huntite and hydromagnesite run after spray drying. Note obvious much better agreement between measured intensity and intensity as indicated by PDF files (calculated patterns) for these minerals compared to previous figure. Note also that minor/trace calcite and magnesite are obvious in this pattern.*

Disadvantages of spray drying

As with any method there are of course some disadvantages with spray drying. Firstly, spray drying produces dust and it is imperative that proper and appropriate precautions and regulations relating to health and safety issues regarding dusts are implemented and followed.

As far as disadvantages for powder diffraction are concerned the main one is that it is inevitable that some sample will be lost in the process. Typically recovery will be 50-80%. The losses occur as material left in the mill (assuming the sample is sprayed directly following wet grinding), material left in the holder from which the sample is sprayed, and material that is not recovered from the oven. This is not normally a problem for a sample if there is plenty of it and many mineral samples fall into this category. For a precious sample, however, of which there is less than 1g spray drying is not yet the answer. At the Macaulay Institute we usually begin by milling 3g of sample and end up collecting ~1.5g in a vial.

For most practical purposes the oven may be cleaned between samples simply by using a jet of compressed air. Experience has shown that trace amounts (<0.5%) of contamination of one sample by another may occur if this procedure is adopted. For many geological materials this is entirely acceptable and an experienced operator can then mill and spray dried as many as 30 samples in a day. If contamination must be avoided at all costs, then the oven must be switched off and cleaned between samples.

The only other disadvantage of spray dying is that some minerals may be susceptible to phase changes at the temperatures used. Typically the sample 'sees' an air steam heated to about 170°C for a few seconds or more. Whilst this does not cause any problems for clay or other common rock forming minerals, phase transformations can occur in many sulphates such as gypsum which dehydrates forming bassanite. Doubtless other temperature sensitive minerals may be similarly affected. One way to combat such problems is to spray dry at lower temperatures using a liquid other than water, and such a procedure may also be adopted for materials which would react with water such as Portland cement which can be successfully spray dried from ethanol (Figure 7). Departures from using aqueous suspensions obviously require that all health and safety aspects should be adequately assessed and appropriately controlled and monitored.

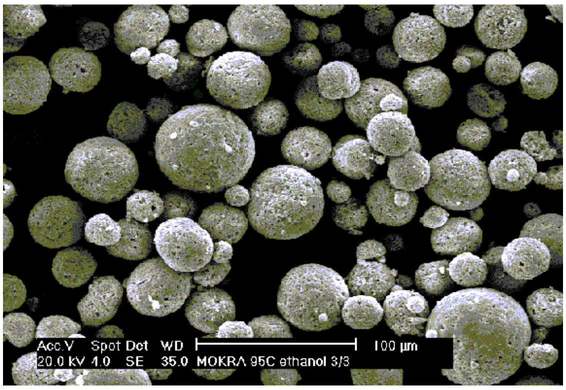

Figure 7. *Ordinary Portland cement spray dried from ethanol.*

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Quantitative Phase Analysis of Sulfide-bearing Mine Wastes Using the Rietveld Method and X-ray Powder Diffraction Data.

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INTRODUCTION

Mining and milling operations are responsible for the production of billions of tonnes of waste rock and finely crushed tailings worldwide (e.g., Fig. 1). Subsequent exposure to abiotic and biotic interactions results in products that adversely affect the environment. Of particular concern is the generation of acid rock drainage (ARD) from the oxidation of sulfide-bearing wastes, which commonly results in effluents that are enriched in potentially toxic metals.

Today, most regulatory agencies require not only that water quality from existing mining wastes be controlled, but also that the possibility of ARD at potential mining sites be predicted. The prediction of ARD involves using various chemical methods and tests to determine how the minerals in samples of waste will behave upon weathering. Of crucial importance is knowledge of the relative amounts of the minerals which have significant amounts of acid-producing potential, AP (pyrite and pyrrhotite), and the minerals which have a high neutralization potential, NP (calcite).

The determination of AP and NP values is critical to successful acid-base accounting (ABA). Regardless of the type of tests done for ARD prediction, quantitative phase analysis of both AP and NP minerals is of prime importance. Here we demonstrate the application of a relatively new method of phase analysis, the Rietveld method, to a typical sulfide- and carbonate-bearing waste rock.

QUANTITATIVE PHASE ANALYSIS

Quantitative phase analysis is the measurement of the relative abundances of the constituent minerals in a sample. Traditionally, geologists have referred to this procedure as modal analysis. The units of the analysis may be in weight, mole or volume percent (calculated from area percent). In Rietveld analysis, the results are determined in weight percent, but these may be later recalculated to any desired unit.

Phase (modal) analysis has traditionally been done using visual methods (point counting, image analysis), relative intensities of peaks in X-ray powder-diffraction patterns (using standards), and normative calculations (using chemical analyses). Each of these traditional methods has disadvantages, which may be overcome using the Rietveld method [1]. Details are given in a previous paper [2].

Figure 1. *Escondida Cu-Au-Ag open-pit mine, Chile. Image from the NASA/GSFC/MITI/ERSDAC/JAROS, and the U.S. - Japan ASTER Science Team. Scale bar is 8 km.*

X-RAY POWDER DIFFRACTION

From the atomic arrangement of a crystal (generally determined by single-crystal X-ray diffraction), we can calculate any powder diffraction pattern. This ability is fundamental to doing quantitative phase analysis using the Rietveld method. In any X-ray powder diffraction pattern, the peak positions are a function of the radiation used, and the size and symmetry of the unit cell; the peak intensities are a function of the kinds of atoms and their arrangement in the unit cell, as modified by various instrumental and method-dependent parameters. Thus, the intensities and positions of peaks in an X-ray powder diffraction pattern are characteristic of a crystalline compound with a particular composition and crystal structure. Therefore, the X-ray powder diffraction pattern of a phase may be used as a “fingerprint” to identify the phase. Traditionally, this simple identification of crystalline compounds has been the familiar goal of most X-ray powder diffraction studies. A database of standards such as that published by the International Centre for Diffraction Data is required.

THE RIETVELD METHOD

The Rietveld method is a standardless, full profile approach to quantitative phase analysis using X-ray powder diffraction data. A calculated diffraction pattern is generated which is compared with the observed data using least-squares procedures to minimize the difference between the whole observed and calculated diffraction patterns. The following parameters may be refined: the structural parameters of each mineral (atomic coordinates, site occupancies, displacement parameters), the various experimental parameters affecting the pattern (zero-point correction, peak shape, background, etc.). Starting values for the atomic parameters are readily available from the literature or from databases such as the Inorganic Crystal Structure Database (ICSD).

Of particular relevance to doing modal analysis of materials is that the Rietveld refinement method can be used to characterize several phases simultaneously, and that the relative masses of all phases contributing to the diffraction pattern can be derived from the refinement using the simple relationship:

$$W_r = S_r\,(ZMV)_r \,/\, S_t\, S_t\,(ZMV)_t$$

where W_r is the relative weight fraction of phase r in a mixture of t phases, S is the scale factor derived from Rietveld refinement, Z is the number of formula units per unit cell, M is the mass of the formula unit (atomic mass units), and V is the volume of the unit cell (Å^3).

FUNDAMENTAL PARAMETERS APPROACH

A strength of the Rietveld method is that overlapping peaks are easily modelled and refined; this is not the case with traditional X-ray powder diffraction methods. However, for complicated phase mixtures with a high degree of overlap, reliable quantitative Rietveld analysis sometimes failed because traditional profile shape functions did not allow for an unambiguous decomposition of peak intensities.

Since the introduction of the so-called fundamental parameters approach [3] even samples with many phases / peaks leading to extreme peak overlap can be quantified successfully [e.g., 4], where traditional profile functions such as pseudo-Voigt and Pearson VII functions fail. With fundamental parameters, the known instrument geometry is used to describe observed line profile shapes according to

$$Y(2q) = (W \text{ Ä } G) \text{ Ä } S$$

where $Y(2q)$ is the observed line profile, W is the spectral distribution, G are any instrumental and S sample contributions. The benefits in using fundamental parameters are manifold including better profile fits based on physical reality in particular of heavily overlapped reflections, but also the standardless determination of microstructure parameters such as crystallite size and microstrain.

SAMPLE PREPARATION

The sample was ground in a McCrone micronizing mill (http://www.mccrone.com/) under alcohol to less than 5 µm in grain size. Fine grain size is essential to minimize micro-absorption corrections, to give reproducible peak intensities and to minimize preferred orientation. The powder was gently back-pressed into a standard aluminium holder against a ground glass slide to further minimize preferred orientation (Fig. 2). X-ray powder-diffraction data were collected over the range 3-70°2θ with CuKα radiation on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer equipped with a diffracted beam graphite monochromator crystal, 2 mm (1°) divergence and antiscatter slits, 0.6 mm receiving slit, incident-beam Soller slit, step 0.04°2θ, time 2 s/step. The long sample holder used (43 mm aperture) ensured that the area irradiated by the X-ray beam under these conditions was completely contained within the sample. The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF2 Data Sets 1-49 plus 70-86 using Search-Match software by Siemens (Bruker).

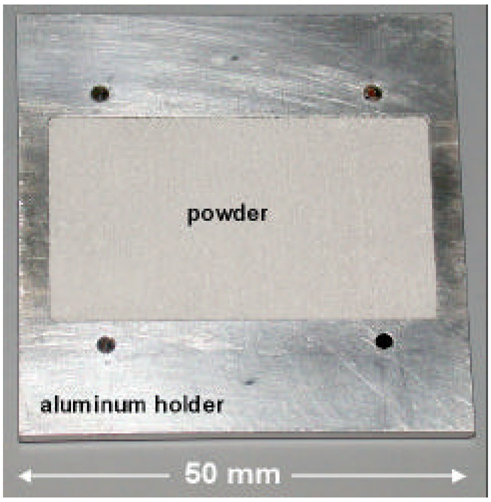

Figure 2. *Sample holder for quantitative phase analysis*.

RIETVELD REFINEMENT

X-ray powder-diffraction data were refined with the Rietveld program Topas 2.0 [5] using the fundamental parameters approach. Isotropic displacement parameters of individual atoms were fixed at values extracted from single-crystal refinements of the structures. Preferred orientation parameters for major phases with marked grain-shape anisotropy were corrected using the March-Dollase method. Micro-absorption contrast between phases was corrected using the method of Brindley [6].

RESULTS

The results of quantitative phase analysis by Rietveld refinement are given in Table 1. Rietveld refinement plots are given in Figures 3A and 3B.

Table 1. Results of Quantitative Phase Analysis

Phase	wt.%
Calcite	8.7 (0.2)
Siderite	2.5 (0.2)
Ankerite	6.2 (0.2)
Quartz	57.1 (0.4)
Muscovite	2.4 (0.3)
Pyrite	0.4 (0.1)
Kaolinite	20.3 (0.4)
Hematite	2.0 (0.2)
Barite	0.4 (0.1)
Total	100.0

Although the X-ray powder diffraction pattern comprises thousands of overlapping peaks, refining the structures of the constituent minerals with the Rietveld method is relatively straightforward. A significant strength of the Rietveld method is that overlapping peaks are fitted and refined; this is not the case with traditional X-ray powder diffraction methods. Regardless of the presence of the other phases, the amounts of carbonate and pyrite can be measured, even at low abundance.

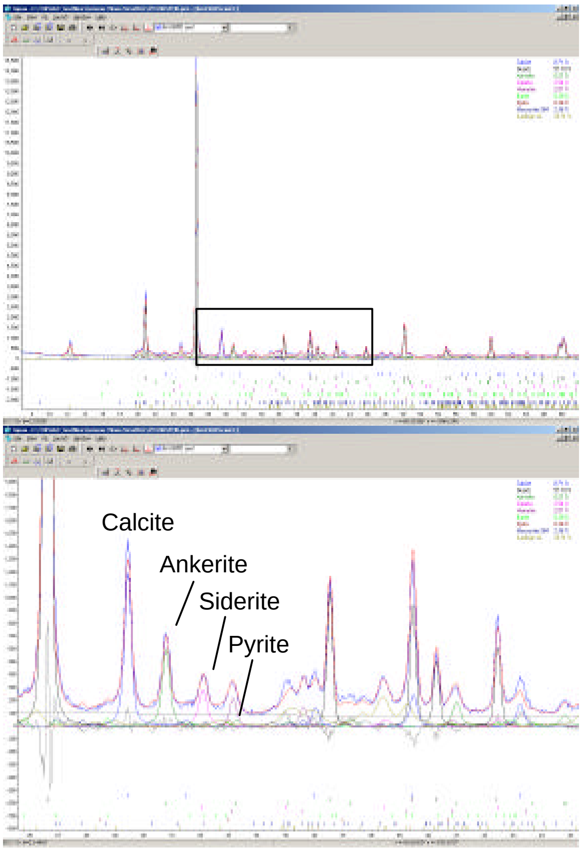

Figure 3. *A: Rietveld refinement plot, 2q (°) vs. Intensity (counts), from Topas 2.0 program for waste-rock sample (blue line - observed intensity at each step; red line - calculated pattern; solid grey line - background, solid grey line below - difference between observed and calculated intensities; vertical bars - positions of all Bragg reflections). Coloured lines are individual diffraction patterns of all phases. Box is area of Figure 3B. B: Enlarged area of box in A showing the main X-ray diffraction peaks of calcite, ankerite, siderite and pyrite.*

SUMMARY

X-ray powder diffraction studies are not restricted to simple "fingerprinting" of crystalline phases. The amounts of calcite-group (calcite, siderite) and dolomite-group minerals, (dolomite, ankerite), and sulfides may be measured quantitatively using the Rietveld method. The amounts of all other minerals may also be measured simultaneously.

Fe and Mn content in minerals cannot be directly distinguished using X-ray diffraction (similar X-ray scattering power) but in certain cases (ankerite) may be determined from the cell dimensions.

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Quantitative Mineral Analysis of Clay-bearing Mixtures: The "Reynolds Cup" Contest

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INTRODUCTION

Quantitative phase analysis (QPA) of sedimentary rocks is a significant challenge because of the presence of clay minerals. Even so-called "clean" sandstones can have significant clays of different types, whereas typical sandstones can have 15 to 25 % clay or more by weight. It is difficult to quantify the mineralogy of clay-bearing rocks because clay minerals have fine particle size, platy shape, and chemical and structural variability. Mixed-layer clays can be especially difficult to analyze quantitatively. Because the clay mineralogy of a basin results from the combined effects of source rock type and sedimentary processes, mineral quantification can yield information about these processes.

Many QPA techniques are used in both commercial and academic laboratories. The Reynolds Cup Contest was aimed at verifying these techniques by analysis of the same mineral mixtures. These mixtures are representative of those found in natural sedimentary rocks. The Reynolds Cup also provided the contestants a valuable opportunity to check and improve their analytical techniques.

Other "round robin" events either used simple mixtures of well ordered phases, such as corundum, zinc oxide and fluorite (e.g. Madsen et al., 2001), whereas others used splits from natural samples where the phase content was not known *a-priori* (e.g. Ottner et al., 2000). Srodon et al. (2001) prepared a small set of "artificial rock" mixtures from relatively pure laboratory mineral standards and sent splits to commercial laboratories for analysis. The results (Srodon et al., 2001) show large cumulative errors from actual values. The idea behind the Reynolds Cup was to make mixtures from pure standards that represent realistic sedimentary rock compositions, and open the contest to any commercial, industrial, and/or academic laboratory that could use any method or combination of methods to obtain the most accurate QPA. The contest was designed to test both preparation and analysis techniques. Based on studies of natural samples (Srodon et al, 2001) and our experience in analyzing core and cuttings samples from sedimentary basins at ChevronTexaco's Mineral Analysis Laboratory, three mixture compositions were chosen. The name Reynolds Cup was chosen in honour of Bob Reynolds for his inspiration and great contributions to clay science.

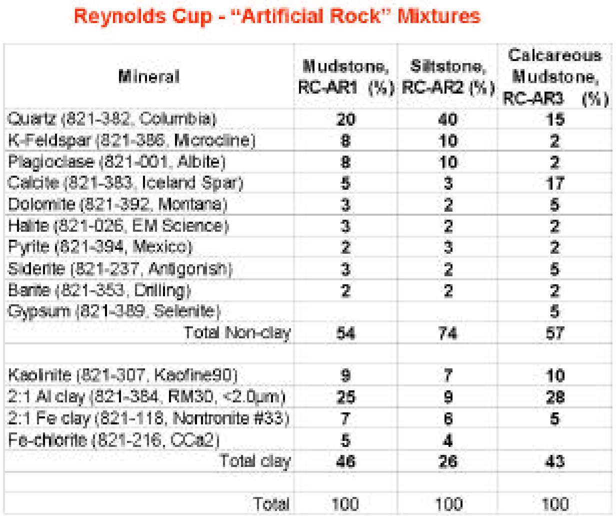
Figure 1. *The Prize: a photograph of the Reynolds Cup*

SAMPLE PREPARATION

Approximately 40 sets of the three artificial clay-bearing samples (~4 g each) were carefully prepared to represent a mudstone, a sand/siltstone, and a clay-bearing carbonate **(Table 1)**. Pure standards of minerals common in these rock types were obtained from commercial sources, including the CMS source clays, and private collections. Standards were screened by XRD and only those with no detectable contamination within reasonable limits were chosen. Pure clay standards were difficult to obtain in significant quantity, and required size fractionation after treatments to remove carbonate and iron oxide cement

The pure dry standards were passively hand ground to pass < 0.4 mm sieve. This chosen size was based on our mixing and splitting experience (Srodon, et al., 2001). We found that <0.4 mm material could be homogeneously mixed and efficiently split into essentially identical samples mineralogically, at least within the lowest experimental error. This size, however, is 20 times greater then the minimum size requirement of 20 micrometers for quantitative analysis by X-ray diffraction (Alexander and Klug, 1948). Therefore, the artificial rock mixtures would be the same for each contestant and test both preparation and analysis techniques and methods. followed by dialysis Jackson, 1985).

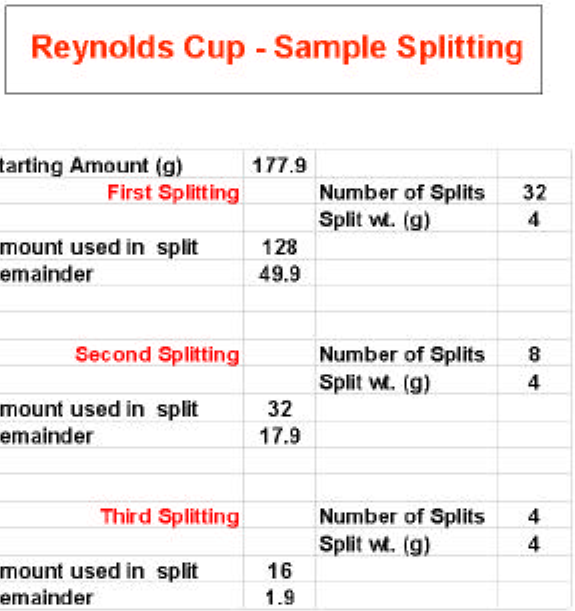
The desired mixtures were split and recombined 5 times. Then, each mixture was put in a 1 liter plastic bottle with three mixing balls and placed in a mechanical roller device for 24 h. A louvered splitter was used to separate the samples into aliquots.



Reynolds Cup - "Artificial Rock" Mixtures

Mineral	Mudstone, RC-AR1 (%)	Siltstone, RC-AR2 (%)	Calcareous Mudstone, RC-AR3 (%)
Quartz (821-382, Columbia)	20	40	15
K-Feldspar (821-386, Microcline)	8	10	2
Plagioclase (821-001, Albite)	8	10	2
Calcite (821-383, Iceland Spar)	5	3	17
Dolomite (821-392, Montana)	3	2	5
Halite (821-026, EM Science)	3	2	2
Pyrite (821-394, Mexico)	2	3	2
Siderite (821-237, Antigonish)	3	2	5
Barite (821-353, Drilling)	2	2	2
Gypsum (821-389, Selenite)			5
Total Non-clay	54	74	57
Kaolinite (821-307, Kaofine90)	9	7	10
2:1 Al clay (821-384, RM30, <2.0µm)	25	9	28
2:1 Fe clay (821-118, Nontronite #33)	7	6	5
Fe-chlorite (821-216, CCa2)	5	4	
Total clay	46	26	43
Total	100	100	100

Table 1: *Composition of the synthetic mixtures*



Reynolds Cup - Sample Splitting

Starting Amount (g)	177.9		
First Splitting		Number of Splits	32
		Split wt. (g)	4
Amount used in split	128		
Remainder	49.9		
Second Splitting		Number of Splits	8
		Split wt. (g)	4
Amount used in split	32		
Remainder	17.9		
Third Splitting		Number of Splits	4
		Split wt. (g)	4
Amount used in split	16		
Remainder	1.9		

Figure 2: *Information on sample splitting*

Due to size restraints on the splitter, it was decided to separate each sample into three portions, 128g, 32g, and 16g. Each of these portions was then split until 32, 8, and 4 four-gram aliquots were obtained respectively. Diffraction data of splits from the 128g and 16g portions along with bulk chemistry were obtained to judge the effectiveness of the mixing and splitting procedure. The splitting scheme is shown in **Figure 2**, and diffraction data from random splits taken from the first and second splitting, are shown in **Figures 3-5** for each artificial rock mixture. Comparison of the chemical analyses by XRF from these splits was performed. The chemical data show that even for trace elements present in low concentration, the percent difference is low, and it is especially low for the major elements. This chemical data, together with the diffraction data, is good evidence that mixing and splitting were effective, and that each contestant's sample set contained essentially the same mineralogy.

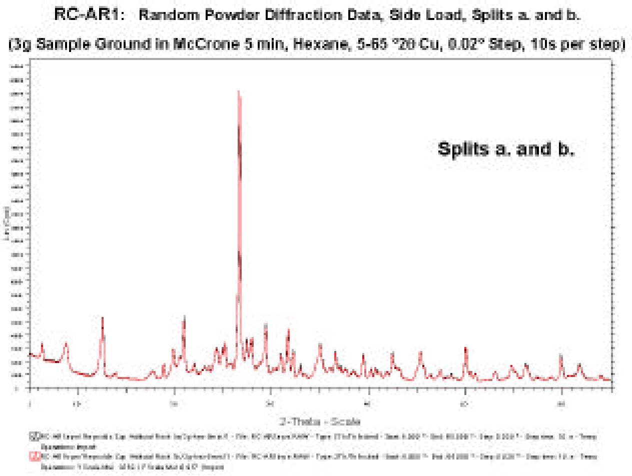


Figure 3: *Powder XRD scan of sample RC-AR1*

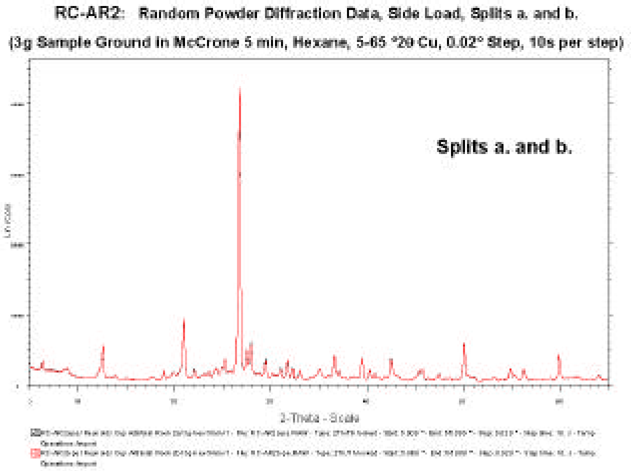


Figure 5: *Powder XRD scan of sample RC-AR3*

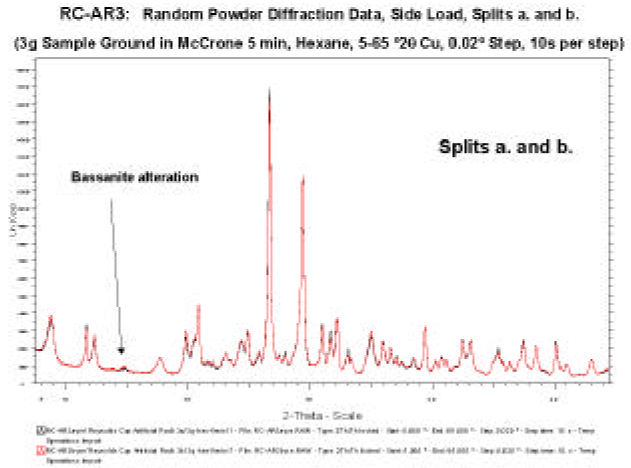


Figure 4: *Powder XRD scan of sample RC-AR2*

CONTEST JUDGING

There are a number of ways that a contest like this can be judged. Our goal was to simply evaluate the laboratory capable of attaining the highest total accuracy for the three-sample set. We decided to do this by cumulative difference from actual content (bias; Madsen et al., 2001). Some of the reported minerals could be compared directly with those used in the artificial mixtures, e.g. quartz, calcite, pyrite etc. Most contestants referred to feldspars by the group name K-feldspar and plagioclase, but if a specific name was given, it was put into appropriate group. Minerals identified that were not present were not counted as a bias. Some of the contestants said later that misidentified minerals should have been counted as a bias. We didn't count them because we assumed that any mineral percentages reported for something that was not present in the sample would, in fact, be unavailable to report for the phases that were present and were reported. Therefore this bias would be taken into account indirectly. Also, in this way the judging was more forgiving. In order to do accurate quantitative analysis one must do accurate qualitative analysis first.

We had to make a decision on how to handle the layer silicates, because a wide range of mineral names was reported. We decided that the fairest and most forgiving way was to group dioctahedral 2:1 layer silicates together. If the contestant did not specify, the terms smectite, illite-smectite, illite were considered to be in this group, so these percentages were added together and compared with the actual amount, which consisted of an illite and a nontronite standard. Trioctahedral 2:1 layer silicates were considered to be a separate group. Therefore, because trioctahedral phases were not present, trioctahedral phases such as biotite were not counted. The winner had the lowest bias for the three artificial mixtures, that is, the smallest difference between the real and the measured weight percentages.

RESULTS AND DISCUSSION

The contest was advertised on listservers from the Clay Minerals Society and the Mineralogical Society of America, as well as by word of mouth. The contest also was advertised on the website for the 2002 Clay Minerals Society Annual meeting. Forty samples were available for contestants and they were sent out on a first come first serve basis. A number of requests were made after all the available samples were sent. Of the forty sample sets that went out, only 15 sets of results were returned. The contestants had about four months to complete the analyses. The cumulative bias results for all three samples are shown in **Figure 6** and those for the three individual samples in **Figure 7**. **Figures 8 and 9** show the bias variation for the individual minerals used to construct the artificial mudstone mixture.

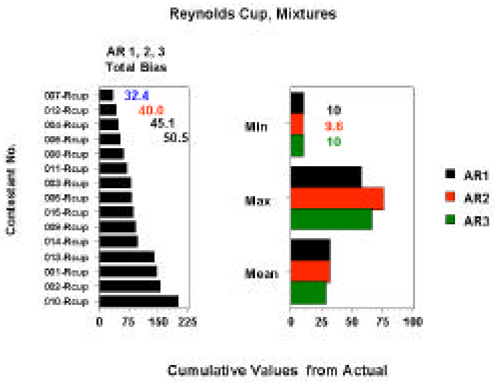


Figure 6: *cumulative bias results for all 3 samples*

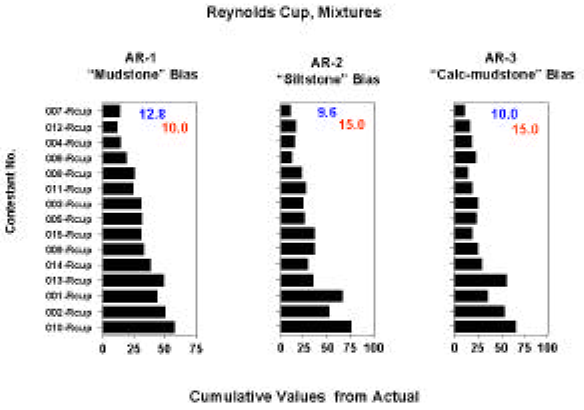


Figure 7: cumulative bias results for the individual samples

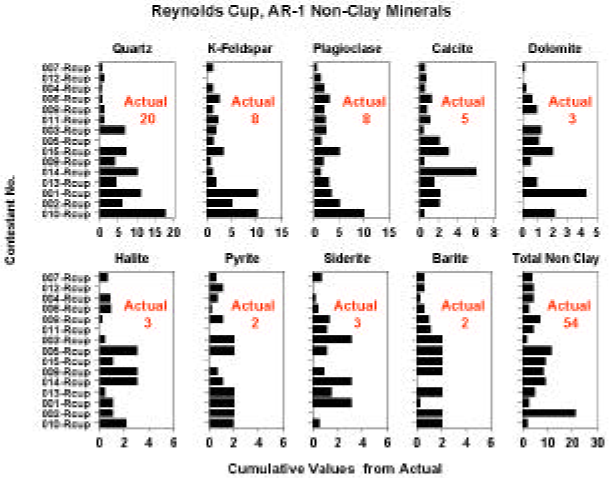


Figure 8: *Participant results on non-clay minerals*

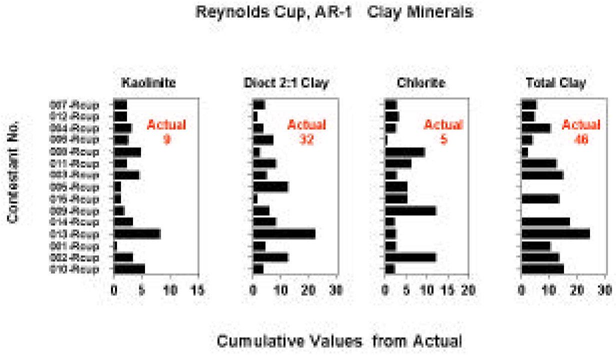
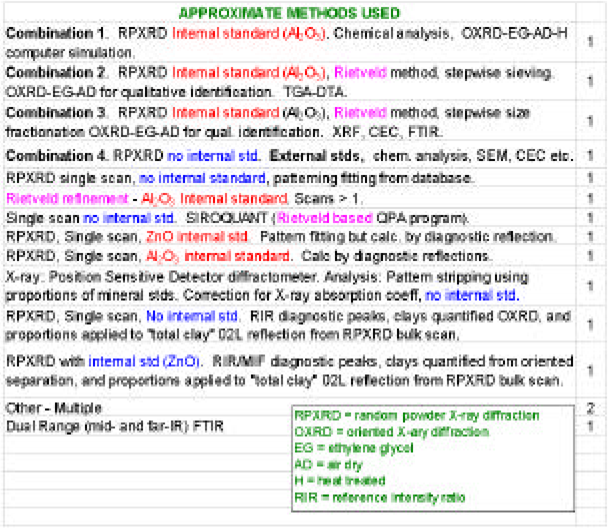


Figure 9: *Participant results on the clay minerals*

In general, the top five or six contestants did a fairly good job, and the top two contestants did a very good job. Each mixture contained 13 minerals, and the highest bias for any of the individual mixtures for the top six contestants was 26 for sample AR2, which is an average difference of 2 wt.% from actual value for each phase present. Many of the contestants in the lower half of the standings were assessed a bias of the actual amount of a particular phase because they failed to report the presence of that phase, because the phase was not identified **(Figure 8)**. This result emphasizes the importance accurate qualitative analysis in evaluating complex mixtures. Aside from the failure to identify phases, quantification of clay minerals seems to be the greatest source of error in a qualitative sense **(Figure 9)**.

A variety of methods were used and a number of contestants used multiple techniques including chemical analysis, oriented clay aggregates, random powder X-ray diffraction, infrared spectroscopy and others. **Figure 10** shows a rough sketch of the methods used not in any arrangement of place. No two methods were exactly the same. The winner, Reinhard Kleeburg **(Figure 11)**, University of Mining and Technology, Mineralogical Institute, Freiberg, Germany, used an internal standard and a Rietveld based method with the program BGMN/AutoQuan for the primary phase quantification, along with a variety of supplemental techniques. The second place contestant, Reiner Dohrmann, Federal Institute for Geosciences and Natural Resources, Hannover, Germany also used the AutoQuan program without an internal standard, along with a variety of supplemental techniques. The organizers congratulate these top place contestants who did a fine job. However, the Reynolds Cup contest also shows that accurate QPA for mixtures such as these is not easy. It is telling that only 15 of 40 contestants returned results.



APPROXIMATE METHODS USED	
Combination 1. RPXRD Internal standard (Al_2O_3). Chemical analysis. OXRD-EG-AD-H computer simulation.	1
Combination 2. RPXRD Internal standard (Al_2O_3), Rietveld method, stepwise sieving. OXRD-EG-AD for qualitative identification. TGA-DTA.	1
Combination 3. RPXRD Internal standard (Al_2O_3), Rietveld method, stepwise size fractionation OXRD-EG-AD for qual. identification. XRF, CEC, FTIR.	1
Combination 4. RPXRD no internal std. **External stds,** chem. analysis, SEM, CEC etc.	1
RPXRD single scan, no internal standard, patterning fitting from database.	1
Rietveld refinement - Al_2O_3 Internal standard. Scans > 1.	1
Single scan no internal std. SIROQUANT (Rietveld based QPA program).	1
RPXRD, Single scan, ZnO internal std. Pattern fitting but calc. by diagnostic reflection.	1
RPXRD, Single scan, Al_2O_3 internal standard. Calc by diagnostic reflections.	1
X-ray: Position Sensitive Detector diffractometer. Analysis: Pattern stripping using proportions of mineral stds. Correction for X-ray absorption coeff, no internal std.	1
RPXRD, Single scan, No internal std. RIR diagnostic peaks, clays quantified OXRD, and proportions applied to "total clay" 02L reflection from RPXRD bulk scan.	1
RPXRD with internal std (ZnO). RIR/MIF diagnostic peaks, clays quantified from oriented separation, and proportions applied to "total clay" 02L reflection from RPXRD bulk scan.	1
Other - Multiple	2
Dual Range (mid- and far-IR) FTIR	1

RPXRD = random powder X-ray diffraction
OXRD = oriented X-ary diffraction
EG = ethylene glycol
AD = air dry
H = heat treated
RIR = reference intensity ratio

Figure 10: *Methods used for quantitative analysis*

Figure 11: *The winner of the Reynolds Cup - Reinhard Kleeberg, University of Mining and Technology, Mineralogical Institute, Freiberg: using the BGMN/AutoQuan for the primary phase quantification*

Figure 12: *Top finishers: left to right: Hillier, Kleeberg, Dohrman, Eberl; with Victor Drits on the far right to present the awards on behalf of Bob Reynolds.*

Quantitative analysis of sedimentary rocks is very important in the oil industry, for example, for both geological and petrophysical applications. The clay content in sedimentary rocks is a primary variable that is used to calculate fluid saturation and determine hydrocarbon reserves. Large errors would occur if the Reynolds Cup samples had been real samples evaluated for this purpose by most of the contestants. The Reynolds Cup competition also demonstrates that accurate QPA is probably unlikely from most commercial sources. However, on the positive side, the competition demonstrates that accurate QPA is possible if the laboratory and analyst take the time and have the experience to do it right. The organizers plan to have a second Reynolds Cup in two years and expect that there will be a higher proportion of accurate results. This contest provides a way to help raise the standard of QPA for natural clay-bearing samples.

ACKNOWLDEGEMENTS

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XRPD in the mining environment - a simple approach to mineral phase quantification

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Background

X-ray powder diffraction (XRPD) analysis has become a widely recognised tool in research (sdpd, modelling of (semi-) amorphous content, crystallite size, stress/strain, quantification of components) and production (quality assurance/control) – mainly due to advances in X-ray optics and detectors (Goebel mirrors, parallel beam optics, Li-PSi and RTMS detectors) and the algorithms used to extract information from the data (Rietveld method, Fundamental Parameters (FP), etc.). The flipside of this is, that we now have two fundamentally different drivers. Research is driven by information maximisation from XRPD data, requiring always better quality data with less or no importance given to the time and cost per sample, while industry is driven solely by their need for results, sample throughput and cost per sample. XRPD is only used in the industry if it is either the only technique capable of providing the desired information or the cheapest technique for providing information fulfilling the requirements (speed, overall information content, accuracy, precision, reproducibility).

Introduction

Based on the requirements above, there are two prerequisites:

1) The XRD machine employed needs to be able to produce good quality data quickly and for large batches: the XRD machine used has a Kevex II PSi detector and 42-sample magazine.

2) The XRD interpretation needs to be done by a highly skilled individual to minimise the time needed per pattern and to provide the highest recognition rate possible.

The XRPD laboratory of a major mining company developed a technique for fast semi-quantitative XRPD analysis, which utilises the maximum peak intensity data (2^{nd} derivative) from only one peak per mineral and an adjusting constant for each mineral based on the FWHM values for that peak as well as a constant based on either Reference Intensity Ratios (RIR), or I/I_{cor} values from the PDF-cards, or experimental constants from synthetic and natural mixtures.

Technique

When the technique was devised it was recognised, that there would be major problems with a one-peak-per-mineral quantification method - mainly arising from peak overlaps, preferred orientation, changes in the overall mass absorption coefficient, changes in grain size and variations in the minerals themselves. To counter these problems, or at least minimise the impact, a couple of strategies were followed:

1) The number of minerals was restricted to the ones commonly found by exploration geologists and at mine sites. This produced a subset of ~600 minerals. Other

minerals are entered as "unknowns", and only if they occur more frequently a constant is set up.

2) Common mixtures were evaluated for peak overlaps and peak ratios and a set of rules established, determining which peak to use, what minerals to look for and how to correct for one in the presence of another.

3) Also, mineral groupings were established to account for ambiguities in the case of small peaks and/or positional variations, eg "Alkali Feldspar".

4) Multiple sets of quantification constants were created and are used to account for drastic changes in the overall mass absorption coefficient between different sample origins, eg metallurgical and exploration samples.

5) A maximum grain size was specified (< 75μm)

The technique itself is based on the acquisition of a full XRPD pattern (5-65 deg 2 Theta, 0.05 deg/step, 1s/step) and a complete interpretation (phase identification) of the collected pattern. The maximum counts (based on the second derivative) for the selected peak of each mineral (and FWHM values for minerals with broad peaks) are then entered into a calculation module which uses these, together with the constant from the selected set to produce a normalised table (to 100% w/w) for all identified minerals following the simple formulas:

$$[C_i] \times [ValFWHM_i] \times [QuantSet_i] = [AC_i] \quad (1)$$

$$[WF_i] = [AC_i] / \sum_{i=1}^{n} AC(i) \quad (2)$$

C_i = Counts for mineral 'i'

$ValFWHM_i$ = Calculated multiplier for FWHM value of mineral 'i'

$QuantSet_i$ = Quantification constant for mineral 'i' in chosen set

AC_i = Adjusted counts for mineral 'i'

WF_i = Weight fraction of mineral 'i' in mixture

n = number of minerals in mixture

Note: If no value is entered for FWHM, the multiplier is = 1

The technique has since been adapted to provide highly reproducible mineral quantification of a single mineral (talc) in a subset of a maximum of ~ 25 known minerals, running a quicker scan over a reduced range (8.5-33.5 deg 2 Theta in 5 minutes) and only focussing on the main mineralogy.

Using the combination of highly skilled people, dedicated machine and simple technique, the laboratory was able to analyse more than 35,000 samples in 2001.

Conclusion

While excellent results in the area of quantification have been achieved using XRPD in connection with the Rietveld method, even in the industry where a small, common set of phases needs to be quantified, it is still too cumbersome and time consuming in most mining environments, due to the diversity and sheer number of samples and cost constraints. While the approach detailed here is surely not the only or the best, it still satisfies all the demands and, what is more important, it follows the guiding principle of providing what is needed, answering the question that should be asked before any experiment: ***"What do I want the data for?".***

Multi-Line Methods for Phase Composition Analysis Using Bragg Intensities: MNI and RIR Strategies

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The authors are responsible for some 500 phase composition analyses per annum on a service basis, as well as overseeing the use of phase composition and related characterisation analyses (strain, crystallite size, texture, etc) for research purposes within the Materials Research Group. While much of the phase analysis work is now performed by Rietveld pattern-fitting, there remain analyses for which traditional methods based on Bragg peak integrated intensities are preferred. These line intensity procedures involve measuring the integrated intensities of a set of Bragg peaks for each phase, by taking advantage of the power of modern peak profile software which largely eliminates the peak overlap problem. The set of peaks for each phase leads to the use of either (i) our preferred multi-line MNI method, or (ii) a multi-line RIR approach. The two strategies reduce the risk of serious bias which can be expected for traditional single-line methods, and may also provide plausible estimates of composition uncertainty from population statistics.

BACKGROUND

Prior to the advent of Rietveld analysis as a powerful general-purpose phase composition analysis (PCA) method, the traditional RIR method and related line ratio procedures were mainly used. Users of the RIR-type methods typically selected the strongest line of each phase to provide line ratio values. The method had a generally poor reputation, and was often described as 'semi-quantitative', due to the strong likelihood of systematic intensities in one or both of the selected lines suffering from systematic errors such as extinction or preferred orientation. The problems introduced by such bias effects were exacerbated by the method providing error estimates which reflect only counting statistics. Anecdotally, some industrial laboratories abandoned PCA methods due to their poor reproducibility.

MNI Method

Principles (Refs 1 and 2)

The integrated Bragg peak intensity for each line in a diffraction pattern may be converted to a *normalised intensity*. The *normalising factor* for each peak of a phase is the integrated peak intensity from the simulated/calculated pattern, derived from the crystal structure of the phase. Ideally all lines for a phase have the same normalised intensity. The normalised intensity for each phase in a mixture is proportional to the volume fraction of the phase.

The integrated intensity for line *j* of phase *i* in a mixture is given by

$$I_{ij} = K\,(m\cdot Lp\cdot F^2)_{ij}\,(v_i\,/\,m\,Vi^2)$$

for constant *K*, phase volume fraction v_i and phase cell volume V_i. Symbols *m*, *Lp* and F^2 have their usual meaning.

The *normalised intensity* for any line is

$$I_{ij}^N = I_{ij}\,/\,R_{ij}$$

where the *normalising factor* is

$$R_{ij} = (m\cdot Lp\cdot F^2)_{ij}\,/\,Vi^2$$

The *phase volume concentration* is proportional to the normalised intensity according to

$$v_i\ \mu\ I_{ij}^N$$

The reliability of the volume concentration result is enhanced by averaging over the set of single-line values to give the phase *mean normalised intensity* (MNI) for the set of nominated lines,

$$v_i\ \mu\ <I_{ij}^N>$$

where the summation is taken over all phases. The volume concentrations may be converted to weight concentrations using the phase densities.

The uncertainty in the phase concentration is readily computed from the variance in the MNI,

$$s^2\,[<I_{ij}^N>\,]\ ®\ s^2\,[v_i]$$

The MNI variance is calculated from the population statistics for the intensities of the nominated lines for the phase – see references 1 and 2.

Practical Points

Example

Figure 1 illustrates the MNI analysis for a two-phase example. The MNI values for the phases SiO_2 and Al_2O_3 are 33.0 and 23.5, respectively. These values translate to volumetric phase concentrations of 58.4 % and 41.6 %, respectively.

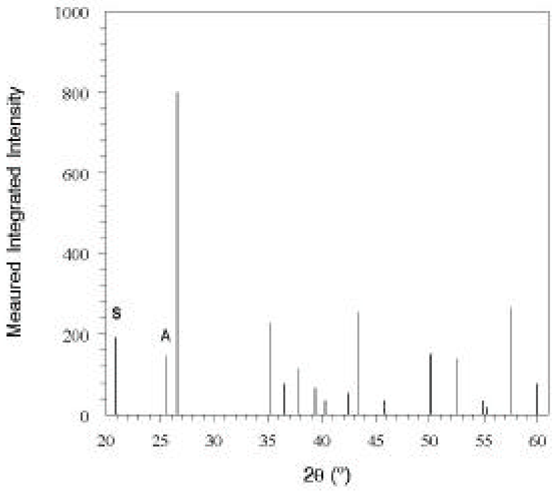

Figure 1. *Measured data (CuKa) for mixture of SiO_2 (a-quartz) and a-Al_2O_3 (corundum): symbols S and A, respectively. (a) – top: measured data; (b) – centre: data after normalisation; (c) – bottom: normalised intensities after elimination of the intense SiO_2 line biased by extinction.*

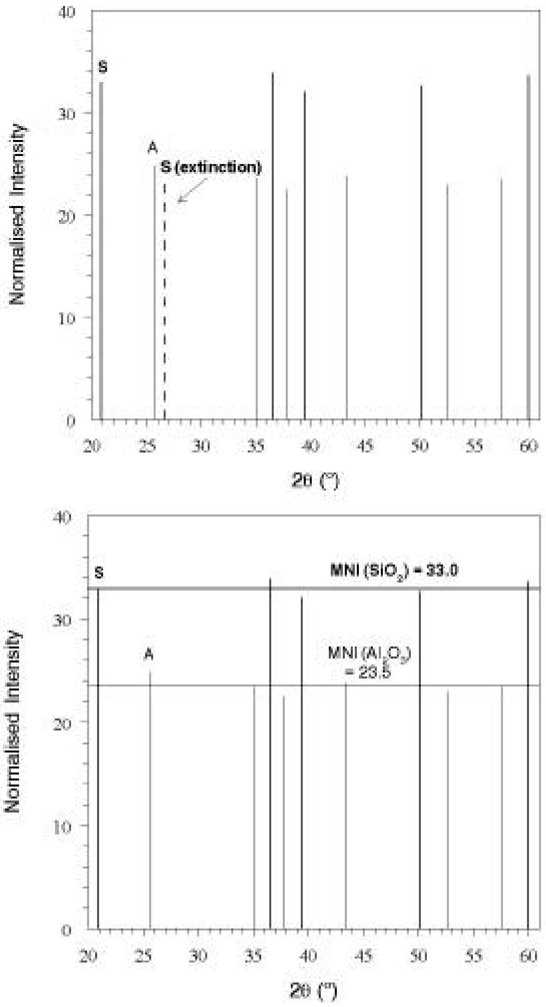

Figure 1. (*continued*).

The example shows the elimination of the intense SiO_2 line at 2θ = 26.6° which suffers from extinction. A powerful feature of the MNI method is the ease by which examination of the variations in the normalised intensities readily reveals the presence of serious systematic errors, or bias, in a line intensity. This test may be used with caution to reject a line suffering from pronounced bias.

Further examples are given in references 1 and 2.

Multi-Line RIR Method

References 3 and 4 give a comprehensive overview of the RIR method, and there are many other references in the literature**.**

Extension of the method to a multi-line procedure considerably extends the power of the single-line approach. It is similar in concept to the MNI approach, but differs by employing intensity line ratios rather than normalised intensities.

The key points in relation to strategy are –

(i) A set of line-pairs is selected for each phase in the mixture, in order to provide a set of line-pair intensity ratios for each phase pair. As for the MNI method, overlapping lines may be employed.

(ii) Each single line-pair ratio is used to compute the relative concentration ratio for the pair of phases.

(iii) The *mean relative concentration ratio* for each pair of phases gives a result which should be superior in quality to the estimate from a single line-pair.

(iv) The method requires determination of a reliable value for the RIR of each line pair. This may be done using (i) software which provides a simulated diffraction pattern for each phase, according to the crystal structure; or (ii) using single-phase standards. Also, the Powder Diffraction File may be used to assemble the set of multi-line RIRs.

(v) The variance in the mean relative concentration ratio is determined from the population statistics of the individual concentration ratios.

DISCUSSION

The authors have a clear preference for the MNI procedure over the multi-line RIR approach mainly due to (i) the value of being able to scrutinise the quality of the measured data using the normalised intensities; and (ii) the use of intensity ratioing in the RIR method degrades the quality of the information**.**

The MNI method is not championed by the authors as a superior alternative to the Rietveld method, but it can compete with the Rietveld method. A strong feature of MNI strategies is way in which these may work well with a selection of lines, whereas Rietveld methodology requires measurement of data to high 2θ angles for PCA work of reasonable quality (ref. 5). Accordingly, MNI is very useful for situations where the full angular range of data cannot be measured or where it is inconvenient to do so, *e.g.* for *in-situ* dynamic studies and for process control in general. The MNI method has particular appeal where minimising the total time for an analysis is important.

In comparing the MNI and Rietveld approaches, the similarity of the methods should be appreciated. This is readily appreciated by noting that the MNI for each phase is the equivalent of the phase scale factor in Rietveld PCA. There is an equivalent MNI expression for each Rietveld PCA expression cited in the literature. It follows that strategies for obtaining absolute phase concentration ratios with PCA standard materials, using either internal or external standards, apply also to the MNI procedure. Another point of appeal for the MNI method is that Rietveld PCA problems, which may be encountered due to parameter correlations, may be avoided (ref. 6).

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Accurate quantification of the modal mineralogy of highly deformed rocks

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An accurate knowledge of the volume proportions of the mineral phases in geological materials is essential in a wide range of applications, and particularly in experimental studies investigating reaction kinetics or the mechanical properties of polymineralic materials. Although phase quantification by powder diffraction is a well established procedure it remains a non-trivial process, and consequently, the most widely used method for determining these proportions is by the analysis of images obtained from two dimensional sections cut through the material. Sample preparation methods including sieving and water column settling, the application of suitable standards for peak intensity measurements, instrumental, sample and individual user-related effects such as constancy of machine alignment, micro-absorption, preferred orientation and sample preparation, and large data collection periods, all combine to make the experimental procedure extremely laborious, and often results in inaccurate assessments of the phase proportions. Furthermore, the data processing generally requires considerable experience of the processing method adopted, a prior knowledge of the crystal chemistry and structures of the phases involved, and specialist crystallographic expertise. The presence of poorly crystalline, poorly characterized compounds, or amorphous materials further complicate the process and reduce precision severely. Consequently, there is a strong need for an alternative method of phase quantification that is both quick and easy to apply, but also provides accurate quantitative phase proportions.

One such method has been made possible with the advent of curved, position-sensitive, X-ray detectors. These permit high-precision/high-resolution X-ray diffraction patterns to be acquired rapidly over large angular ranges of 2θ. To take advantage of this capability, Cressey and Schofield (1996) [1] developed a whole pattern, profile stripping method for the analysis of such data, and this method now presents a much easier and faster route to phase quantification by X-ray powder diffraction than the techniques previously available. By collecting diffraction patterns for a multiphase mixture and for standards that represent each phase within this mixture, all under identical, unchanging experimental conditions, the proportions of the component phases may be measured by proportioning and stripping the diffraction patterns of the standard phases from that of the multiphase mixture. The accuracy of the basic method was demonstrated [1] using a number of multiphase powders mixed in known volume proportions from the end member phases, and its efficacy has also been proved for a series of mechanical mixtures distributed in the IUCr sponsored quantitative phase analysis round robin [2,3]. Subsequently the technique has been developed to account for the effect of micro-absorption [4], and has been successfully applied to clay-bearing samples [5], microcrystalline silica polymorphs [6], and to soils/sediments [7]. Furthermore, its utility for phase quantification in materials containing significant residual strains, such as may be produced by deformation and/or by mineral reactions involving large volume changes, has recently been demonstrated [8], and some of the data from this work is presented here.

The rock analysed here is a mantle-derived harzburgite that has been strongly deformed at high temperatures so that microstructurally they are now porphyroclastic mylonites.

The rock was prepared as a powder comprising predominantly of grains between 5 and 15 µm, which was a sufficiently small grain size to avoid problems associated with micro-absorption [3]. As it was not possible to separate out phase-pure material from the bulk rock, mineral standards with closely matching structures and chemistries to those in the rock were chosen from the collections at the Natural History Museum, London UK.

X-ray powder diffraction data were collected using an Inel curved, position sensitive detector (PSD) within a static beam-sample-detector geometry and copper Kα_1 radiation. Powdered samples of the rocks and mineral standards were top loaded, in turn, into a circular well mount, packed, smoothed and spun continuously in the plane of the sample surface. Data collection of 10 minutes only were required for each standard and the rock to be quantified, which means that the four-phase rock of this study was quantified in less than 1 hour from start to finish. Indeed, the full quantification process, including data collection and analysis, for a suite of 12 such rocks could be fully completed in less than 3 hours. Quantification of the Oman harzburgite was performed using a linear least-squares routine, fitting the standard patterns to that of the bulk rock, and is demonstrated in Figure 1. Data from the XRD-PSD method are compared in Table 1 to data from a four-phase Rietveld analysis of time-of-flight neutron powder diffraction data (Figure 2) collected on the POLARIS diffractometer [9] at the ISIS neutron spallation source.

Oman Rock	PSD-XRD method		Rietveld Analysis of Neutron Data	
	weight %	volume %	weight %	volume %
olivine	71.7(4)	71.4(4)	70.5(7)	70.5(7)
orthopyroxene	25.1(3)	25.5(3)	25.3(7)	25.8(7)
clinopyroxene	2.7(1)	2.7(1)	1.8(8)	1.8(8)
spinel	0.5(3)	0.4(3)	2.4(5)	1.9(5)

Table 1: *Phase quantification of the Oman harzburgite from profile stripping of PSD X-ray data and Rietveld analysis of the neutron powder diffraction data.*

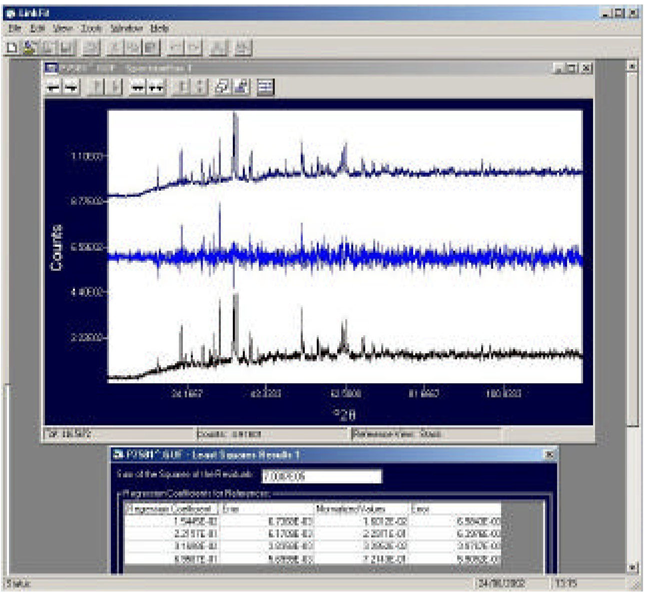

Figure 1. *Whole pattern, linear least-squares fitting of the PSD-XRD data for the Oman rock. The calculated pattern (top), experimental pattern (bottom) and the residual (middle) are shown in the top window, and the numerical result is shown in the lower window.*

The larger residuals from the PSD-XRD analyses, compared with those of the Rietveld fit to the neutron diffraction data, are the result of using standard patterns that are not exact matches to the phases in the mixture. The standard data generated were experimental patterns recorded from pure phase materials selected from the Museum collection as materials with diffraction patterns that are a close match to the phases identified in the mixtures. Slight differences in chemistry, cell parameters, site occupancies, defects and strains between the standards and the phases in the mixtures are minor incompatibilities compared with those arising from preferred orientations or an occasional larger crystallite that can affect the intensities of certain peaks in either the standard or the mixture powder pattern or both. These incompatibilities in intensity are most noticeable at low angles in the PSD-XRD residuals. However, because the whole-pattern profile is used in the fitting procedure, rather than just specific peaks, small poorly fitted regions of the diffraction patterns can be ignored without there being a significant effect on the final best-fit proportions returned by the least squares fitting.

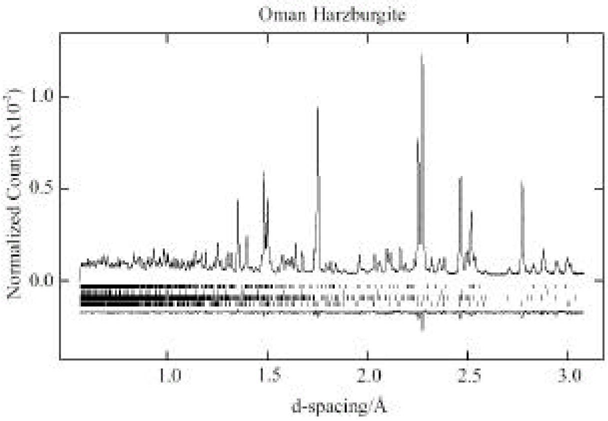

Figure 2. *Time-of-flight, neutron powder diffraction profile of the Oman rock. The dots represent the observed data and the solid lines represent the calculated profile from multiphase Rietveld refinement. The residual reflects ± 3s. The tick marks indicate the expected positions of diffraction peaks for the four phases clinopyroxene, spinel, orthopyroxene and olivine from top to bottom.*

The most important aspect in the X-ray diffraction pattern matching procedure is to ensure that the final residual background level after subtracting the patterns of all the phases present is close to zero, particularly at moderate to high angles of 2θ. This is a sensitive measure of the success of the procedure, especially when Fe, Mn, and/or Cr bearing phases produce a high fluorescent background through interacting with Cu Kα_1 radiation. This is important in the quantification process used here because the fluorescence signal together with the Bragg peaks are used as an effective measure of the high-absorber phase proportions. The largest uncertainty is associated with the chrome-spinel where an exact match between sample and standard proved difficult to find. Furthermore, the Bragg signature peaks for the chrome-spinel are sparse and low in intensity, unlike those of the other fluorescing Fe-containing phases (predominantly olivine and enstatite). Nevertheless, despite being present at the one volume percent level, the intense fluorescent background produced by the chrome-spinel is an additional aid in determining accurate phase proportions.

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The RTMS technology: dream or reality?

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INTRODUCTION

An exciting new era in powder diffraction has started with the introduction of a new kind of detector technology: Real Time Multiple Strip (RTMS). The X'Celerator is based on this new technology. The RTMS technology offers direct detection of the diffracted X-rays, unlike other technologies that rely on the delayed response of, for example: gas ionization. The detector works as if you have over 100 detectors all working at the same time together with the ability to process high count rates, see Figure 1.

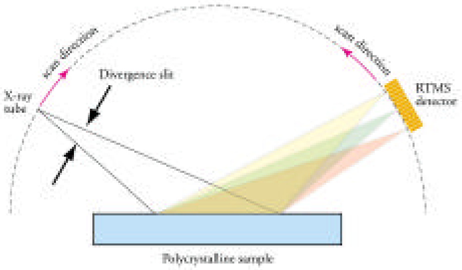

Fig 1: *Schematic drawing of data collection with the X'Celerator.*

Armel Le Bail stated on his web-site [1]: 'The main advantage of the X'Celerator is the gain in time with no loss of resolution.' This opens a world of application opportunities, for example in-situ observations of rapid phase transformations or routine process control of large amounts of samples. For crystal structure solution and refinements very good laboratory data can now be collected with a focussing incident beam (Johansson) monochromator in a reasonable time [2].

COMPARISON: X'CELERATOR VERSUS POINT DETECTOR

In order to compare the performance of the X'Celerator with a conventional point detector, two sets of data were collected on the same parafocusing diffractometer (Philips X'Pert PRO MPD). The incident beam configuration was identical; Cu-LFF tube, 45 kV, 40 mA, fixed divergence slit (1/4º), Soller slit (0.02 rad) and a Ni-filter. The diffracted beam configuration with the point detector was equipped with an anti-scatter slit (1/4º), receiving slit (0.1 mm), Soller slit (0.04 rad) and a proportional detector. The X'Celerator configuration had an anti-scatter shield and a Soller slit (0.04 rad). The measurements were performed on SRM 2910 (Calcium Hydroxy Apatite); a NIST standard reference material. To avoid texture effects, backloading was used in sample preparation. The scan times were 00:08:16 (hh:mm:ss) for the measurement with the X'Celerator and 18:30:40 (hh:mm:ss) with the proportional detector. The step sizes were 0.01673º 2θ and 0.017º 2θ respectively. The two scans are very similar, except for a slight increase in the background at low angles in the case of the X'Celerator. The main difference however, is the data collection time: about 100 times longer for the scan with the proportional detector. In figure 2 a zoomed part of the two scans plotted together in the same graph without scaling shows that the peak shapes and intensities are nearly identical, the main difference is due to counting statistics.

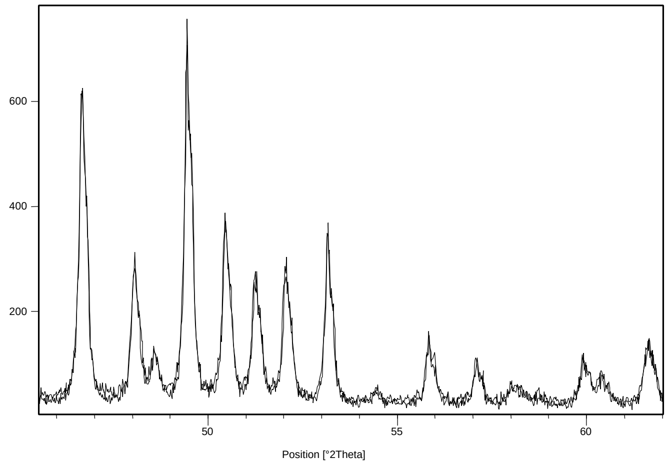

Fig 2: *The two scans in the same plot: peak shapes and intensities are very similar.*

RIETVELD REFINEMENTS

To compare the quality of the two scans with each other and with the NIST standard, Rietveld refinements were performed [3]. Figures 3 and 4 show the Rietveld refinement from respectively the X'Celerator scan and the proportional detector scan. In table 1 the refined lattice parameters are compared with the NIST reference values [4]. Although the procedure followed in this study was less rigorous than described in the NIST certificate, for example no internal standard was added to the sample, the lattice parameters of both refinements are very close to the ones reported by NIST.

	a-axis Å	**c-axis Å**
NIST SRM 2910	9.42253(13)	6.88501(9)
X'Celerator	9.4230(2)	6.8850(2)
Proportional counter	9.4225(2)	6.8842(2)

Table 1: *Comparison between the lattice parameters values for the NIST SRM 2910 and the ones obtained by Rietveld refinement from the scans made with the X'Celerator and proportional detector.*

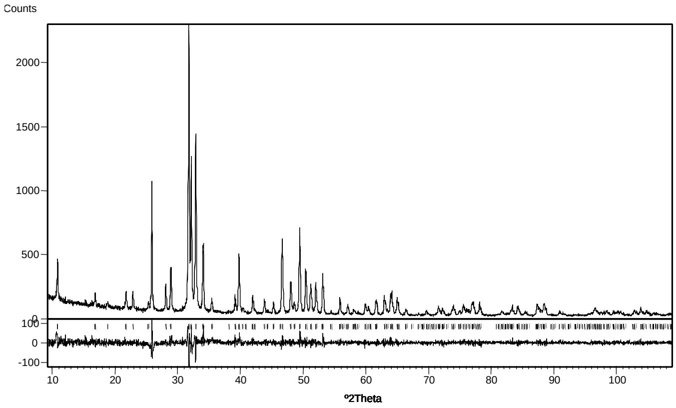

Fig 3: *Rietveld refinement of the X'Celerator measurement of SRM 2910*

INDUSTRIAL APPLICATION

The above results indicate that the X'Celerator can be used for Rietveld refinements in industrial environments where high throughput of samples greatly restricts the measuring time. To test this, an X'Celerator scan of 1 minute was made on the NIST clinker standard SRM 8488, see figure 5 [5]. The quantitative results obtained with a Rietveld refinement were comparable with the ones listed by NIST, see table 2.

Phase	**NIST SRM 8488**	**X'Celerator**
Alite (C3S)	64.97 (0.56) %	65.2 (0.5) %
Belite (C2S)	18.51 (0.58) %	18.2 (0.8) %
Aluminate (C3A)	4.34 (1.35) %	4.7 (0.2) %
Ferrite (C4AF)	12.12 (1.50) %	11.9 (0.7) %

Table 2: *Quantitative results obtained with a Rietveld refinement from a 1 minute scan with the X'Celerator on SRM 8488.*

As can be seen above, with the X'Celerator the measuring time is no longer the limiting factor in industrial applications. The remaining problem in process control applications with Rietveld is good crystal structure knowledge for every phase. Many of the needed phases differ from one case to another and are not known, therefore the individual crystal structures have to be determined first. After all the relevant information is gathered application scientists can set-up push button applications.

CONCLUSIONS

The RTMS technology has made it possible to create a new kind of detector: the X'Celerator. The main advantage of the X'Celerator is the gain in time, up to one hundred times,

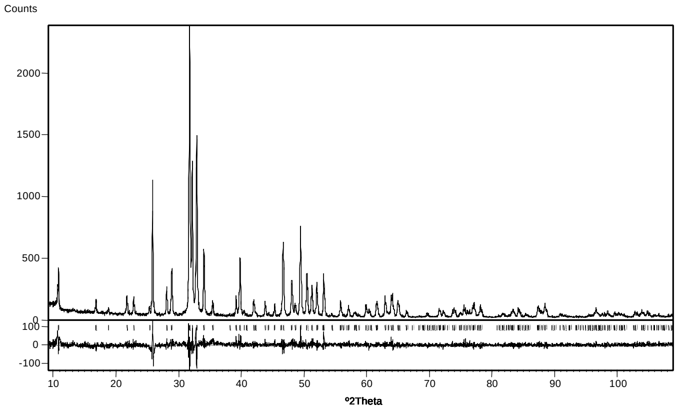

Fig 4: *Rietveld refinement of the proportional counter measurement of SRM 2910*

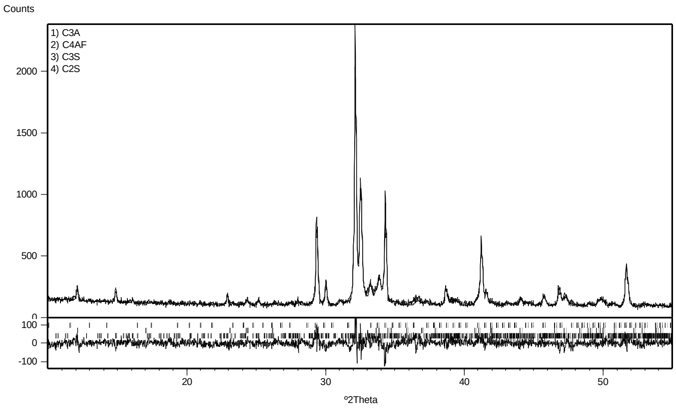

Fig 5: *Rietveld refinement of the X'Celerator measurement of SRM 8488*

without any compromise on data quality or ease of use. The X'Celerator makes it possible to perform experiments which a year ago could only be dreamed of.

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Variable Count Time data collection in Powder X-ray Diffraction

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Historically, powder diffraction data was first collected on film using Debye-Scherrer cameras, with all parts of the film being exposed for equal time. Little changed with the development of digital diffractometers except that the data were now collected on a point-by-point basis for a fixed time with the output originally being sent to a paper chart recorder that moved at constant speed. Most modern commercial diffractometers still seem to collect data based on a strategy that was forced on them through the use of film, and subsequently chart recorders, in that the data is still collected at a constant step rate in time, i.e. x degrees 2 theta at n seconds per point. This is despite modern developments in structure solution by powder diffraction, for which this strategy for data acquisition is far from optimal. With regard to data acquisition, several questions need to be asked: Firstly, what is the strategy that provides the best chance of success, and, secondly, how can that strategy be implemented if the acquisition software is limited in its capabilities by the commercial supplier of the X-ray diffractometer?

The choice of strategy depends on the object of the experiment. To illustrate one method for variable count times in powder X-ray diffraction, we will consider the case where the object of the method is structure solution. The simplest strategy in this instance would be to count all peaks with similar precision, a strategy that is not achieved by the constant time per point step scan, which is represented by the horizontal grey line shown in Figure 1. Assuming that the position and intensity of the peaks is not known a-priori, factors that one must take into account in order to satisfy our strategy include the following: geometric factors (Lorentz and polarisation), reflection density, weighted-average X-ray scattering factor, and a typical overall thermal displacement factor. The peak density function varies slightly according to crystal system, but in all cases it has a minimum at 0° and 180° and a maximum in the range 90° to approximately 110° (for cubic down to triclinic symmetry, respectively). Average X-ray scattering factor and overall thermal displacement factor will depend on the nature of the material: most organic molecules containing only C, H, O, and N will scatter X-rays strongly at low angle and only weakly at higher scattering angles, in contrast to, say, ceramics. Taking the reciprocal of all these factors multiplied together gives the typical curve shown in dark grey in Figure 1, which represents our "ideal" data collection strategy in terms of time per point. If we assume that our software package is only capable of measuring scans in terms of a constant time per point, is it still possible to measure the diffraction pattern so that we approximately follow the curve as shown?

The solution is to collect several constant time per point scans, but not all with the same 2? range as shown in the Figure. By making the first scan at 10 s/point cover the range 0° to 130°, the second and third scans 50° to 130°, fourth and fifth scans 65° to 130°, … , up to the eleventh and last scans with the 2? range 90° to 110°, we can achieve

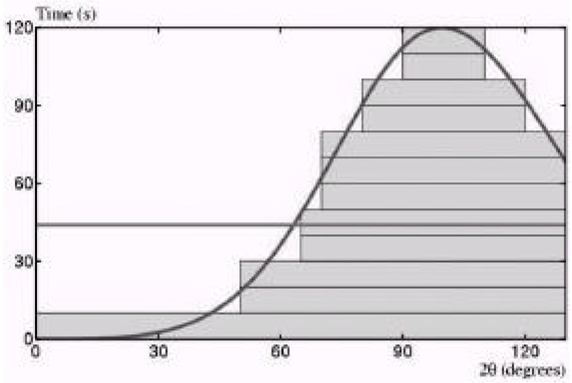

Fig 1: *Schematic diagram of a variable count time strategy.*

a total count time that roughly follows the smooth curve shown. You should note that even this strategy still overcounts the low-angle data relative to the higher-angle data, especially if the complete 2? range is collected at the end of the experiment as a check against sample and instrument stability during the period of the experiment.

The practical question that usually arises is: “how do I merge all of these separate scans into a single data set?” The answer is simple, and can be achieved either with a spreadsheet program such as Excel or, for those with programming skills, by knocking up a simple computer program specifically for the task. Firstly, export the individual binary data sets to text-based column data as total count y_i(2?) and time t_i(2?) (as opposed to counts per second) so that they can be imported into your spreadsheet. For each 2? point, total all of the y_i and t_i values separately to get Y_i = ? y_i and T_i = ? t_i. At this point, calculate the error on the total count of each point as s$_i$ = vY_i. The final step is to normalise both the total count and its associated error back to counts per unit time (which could be seconds) by dividing both Y_i and s$_i$ by T_i. However, one word of caution: beware of converting the final data back into integer format when the count rate is low.

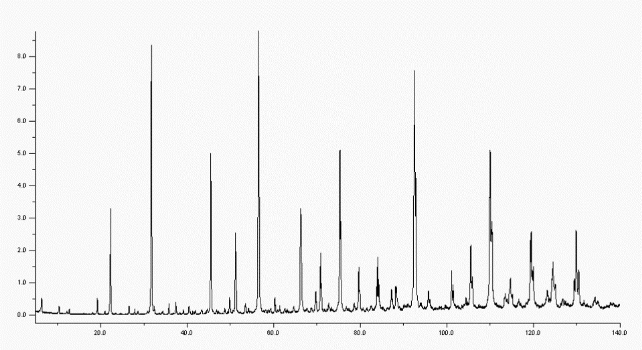

Fig 2a: *Example of variable count time dataset*

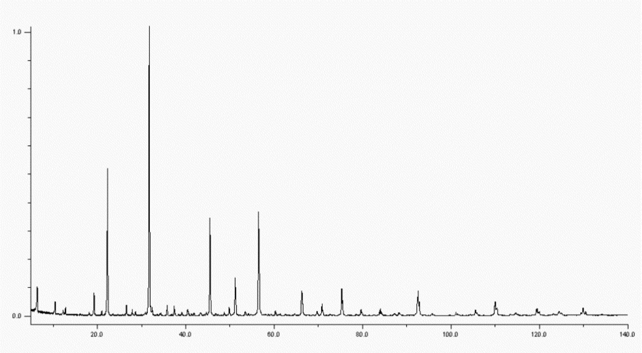

Fig 2b: *Example of above variable count time dataset normalized to look like a fixed count time dataset*

If integer data is required, the simplest solution is to normalise the data and error arrays to counts per minute (or even per hour).

The above data-acquisition strategy may be fine for a structure-solution problem, but is unlikely to be suitable for some indexing or qualitative/quantitative analysis problems, where one may require high precision for the profile of weak peaks at, for example, low scattering angle. However, although the strategy may be different, a similar solution to the previous case can be applied, e.g. a constant time per point scan may be collected initially, and this may be followed by one or more repeat scans over smaller 2? ranges that contain the weak peaks of interest. By this method, the quantity of a small amount of an impurity phase may be determined with increased precision (due to better peak intensity information) or the *d* spacing of a weak reflection required for indexing may be determined more reliably (due to better peak position information).

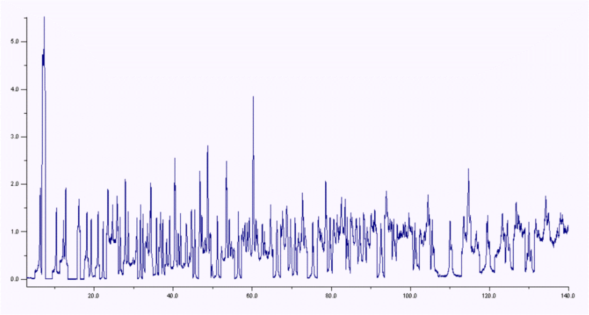

Fig 3a: *Example of variable count time dataset where each reflection is collected to roughly equal counting statistics (suitable for phase Identification, powder indexing, high accuracy quantitative analysis of trace phases, unit cell refinement, etc)*

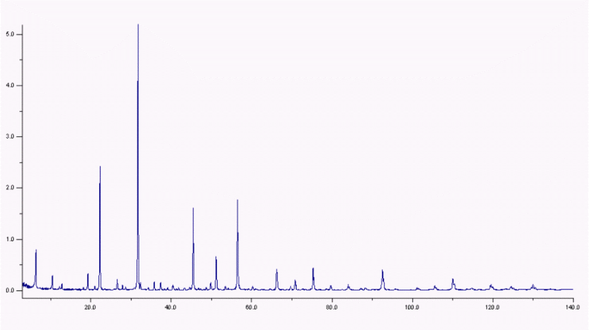

Fig 3b: *Example of above variable count time dataset normalized to look like a fixed count time dataset*

Finding a mineral problem to solve

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For being IMA-approved, a new mineral needs a chemical formula, a location, and some specific characterizations not necessarily including the crystal structure (CS). This results in many minerals still waiting for their CS determination. However, if the CS was not determined, then this is generally because of some difficulties: microcrystallinity, twinning, disorder, etc. I was aware that many of these unknown CS’s could be good candidates for a Structure Determination by Powder Diffractometry (SDPD). Indeed, many mineral CS’s were determined from powder diffraction data [1], because a single crystal approach was impossible, and this includes some zeolites but also kanemite, tinticite, etc. How many minerals are remaining structurally uncharacterized was an interesting question for somebody like me, trying to promote SDPD. Thus I made some efforts to identify them. The first step was easy : finding those minerals whose CSs are known. The most complete list was obtained from the ICSD database [2], and it was checked against other lists, including those from the Mineralogical Society of America [3] and the MINCRYST [4] Web sites. Then, it is in principle obvious that any mineral not included in this first list is one of these unknowns. A subtraction from a complete list of minerals of the ICSD list should give the expected result. How to find a complete list of minerals ? The Internet produced answers (WebMineral site [5], EUROMIN Project [6], etc). Thus, a list of more than 300 minerals with probably unknown CS was established with the help of a software comparing the previous lists. At the beginning, that list of unknown CSs was for my personal use, but, given this large number, and according to the "it's more fun to compete" rule, the list was made available on the Web [7] and its existence was announced at some mailing lists and Newsgroups in July 2001. There were some fast reactions of people claiming that they had submitted recently for publication the CS of one or of several members of the list. A label "too late" was then added in front of these mineral names in the list. Of course, mineralogists trying to determine a mineral CS are never sure that the same job is not made simultaneously elsewhere by another team, that is a constant question in world research. Other reactions about that list were from people asking for the reference of these "too late" minerals. Maintaining the list will not be done (anyway, it was certainly not exhaustive, nor exact, and you should not trust it without doing some bibliography) because this is too much work, and also because it seems to be a bit diabolic regarding competition, precisely (people prefer not to compete in fact, they prefer to keep some secret on their activity). I do not know if that list has already given ideas to people seeking for mineral CS problems to solve. When I record powder patterns of some of these CS-unknown minerals, I add them into the list, with comments. In one case, I preferred not to show the powder pattern, because I tried the SDPD myself. The job was not simple (triclinic, 19 independent atom sites) and required the use of synchrotron powder diffraction data as well as applying the direct-space Monte Carlo software ESPOIR [8] in "scratch" mode (random atoms as starting solution). The manuscript is submitted [9], and this is why you can find "too late" in front of the gormanite and souzalite names in the list mentioned above [7]. Will the paper be accepted ? This is another question. But at least, one of my youth dreams is fulfilled in a way (becoming a geologist or a mineralogist).

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[5] Mineralogy Database : http://www.webmineral.com/
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A slice of history - quantitative phase analysis in a unique film setting

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The name "SASOL" has been associated with the conversion of coal into fuels and chemicals for fifty-two years, a time in which it became a world leader in the use of Fischer-Tropsch technology. This was not so on start-up of the first Kellogg reactor in 1955. Lack of experience with the new technology caused the circulating fluidised-bed reactors to block frequently, resulting in emergency shutdowns during which the fouled catalyst had to be removed with jackhammers. In the determination of the causes of the failure, the constituent phases, oxides and carbides of iron, wax, as well as carbon, could be identified using X-ray diffraction. In order to quantify the iron phases, a novel solution (for the time) was devised, employing a technique not yet mentioned in the literature or the book of Klug and Alexander (1954). The technique was that of comparing intensity ratios in an unknown sample with those of a series of standards. It could also be used for determining the degree of reduction of iron oxides and turned out to be so useful that it remained in use for almost forty years, until it was replaced by the Rietveld technique.

A series of relatively pure standards were available at the time, their exact compositions were determined using wet chemical and other methods. A series of Debye-Scherrer photographs were then obtained from known weights of binary mixtures of these standards. The mixtures were made using increments of 10 %, so that the ratios were 10:90, 20:80 etc. The photographs obtained were mounted on a glass table and illuminated from below.

The composition of an unknown sample was determined by comparing the ratio of the intensities of two lines (peaks) of different phases in the unknown, with the ratio of the intensities of the same two lines (peaks) in the standards. When a standard with a similar ratio was found, its composition was taken for the unknown. Sometimes it was even possible to interpolate between two standards. The composition of samples containing three or four phases could also be determined by using magnetite as a common phase in more than one series of binary mixtures. If the ratio of magnetite to iron and the ratio of magnetite to hematite had been determined, the composition of an unknown sample containing all three iron phases could be calculated using a simple ratio sum.

It may be argued that the errors were large – mainly as a result of the large increments. This certainly is true, but the technique on the other hand was quick and gave results that were precise enough for their purpose. The exposure times for the Debye-Scherrer photographs were 20 minutes each and two photographs could be obtained simultaneously. In case of an emergency, the interpretation was frequently done while the photograph was still wet. It was thus possible to phone a result to the production plant within half an hour of a sample being received.

The author wishes to thank Drs. Jan Louw and Leon Ferreira, both retired, for sharing their experiences of a very exciting period at Sasol.

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The new BGMN and its use in Quantitative Phase Analysis of Mineralogical Multiphase Samples

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BGMNwin is a JAVA based graphical user interface, designed for a more convenient use of the Rietveld program BGMN [1]. The actual release 0.92 beta includes the following features:

- Installer for WINDOWS to avoid the problems in manual setting of environment variables and paths
- Editor for BGMN control files *.sav and structure files *.str
- Start of the programs for calculation of geometric profiles (GEOMET, VERZERR, MAKEGEQ) and of the refinement kernel BGMN
- Graphical representation of pattern refinement during calculation including zoom function and d-spacing calculation of the actual cursor position
- Listing of refinement results and peak parameters
- Some first help functions.

The program can be used if JAVA 1.3.0 or higher is installed. Some examples for quantitative phase analysis are included in the full version as well as in the demo version. The demo version (restricted to 1601 data points) can be downloaded from: http://www.bgmn.de/download.html

As a special support for the use of BGMNwin in quantitative analysis, some ready-to-use structure description files can be downloaded from: http://www.bgmn.de/download-structures.html

The BGMNwin interface enables the use of the full power of the BGMN structure description language in phase analysis as well as in structure refinement and in peak profile analysis. However, in this paper the application in Quantitative Phase Analysis (QPA) will be demonstrated.

Example: Granodiorite from the IUCr Round Robin in QPA [2], [3].

The natural granodiorite sample from the IUCr QPA Round Robin sample suite was ground manually stepwise to pass completely a 20 µm sieve. The sample was prepared by the simple front-loading technique. A relative fast routine measurement (step 0.03 °2Θ, 5 sec/step) in the angular range 5-100 °2Θ Co-radiation was performed.

The control file (Fig.1) contains some global parameters, the geometric profile model, a list of structures to be quantified and a prescription to calculate the relative phase abundance and the e.s.d.'s.

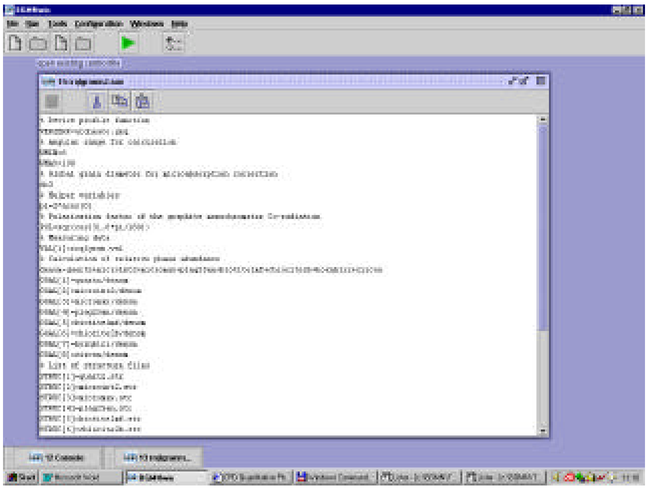

Fig. 1: *Screen shot of the BGMNwin edit mode*

The refinement was started by simply choosing the prepared control file. Phase specific parameters, their limits and the models for preferred orientation correction [4] as well as peak broadening models [5] are previously defined in the structure description files.

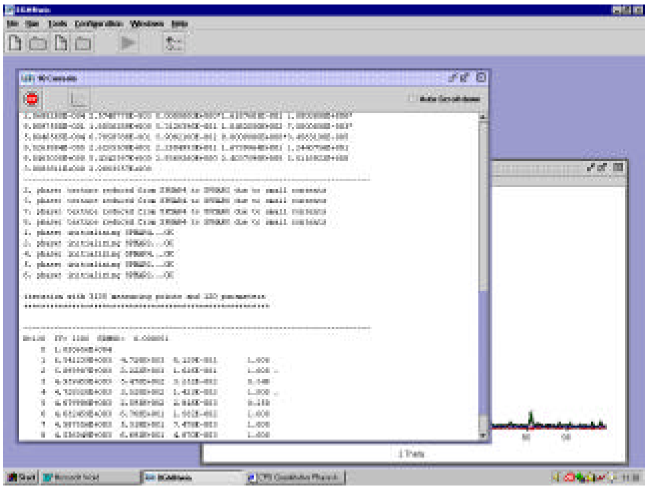

Fig. 2: *Automatic decision of applicability of PO correction models during refinement of the multiphase sample granodiorite.*

The special features of BGMN [1] ensure an automatic refinement without any user interaction. As an example, the use of some possibly over-parameterised models for PO correction and anisotropic line broadening is controlled by automatic pre-estimating of errors and their start will be prevented automatically by the program (Fig. 2). This tool helps to avoid the application of a too complex starting model that would be unable to refine from poor measuring data in routine analysis.

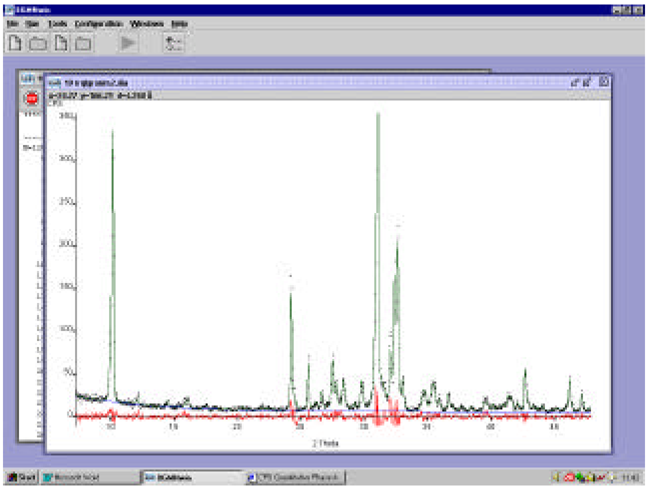

Fig. 3: *Rietveld refinement plot online during calculation.*

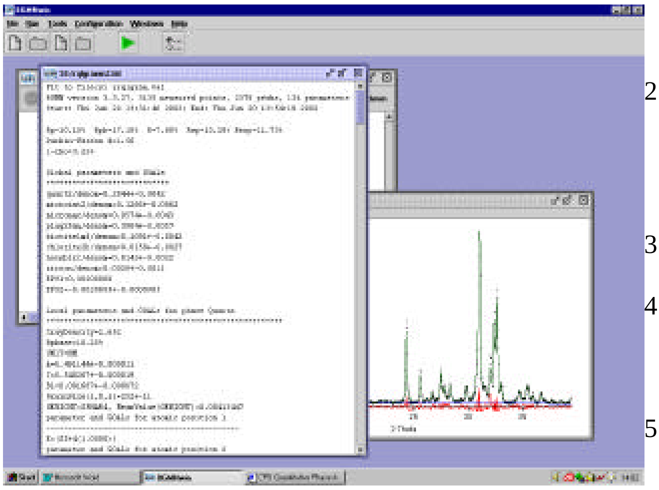

Fig. 4: *Listing of refinement results. Relative phase abundance is calculated including e.s.d.'s (1s) by the BGMN goal concept.*

The QPA results agree well with the means published in [3], although the quality of the measurement was rather poor and about 134 parameters had to be refined in full automatic mode. Additionally, two different K-feldspars have been identified in the granodiorite and could be refined together in one model. Only the biotite content was somewhat overestimated, possibly by the application of a too complex disordering model [7].

The graphic representation of measurement, calculated pattern and difference plot during the calculation process may be used to identify minor phases not included in the actual phase composition. In our experience in using the commercial package AUTOQUAN, the inspection of the difference plot is the most effective tool to complete the qualitative phase analysis of complicated mixtures [6].

Future prospects

The BGMNwin GUI makes the use of BGMN more convenient. Later versions will be improved, especially with respect to print options, result representation and help functions.

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FULLPAT: a full-pattern quantitative analysis program for X-ray powder diffraction

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FULLPAT is a quantitative X-ray diffraction methodology that merges the advantages of existing full-pattern fitting methods with the traditional reference intensity ratio (RIR) method [1]. FULLPAT is based on the premise that patterns for each individual phase in a mixture can be added in the correct proportions to reproduce the observed pattern. Like the Rietveld [2,3] and other full-pattern quantitative analysis methods [4,5,6], it uses complete diffraction patterns. However, FULLPAT can explicitly analyze all phases in a sample including partially ordered or amorphous phases such as glasses, clay minerals, or polymers. Addition of an internal standard to both library standards and the unknown samples eliminates instrumental and matrix effects and allows unconstrained analyses to be conducted by direct fitting of library standard patterns to each phase in the sample. Because the amount of corundum used in standards and unknowns is identical (20%), each analysis is reduced to nothing more than scaling and matching of library patterns to the patterns of those phases in the observed pattern. The amount of a phase in the unknown mixture is equal to the amount the library standard must be scaled to match the pure-phase library pattern with that phase's portion of the unknown sample pattern. Standard patterns may include data for any solid material including glasses, and calculated patterns may also be used.

If all individual library standards are normalized to be equal on the basis of the intensity of the corundum internal standard, one can conduct an "external standard" or "adiabatic" method analysis as described by Chung [8], without the addition of an internal standard to the unknown. External standard analyses are performed by scaling the library patterns to match the observed pattern, but relative percentages are now obtained for all phases. External standard analyses require the constraint that the abundance of all phases must sum to 100%. Most existing QXRD methods, including the traditional RIR [7], Rietveld [2,3], and the Smith et al [4] methods require that an internal standard be added to a sample for absolute quantification as none of them explicitly deals with amorphous phases present.

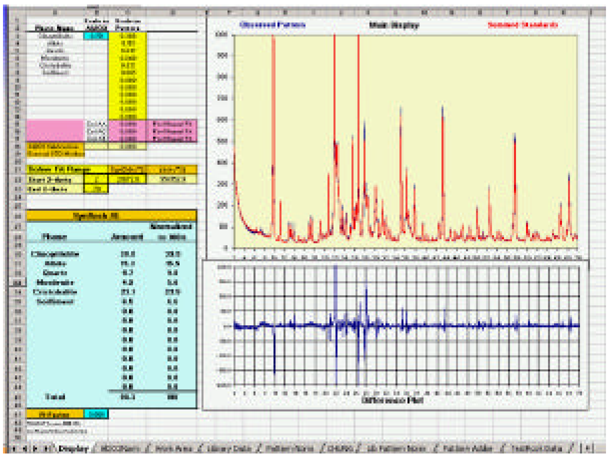

Fig 1: *Main display page of FULLPAT running within Microsoft Excel, showing the analysis of a synthetic mineral mixture composed of clinoptilolite (40%), cristobalite (25%), albite (15%), quartz (10%), mordenite (5%) and smectite (5%). Note: both the observed and a simulated ("summed standards") pattern are included in the above diffraction pattern but are virtually indistinguishable.*

By fitting the entire pattern, including background, amorphous components can be explicitly included in a FULLPAT analysis. Amorphous content is therefore no longer determined as the difference from 100% (i.e., %amorphous = 100% - S crystalline phases) but is measured directly.

FULLPAT uses least-squares minimization to optimize the fit between the sum of standard patterns and the observed pattern, which is extremely important. Not only does this improve the quality of each analysis, it also removes a significant component of operator intervention, thereby giving reproducible results independent of operator bias. FULLPAT is coded into Microsoft EXCEL using standard spreadsheet functions. As such, it should be readily transportable to any computer on which EXCEL is installed.

Program Availability and caveats:

The program is available free of charge and can be obtained by contacting the authors directly and (in the near future) via the web at http://www.ccp14.ac.uk/ccp/web-mirrors/fullpatt/. The program is distributed with full documentation describing its installation and use. In using FULLPAT, it is important to recognize that the quality of each analysis is strongly dependent on the quality of the standard library patterns. Given the variety of methods and instruments used in different laboratories, library patterns should not generally be shared between different laboratories. FULLPAT is distributed with only a limited number of example library patterns, as individual laboratories should measure their own standard patterns to ensure that the patterns are appropriate for their instrument and sample configurations.

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FOX 'Free Objects For Xtallography' : ab initio structure solution from powder diffraction tailored for inorganic compounds

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Introduction

Ab initio structure determination from powder diffraction is still a difficult problem for cystallographers, even if vast progress has been made during the last 10 years (for a review, see http://www.cristal.org/iniref.html). Despite the progress in the development of direct methods for structure solution [1], these methods are often limited by the difficulty of extracting reliably intensities of weak, high-angle reflections which are required by direct methods.

This is why direct-space methods have been intensively developed for structure solution from powder diffraction, using Monte-Carlo algorithms, Simulated Annealing, or Genetic Algorithms. However, relatively little effort has been spent on the modeling of inorganic compounds, with the exception of zeolite structures for which specific programs have been developed [2,3]. The most important features lacking were the handling of special positions, and the description of the structure using custom "building blocks". We have developed the free, open-source program Fox [4], "Free Objects for Xtallography", to address these issues, with the following requirements:

(i) The crystal structure can be described using any combination of building blocks: isolated atoms, molecules, polyhedra. The correct structure can be found without any assumption on the actual connectivity between building blocks, nor any a priori knowledge about atoms on special positions.

(ii) Several optimization algorithms can be used, with easy path from one to another and with easy upgrade of algorithm. All optimized objects (crystal structure, powder pattern) can define their Cost Function (CF) and any combination of CF's can be used as a criterion.

(iii) It is possible to use jointly all available diffraction data sets.

(iv) Object-oriented programming makes updating of the algorithms and parameterization easy.

Global Optimization: Algorithms and Cost Functions

The algorithms used by Fox are derived from the so-called *reverse Monte-Carlo* approach: starting from a random configuration, the free parameters of the structure are varied randomly, and all configurations are compared using 'Cost Functions', which are characteristic of how good the structure is (from either *a priori* knowledge on the compound and/or experimental data). The most efficient algorithm implemented is Parallel Tempering [2], in which parallel optimizations are made at different 'temperatures' (a higher 'temperature' allowing the generation of less favorable configurations), which allows it to move out of local minima without user intervention.

The criteria used to validate all structures generated by the algorithm (the Cost Functions) can be either the standard full-profile weighted R-factor (Rwp), or an integrated Rwp (comparing the integrated intensities around each reflection on the calculated and observed full profiles). This method does not require precise profile parameters and is useful at the structure solution stage, especially for multi-phased data or badly defined profiles [4]. No energetic criterion has been added yet in Fox, because of the high specialization of the interaction potentials with specific type of materials. It is, however, possible to use a generic 'anti-bump' cost function to avoid interpenetration of different types of atoms.

Inorganic structures: using polyhedra and handling special positions

One advantage (compared to molecular structures) of inorganic structures is the generally *high symmetry*, which reduces the number of independent atoms. Another simplification is the fact that inorganic chemists can very often predict the type of *atomic coordination* from the formula or the family of compounds studied. However in practice this information of stacking and symmetry is not fully used in structure solution algorithms, because it is difficult to handle *ab initio* special positions and building blocks without *a priori* knowledge about their connectivity (hence the infamous use of P1 symmetry for optimization).

In Fox, *the crystal structure can be described by any combination of atoms and 'building blocks'* (Fig. 1). The latter are described by bond lengths, bond angles and dihedral angles, using a 'natural' approach and therefore chemically meaningful constraints. The user can either use built-in tetrahedra, octahedra, prisms, etc. or build his own cluster of atoms. All parameters (bond lengths & angles) of building blocks can be individually fixed or constrained within user-chosen limits, allowing the definition of fully rigid or more or less flexible bodies.

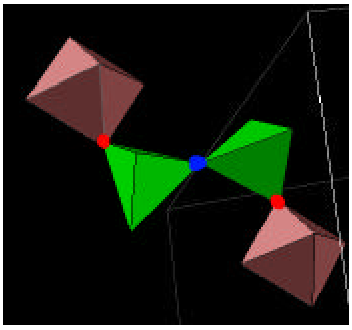

Fig.1: *the crystal structures can be described using flexible or rigid building blocks (built-in such as tetrahedra and octahedra, or custom-built). When one atom falls in special position (central blue dot on a twofold axis), or several atoms are shared (red dots) between two building blocks, the occupancy of the overlapping atoms are reduced dynamically during the global optimization random moves (without a priori knowledge or user intervention) so that the scattered intensities computed correspond to a single atom.*

To take into account the sharing of atoms between different building blocks, we use a '*Dynamical Occupancy Correction*' (DOC) which also corrects special positions. When *n* identical atoms (oxygen) overlap (Fig.1) during the global optimization (whether due to a special position or the overlapping of several atoms of different building blocks), the occupancies of the atoms are dynamically reduced to 1/*n*, so that the resulting electronic (or nuclear) density is equal to that of a single atom.

This simple approach is valid for *any* type and *any* number of overlapping atoms, and can be done continuously during the optimization (the occupancy is slowly decreased as the atoms are merged), and avoids "breaking" any building block since no atom is removed. One extra advantage of this DOC is that *the exact cell contents need not be known in advance*, as excess atoms can be merged during the optimization.

Fox Features

Fox can analyze powder diffraction patterns from X-ray (laboratory source or synchrotron) or neutron diffractometers, and can handle *multiple phases* and *preferred orientation* using the March-Dollase model. It is also possible to optimize single-crystal data in $F(hkl)^2$ form. The modular approach of the algorithms allows the use of any combination of cost functions as a criterion, so that multiple diffraction data sets can be combined to determine a given crystal structure (e.g. *joint optimization* on X-ray and neutron powder patterns).

Fox uses a Graphical User Interface to define the crystal structure, select the powder diffraction data, and choose algorithm parameters (Fig. 2). It has been used to determine *ab initio* new structures for inorganic (oxides, hydrides) and hybrid (metal-organic) structures, and has also been tested on known molecular compounds.

Availability

Fox is available from http://objcryst.sourceforge.net and from CCP14 mirrors, in precompiled form or as source code, for Linux and windows (98 and above). It is free and open-source, available under the General Public License.

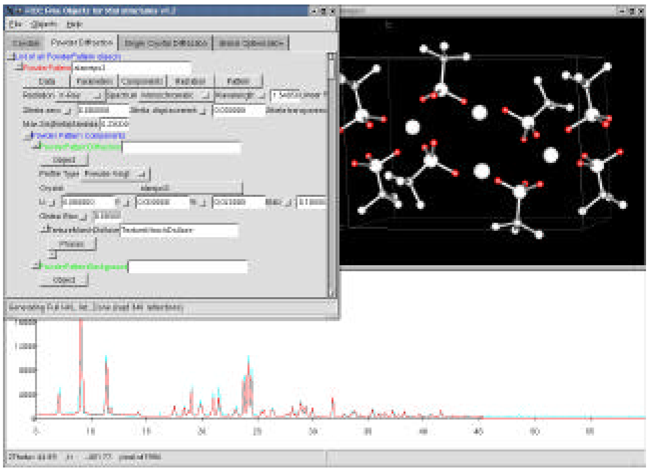

Fig.2: *the Fox Graphical User Interface, with one main window to define all components (crystal structure, powder pattern, algorithm), a 3D window to display the crystal structure, and a window to display the observed and calculated powder pattern*.

Future developments

This program is built around an object-oriented crystallographic computing library (ObjCryst++, http://objcryst.sourceforge.net), which was designed (through inheritance and overloading properties) to be easily extendable to new types of scatterers (building blocks), diffraction data and algorithms. It is also easy to add new criteria (cost functions) for the evaluation of intermediate structures. Of course, as a free and open-source software, Fox and ObjCryst++ welcomes contributions from other crystallographers.

Acknowledgements

We would like to thank Yuri Andreev from the University of St. Andrews for a fruitful discussion on global optimization methods, Ralf Grosse-Kunstleve from Lawrence Berkeley National Laboratory for his help in using the SgInfo and AtomInfo libraries, and Lachlan Cranswick for useful suggestions and mirroring the project on the CCP14 web site. This work was supported by the Swiss National Science Foundation through grant No. 2100-053847.98.

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[3] Grosse-Kunstleve R.W., McCusker L.B. & Baerlocher Ch., J. Appl. Cryst. 30 (1997), 985-995

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Powder Indexing with Crysfire 2002

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One of the barriers to the current renaissance in ab initio structure determination from powder diffraction is the stubborn fact that, before structural work can be done on a material that is only available in powder form, its unit cell must be determined. Unless the powder pattern can be indexed, the intensity associated with each reflection cannot be assigned to its location in reciprocal space, and further progress is impossible. With recent advances in methods for structure solution from powders, and especially in Rietveld refinement, this initial indexing stage is increasingly the main bottleneck in determining powder structures.

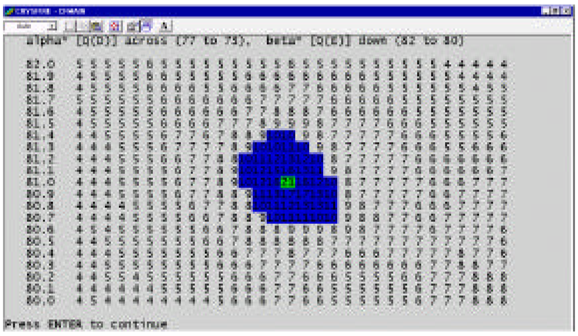
Though the unit cell completely determines the powder pattern (with intensities, instrumental factors, etc.), this is not logically reversible, since we can only resolve a relatively small, degraded and partly overlapping portion of the pattern that lies near the origin of reciprocal space. Powder indexing involves a complex process of induction that is far beyond manual methods in all but the simplest cases. Fortunately, there exist powerful and mature indexing programs, with intelligent front-ends and expert systems to assist the non-specialist in using them.

One of the most widely used has been Crysfire. Despite its relatively unsophisticated interface, Crysfire has brought an unparalleled range of heavy-duty indexing software to non-specialist users. Eight programs contributed by various indexing specialists were included in its August 2000 release, including some not readily available elsewhere, plus a large toolbox of support facilities. A central feature was the generation of a log-file and a cumulative summary file for each dataset, which builds up as the investigation progresses, and shows a line-per-solution summary of each trial cell found by the various programs, sorted into descending order of lines indexed and figure of merit.

However, the Crysfire 2000 core was up against compiler-address-space limits. The new release, Crysfire 2002, required a port of the core to a different language, giving a largely rewritten version that has been completely revised internally and contains three times as many lines of code. The front-end interface remains familiar (since ability to reproduce the output from the previous version was used as a criterion of correctness), but the new Crysfire is now a close-coupled system, faster, more robust and easier to use. Nothing has been lost and there are several powerful new facilities.

Although Crysfire 2002 will take advantage of many of the facilities of Windows when it finds itself running in that environment, it is still essentially a DOS suite, designed to be able to run on almost any PC anywhere in the world, including the rather basic equipment that may be all that is available to students in developing countries. Of course, since indexing can be a computationally intensive process, Crysfire will be seen at its best when running at GHz speeds on a modern Pentium or Athlon PC, under Windows 95 or later. Nevertheless, it will still get there eventually on any PC that meets its very basic requirements (640K RAM, a hard disk of some sort, and DOS 5 or later).

An obvious improvement is the new IN (=index) command, which launches indexing programs directly, automatically reloading the current dataset on returning (these previously required additional user commands). All previous indexing programs are supported (often with considerable improvements), plus a completely new program Mmap, which can be used both for ab initio indexing and for topographical scans of solution space, since it generates a visual map of the hills and valleys of figure of merit plotted against lattice parameters.



```
alpha* [Q(D)] across (77 to 73),  beta* [Q(E)] down (82 to 80)
Press ENTER to continue
```

Fig 1: *Centred figure-of-merit map for a trial solution in an alpha*/beta* section, generated in topographical mode by the new Mmap program in Crysfire 2002. A narrow, compact peak like this is likely to be the physically-correct solution.*

For example, Fig. 1 shows the figure-of-merit surface surrounding a trial solution for a triclinic biological material, made more difficult to index by a dominant zone and very small particle size (producing some line-broadening). The dominant zone generates numerous mathematically-possible solutions, many of which might be plausible if the only criterion were refined figure of merit. A merit-surface map provides a clearer picture in which the central peak reveals itself as likely to be a physically correct solution because of its narrow and compact cross-section, while others (not shown), which are merely pseudo-solutions, prove to lie on ridges and other extended features in solution space. A new LC (Load Cell) command allows trial solutions to be loaded from Crysfire or Chekcell summary files for such investigations.

Another new feature is that, after the summary has been displayed, all solutions are run through a system version of Ton Spek's Le Page program then redisplayed for comparison in reduced-cell form. This highlights the relations between trial solutions, including those which are actually equivalent, though previously found in different settings (and, equally important, those that are non-equivalent derivative cells, though their volumes might have suggested that they were different settings of the same solution).

Also new is an approximate ab-initio volume estimate which is reported whenever a dataset is loaded, with a suggested rescale factor if it seems likely to be outside the volume range for which most indexing programs have been optimised. This can become important as SDPD attempts increasingly ambitious structures, even including proteins (e.g. a new form of zinc insulin: Von Dreele, 2002).

At the other end of the scale, high-pressure/high-temperature experiments often unavoidably yield sparse datasets from phases that are not observable under ambient conditions, and which contain fewer than the 20 observed lines regarded as the absolute minimum by many indexing programs. A new EP (Extend Pattern) command can automatically extend any sparse pattern by adding higher orders of observed lines until the total has been expanded to 20. While this obviously cannot increase the amount of information present, it permits more programs to run, providing a broader basis for hypotheses about the cell (or at least sub-cell) that is present.

The author wishes to acknowledge, with thanks, all those who have contributed indexing and cell-transformation software to the Crysfire 2002 system, especially Franz Kohlbeck, Daniel Louër, Ton Spek, Daniel Taupin, Jan Visser and Per-Eric Werner, and also to draw attention to the fruitful symbiosis that exists between Crysfire and the Chekcell program by Jean Laugier & Bernard Bocchu, for graphically examining proposed solutions and investigating their probable symmetry.

Like its predecessor, Crysfire 2002 is distributed from the CCP14 website and is free for academic and other non-profit use. It can now also be licensed for industrial use (a pro forma invoice is provided in the distribution, the fee being specifically for the overall system integration, the front-end, and for special software like Mmap - no charge is made for contributed code). A separate, semi-automated 32-bit Windows version (Industrial Crysfire), usable by technicians and other non-crystallographers, is in the development pipeline.

Search-Match Round Robin – 2002

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Web: http://www.cristal.org/

Phase identification from a powder diffraction pattern is a widely used method. Modern computer search-match programs coupled with the ICDD Powder Diffraction File (PDF) database (or with custom databases, Pauling, etc) are now probably more than 20 [1-4], and use various algorithms. However, their respective efficiency was unknown to date. Wasting time because a compound was wrongly believed to be new, since a search-match was negative, is something that should not happen these days. We thus decided to organise a Search-Match Round Robin (SMRR), completely open to academic researchers, manufacturers, developers and others. The SMRR appeared timely, because the PDF was supposed to make a breakthrough, by the end of 2002, by including patterns calculated from the Cambridge Structural Database atomic coordinates, increasing enormously the ability to identify organic and organometallic compounds by search-match procedures. At the time this Newsletter will be read, the SMRR will be closed, but at the writing time, only the SMRR first step was accomplished by 25 participants (although there were more than 200 data downloads)

Procedure of the SMRR-2002

The SMRR-2002 started in early May 2002. Participants had to identify the phases in four powder diffraction patterns which were downloadable at http://sdpd.univ-lemans.fr/smrr/ and the CCP14 mirrors in various formats.

The collection of results occurred in two steps:
step 1, deadline June 15, 2002 - samples without information about their chemistry.
step 2, deadline June 30, 2002 - samples with chemistry information as given on June 16.

Choice of the four samples :

Sample 1: Geological Sample
Sample 2: From a synthetic chemist
Sample 3: Organic from a pharmaceutical engineer
Sample 4: Industrial processing plant sample

The samples correspond to typical real cases. And the PDF contains solutions or at least close solutions to these problems. During the round robin, minimal information was given about the samples since many identifications by search-match methods are frequently made without prior knowledge or having only an idea of the chemical content. Real-life samples have certainly not always exact solutions in the PDF. A search-match program should be efficient enough to give the maximum fits.

Some Results for step 1 of the SMRR

Software used

Three main software packages were used by the participants in step 1 of the SMRR (Fig. 1): Jade, from MDI, (16%) X'Pert Graphic & Identify, from Philips (16%); and for nearly 50% EVA from Socabim / Bruker.

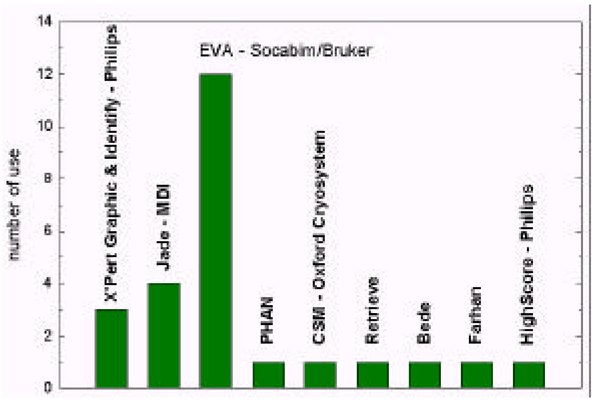


Fig.1: *Software used, all version merged*

ICDD-PDF release	2001 up to set 51	2000 up to set 50	1999 up to set 49	up to set 47	up to set 45	not given
Number of participants	7	5	2	3	1	7
%	28	20	8	12	4	28

Table I: *ICCD-PDF release*

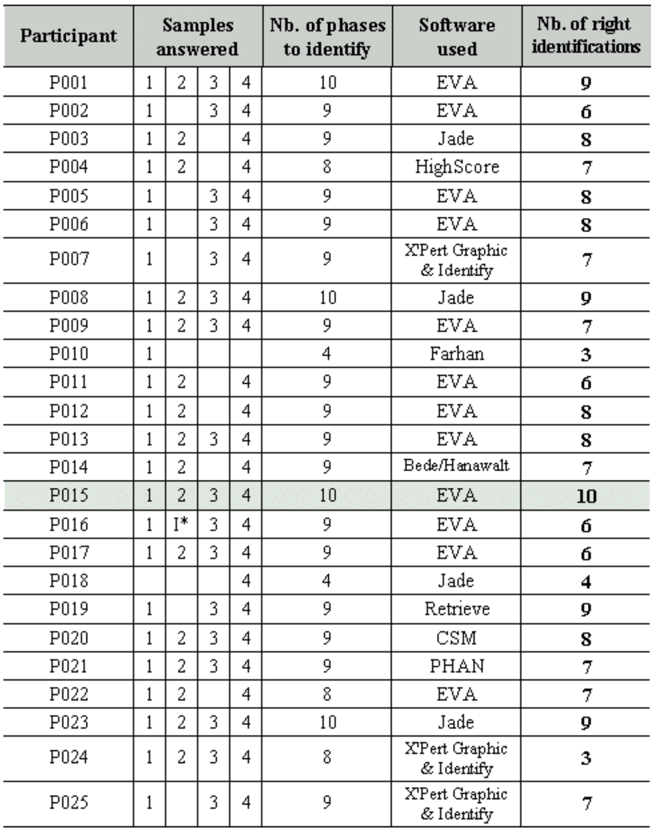
Databases used

Table I shows the versions of the ICDD-PDF used by the participants. 56% of them use a release from 1999 at least. This number is probably higher because 28% of the participants did not give this information.

At least 16% of the participants could not identify sample 2 because they were using an old ICDD release.

Participants results (only step 1)

The participants could send the answers for all the samples, or only for those of their choice. Some answers do not include all samples but 92% of the participants give at least their answers for 3 samples. A summary of the results is proposed in Table II (we do not give the details of the answers in this article).



Participant	Samples answered				Nb. of phases to identify	Software used	Nb. of right identifications
P001	1	2	3	4	10	EVA	9
P002	1		3	4	9	EVA	6
P003	1	2		4	9	Jade	8
P004	1	2		4	8	HighScore	7
P005	1		3	4	9	EVA	8
P006	1		3	4	9	EVA	8
P007	1		3	4	9	X'Pert Graphic & Identify	7
P008	1	2	3	4	10	Jade	9
P009	1	2	3	4	9	EVA	7
P010	1				4	Farhan	3
P011	1	2		4	9	EVA	6
P012	1	2		4	9	EVA	8
P013	1	2	3	4	9	EVA	8
P014	1	2		4	9	Bede/Hanawalt	7
P015	1	2	3	4	10	EVA	10
P016	1	I*	3	4	9	EVA	6
P017	1	2	3	4	9	EVA	6
P018				4	4	Jade	4
P019	1		3	4	9	Retrieve	9
P020	1	2	3	4	9	CSM	8
P021	1	2	3	4	9	PHAN	7
P022	1	2		4	8	EVA	7
P023	1	2	3	4	10	Jade	9
P024	1	2	3	4	8	X'Pert Graphic & Identify	3
P025	1		3	4	9	X'Pert Graphic & Identify	7

Table II: *Summary of results. “I” stands for indexed pattern only.*

Conclusion:

Experience certainly plays a large role here, and only one participant could identify the whole set of ten phases present in the four powder patterns. Some participants could identify 9 of these 10 phases but many others were not as successful. We suggest you read the SMRR conclusions at http://sdpd.univ-lemans.fr/smrr/ before deciding on a new search-match software, this is the least you can do.

[1] D.K. Smith & S. Gorter, "Powder Diffraction Program Information 1990 Program List," J. Appl. Cryst. 24 (1992) 369-402. and, from the same authors, see the last release of the "World Directory of Powder Diffraction Programs."
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http://www.ccp14.ac.uk/solution/search-match.htm and http://www.ccp14.ac.uk/poster-talks/phase-id-1999/
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http://sdpd.univ-lemans.fr/iniref/tutorial/indexa.html

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ICDD Holds Its Annual Spring Meetings

During the week of 18–22 March 2002, the International Centre for Diffraction Data (ICDD) welcomed its members to the headquarters office in Newtown Square, Pennsylvania for its Annual Spring Meetings. An international gathering of the ICDD members, representing a wide range of scientific disciplines, participated in the various committee, subcommittee, and task group meetings held throughout the week. In addition, the ICDD Board of Directors met to discuss the financial, business, and long-range planning functions of the ICDD.

The Technical Committee meeting on Thursday, 21 March 2002, served as a summary of all subcommittee activities and included reports by ICDD's Regional Co-chairs: Shao-Fan Lin, China; Nubuo Ishizawa, East Pacific Rim; David Taylor, England; David Rafaja, European Community; James A. Kaduk, North America; Evgeny Antipov, Russia; José M. Delgado, South America; Brian H. O'Connor, Southeast Asia. The co-chairs reported on the activities in their region related to the ICDD and those of general interest to the X-ray analysis community. Results of global X-ray conferences, workshops and clinics were described as well as proposals for future activities in each region. In a typical year, the ICDD financially supports or directly conducts over a dozen forums for technology exchange across the globe, targeted toward scientists working in X-ray analysis.

The Annual Meeting of Members was also held on Thursday, where Cam Hubbard, ICDD's Chairman, discussed the high productivity and major progress on the Powder Diffraction File™, and the overall evolution of ICDD over the last several years.

Evgeny Antipov, Moscow State University, received the Distinguished Grantee Award and also gave a presentation of his work in the ICDD Grant-in-Aid Program, which includes reference patterns for industrially important, advanced inorganic materials. Dr. Antipov was also cited for the high quality of his contributions to the PDF and his role in the development of the powder diffraction community in his region.

The retiring members of the Board, Jeffrey N. Dann, Charles T. Prewitt, and Jeffrey E. Post were recognized for their service. As per the results of the recent election of officers and directors, the new slate of directors serving the term 2002–2004 was also announced:

Chairman: Camden R. Hubbard
Vice Chairman: Brian H. O'Connor
Treasurer: Julian Messick
Corporate Secretary: Terry Maguire
Executive Director: Timothy G. Fawcett
Chairman, Technical Committee: James A. Kaduk
Directors-at-Large: Evgeny Antipov, Raymond P. Goehner, Ron Jenkins, Daniel Louer, and David F. Rendle
Past Chairman: Robert L. Snyder

Front row: Evgeny Antipov, Terry Maguire, Julian Messick, Cam Hubbard, Tim Fawcett, Brian O'Connor, David Rendle. Back row: Bob Snyder, Jim Kaduk, Ray Goehner, Daniel Louer. Missing from picture: Ron Jenkins.

Members play an essential role in the development of the ICDD, its database products, and services, tailoring those products and services to the needs of the global scientific community. Interested in becoming an ICDD member? Please visit our web site at www.icdd.com, or contact our Membership Committee Chairperson, Dr. Winnie Wong-Ng, at winnie.wong-ng@nist.gov.

Educational News

XRF & XRD Clinics

In pursuing its dynamic commitment to education, the ICDD once again held its annual training clinics in XRF and XRD at its headquarters in Newtown Square, Pennsylvania. These clinics offer both novices and professionals in the field of X-ray analysis an opportunity to learn techniques from the experts as well as the opportunity to discuss field experiences with peers.

The instructors for the XRF Clinic included: John Anzelmo and Larry Arias of Bruker AXS, Inc.; Gene Bertin, Emeritus, RCA Labs; Richard Bostwick of SPEX CertiPrep, Inc.; Larry Creasy of Titanium Metals Corp.; John Croke, Emeritus, Philips Analytical, Inc.; Tim Fawcett, ICDD; and Mary Ann Zaitz of IBM Microelectronics.

The instructors for the XRD Clinic included: Tom Blanton, Eastman Kodak Company; Holger Cordes, Bruker AXS, Inc.; C. M. Foris, DuPont Central Research & Development; Richard Hamilton, Emeritus, Air Products and Chemicals, Inc.; James A. Kaduk, BP Amoco, Mark Rodriguez, Sandia National Laboratory; Susan Quick and Earle Ryba, both of The Pennsylvania State University; Bernie Squires, Rigaku/USA, Inc.; and Harlan Clark, John Faber, Tim Fawcett, Suri Kabekkodu, Frank McClune, Fangling Needham, Chuck Weth, all of the ICDD.

The ICDD wishes to thank NeXray, Bruker AXS, Inc., and Rigaku/USA, Inc. for their assistance in providing X-ray instruments for use during the courses. Through these generous donations, the clinic curriculums were reinforced by providing hands-on experiences to the attendees.

ICDD Workshop at EPDIC-8

The ICDD held a full-day workshop entitled *Advances In Powder Diffraction* on Thursday 23 May, during EPDIC-8. Led by Dr. Tim Fawcett, ICDD's Executive Director, and Dr. John Faber, ICDD's Principal Scientist, the workshop focused on data mining and next generation software; Round Robin tests; and X-ray optics. Approximately 40 EPDIC attendees participated in the workshop.

Ludo Frevel Crystallography Scholarship Recipients Named

Congratulations to the 2002 Ludo Frevel Crystallography Scholarship recipients who were recently selected. Named in honor of the program's founder, Dr. Ludo Frevel, this program was created to encourage promising graduate students to pursue crystallography-oriented research. Each $2,250 stipend provides assistance to students in their research efforts, to help defray tuition and laboratory fees, and enables them to attend scientific meetings related to crystallography.

Since the program's inception in 1991, over $93,000 in scholarships have been awarded to 45 graduate students. As a reflection of the international scope of this award, students representing ten different countries have benefited from these scholarships.

The recipients selected to receive the 2002 awards, along with their chosen field of research, are:

> Dane A. Boysen of The California Institute of Technology, Pasadena, California with research involving "Hydrogen-Bonding, Phase Transitions, and Proton Conductivity in MH_2PO_4-Type Solid Acids (M=Li, K, Na, Rb, Cs and NH_4)"
>
> Desiree H. Fong of The McGill University of Montreal, Quebec, Canada with exploration into "Structural Analysis of an Antibiotic-Detoxifying Kinase"
>
> Jeffrey H. Haeni of The Pennsylvania State University, University Park, Pennsylvania with major interest in "Growth and Characterization of Metastable $BaTiO_3/SrTiO_3$ Superlattices"
>
> Michael W. Lufaso of The Ohio State University, Columbus, Ohio with studies focusing on "Evaluation and Prediction of the Crystal Structures of Single/Ordered/Disordered Octahedral Cation Perovskites Using the Software Program SPuDS"
>
> Jeffrey P. Maranchi of The Carnegie Mellon University, Pittsburgh, Pennsylvania with research concerning "Novel Chemical Synthesis and Characterization of Electrode Materials for Thin Film Lithium-Ion Batteries"
>
> Christine M. Clark McCracken of The University of Manitoba, Winnipeg, Manitoba, Canada who's investigating "The Crystallography and Chemistry of Tourmaline."

New Product Releases

This year, the ICDD will release two new commercial products designed to bring unprecedented database capabilities to the global X-ray diffraction community. The first product, now available, contains 136,800 materials and is the next generation of the historic Powder Diffraction File (PDF®)—PDF 4/Full File 2002. The second product, a collaborative effort with the Cambridge Crystallographic Data Centre, is scheduled to be released in November and contains 146,000 organic and organometallic materials—PDF 4/Organics 2002.

Both databases are in a relational database format that allows complex Boolean search queries of more than 30 separate fields. This format allows users to search on diffraction data (d's, I's), unit cell parameters, chemistry, melting points as well as a wide range of physical and optical properties and bibliographic references. Combined, these databases contain 257,000 unique entries, which can also be searched by material subsets such as pharmaceuticals, minerals, metals & alloys, polymers, superconductors, zeolites, etc.

Further Information

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

Computer Corner

Updates on Freely Available Crystallographic and Powder Diffraction Software

(Suggestions, corrections, comments appreciated; especially if you know of new program features, program updates and announcements that should be mentioned here).

Lachlan M. D. Cranswick
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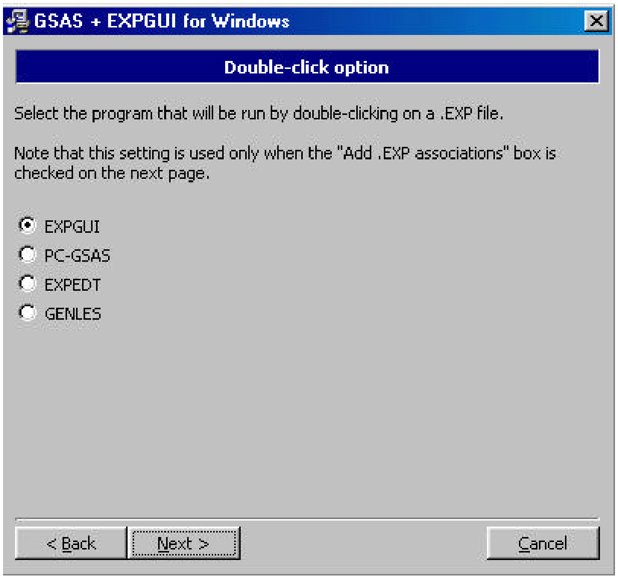
WWW: http://www.ccp14.ac.uk - http://ccp14.sims.nrc.ca - http://ccp14.semo.edu - http://ccp14.minerals.csiro.au

Latest GSAS and EXPGUI installer for Windows and Linux

There is a new version of the Windows installer created by Brian Toby for the latest version of EXPGUI and Bob von Dreele and Alan Larsen's GSAS available at ftp://ftp.ncnr.nist.gov/pub/cryst/gsas/. The Windows installer is dated Tue May 07 2002, the Linux RPM installer, Mon Dec 17 2001. Be wary that for the Linux RPM to install on Redhat Linux, you may have to install a BLT RPM which is one of the dependencies (assuming also that you have Tcl/Tk installed as part of your Linux operating system).

The Windows installer titled gsas+expgui.exe makes it very easy to install and start using GSAS in that it also handles setting all the relevant environment variables.



Select the program that will be run by double-clicking on a .EXP file.

Note that this setting is used only when the "Add .EXP associations" box is checked on the next page.

● EXPGUI
○ PC-GSAS
○ EXPEDT
○ GENLES

Fig 1: *Part of the GSAS/EXPGUI installer process, in this case querying which program should be associated with the EXP file (EXPGUI, PC-GSAS, EXPEDT or GENLES).*

New version of Jana single crystal and Rietveld software by Vaclav Petricek and Michal Dusek

A new upgrade of Jana for normal and incommensurate structures, anharmonic refinement and charge density is available via the web. Jana can now handle up to 500 atom structures, improved CIF output and Shelx INS file input, as well as various bug fixes.

As part of the anharmonic thermal refinement options, it might not be appreciated by people who haven't tried this option that Jana automatically applies the correct symmetry constraints via its menu based operation.

The main Jana webpage is at http://www-xray.fzu.cz/jana/jana.html with program download at ftp://ftp.fzu.cz/pub/cryst/jana2000 (as well as CCP14 mirrors)

Programs that link into Fujio Izimi's Rietan Rietveld

A wide variety of programs link into the Rietan Rietveld software by Fujio Izumi and are described at http://homepage.mac.com/fujioizumi/rietan/angle_dispersive/angle_dispersive.html#Auxiliary. Many of these are Japanese language based while remaining are in English. These include Graphing programs, Rietveld plot viewers, structure viewers and general diffraction data display software.

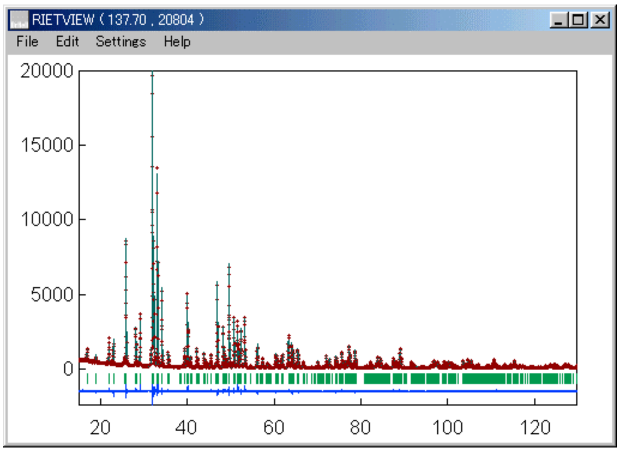


Fig 2: *Screen image of Rietview for Windows by Dr Hell for viewing Rietan plot files. The program is available at http://members.tripod.co.jp/DrHell/labo/index.html*

The usefulness of Ton Spek's LePage software as part of the ab initio powder indexing process

"Those who know, know", but many performing powder indexing may not realise how very useful Ton Spek's

LaPage software can be for trying to deriving sub-cells and/or super-cells (A. L. Spek, J. Appl. Cryst., 21, (1988), 578-579) Fortran source code for LePage is available at ftp://xraysoft.chem.uu.nl/pub/unix/lepage/ and CCP14 mirrors (with a Graphical Windows port as part of the LMGP suite). The LePage super-cell and sub-cell searching can routinely find a better unit-cells from trial cell solutions which turn out to be the true solution. This can be particularly useful in problems where molecular geometry or chemical crystallographic intuition favours one cell type over others (e.g., hexagonal) but which has not been found by any of the indexing programs. Some examples follow where LePage is able to find the "true" cells from the solution list provided by various indexing programs:

Example 1:

Top FOM trial cell (Orthorhombic):

16.147 9.322 7.651 90 90 90

Hexagonal cell found by LePage using super-cell / sub-cell searching on the above solution:

18.644 18.644 7.651 90 90 120

Example 2:

A good looking tetragonal trial cell:

7.501 7.501 5.304 90 90 90

Cubic cell found by LePage using super-cell / sub-cell searching on the above solution:

10.608 10.608 10.608 90 90 90

Example 3:

Top FOM trial cell (Monoclinic):

18.646 2.554 4.425 90 94.53 90

Rhombohedral cell found by LePage using super-cell / sub-cell searching on the above solution:

18.820 18.820 18.820 15.60 15.60 15.60

5.108 5.108 55.762 90 90 120

All the above LePage found cells give better "parsimony of extra reflections" results over the starting cells. Some "good" trial cells which structure solution has been problematic have been found by LePage to have better cells, from which structure solution becomes more feasible.

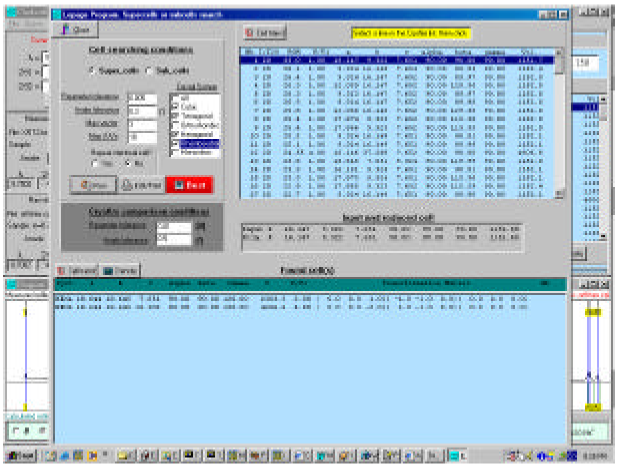


Fig 3: Described in the July 2001 edition of this newsletter, *Jean Laugier and Bernard Bochu's Chekcell has LePage inbuilt; going a LePage check is very easy and just as easy to evaluate any LePage derived cells via its "Best Solution" parsimony of extra reflections check.*

The upcoming Crysfire 2002 June/July release has LePage in-built to routinely provide the reduced cell; while Jean Laugier and Bernard Bochu have ported LePage for Windows and also incorporated it into the Chekcell powder indexing helper tool.
Crysfire: http://www.ccp14.ac.uk/tutorial/crys/
Wlepage and Chekcell (which has LePage inbuilt) part of the LMGP suite: http://www.ccp14.ac.uk/tutorial/lmgp/

Jean-Jacques Rouseau's Spacegroups Java Webpage

A free on-line alternative to the IUCr International Tables spacegroup diagrams is Jean-Jacques Rousseau's spacegroup tables. They can be viewed by any Java compliant web browser and are available at the University of Le Mans web-site via: http://www.univ-lemans.fr/enseignements/physique/02/cristallo/cristal.html.

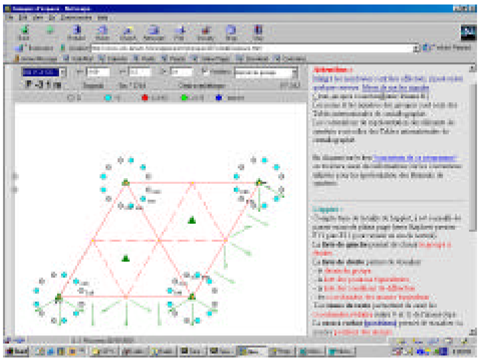


Fig 4: *Example of J.J. Rousseau "Les 230 groupes d'espace" freely available via the web. On-line spacegroup diagrams. In this example showing P –3 1 m.*

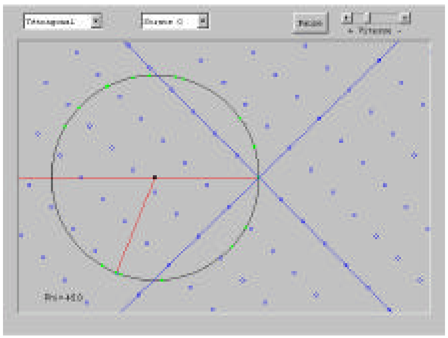


Fig 5: *Another web applet from J.J. Rousseau's webpage – titled "Cristal tournant" with an interactive animation of the "sphère d'Ewald".*

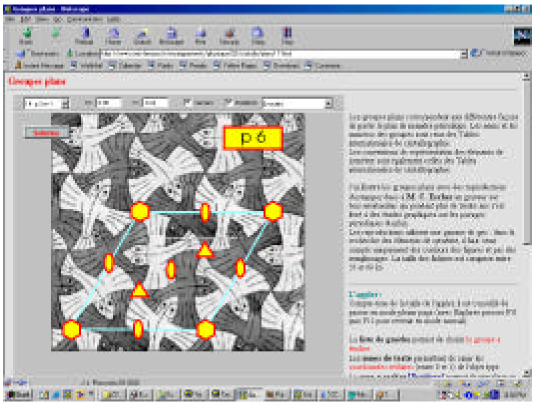


Fig 6: *Example of the "Les 17 groupes plan" web applet where the user has to determine the symmetry of various*

Escher drawings. A solution Icon confirms the solution by overlaying the symmetry elements.

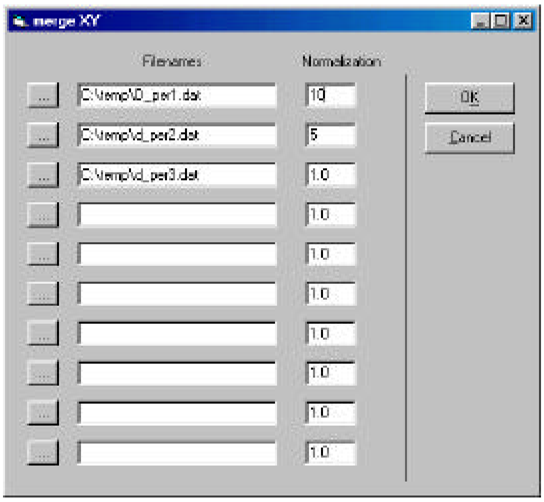
Other Java applets useful for teaching and performing crystallography by Professor Rousseau are also available on the above web page. The website is in French. However, given English has been described by some scholars as a dialect of French, it should not be a problem for those who mainly understand English to make good use of this site.

Christian Baerlocher's DLS-76 for Windows ported by Ross Angel (and Mac version)

A new port for Windows of Christian Baerlocher's DLS-76 by Ross Angel (and also a Macversion) is now available on the web at http://www.kristall.ethz.ch/LFK/software/. A feature of DLS-76 lacking in other DLS software is the ability to vary the unit-cell parameters as part of the DLS refinement.

New version of Convert 4 for Windows by Nita Dragoe

The latest beta test version of Convert 4 by Nita Dragoe now allows for the merging and normalisation of up to 10 diffraction datasets with the recalculation of appropriate esd's. This makes it feasible for the collection of multiple fixed count time diffraction patterns and for their merging into a variable count time (VCT) dataset with appropriate esd's. Powder v4 is available via http://www.ccp14.ac.uk/ccp/web-mirrors/ndragoe/zip/. A tutorial on using this new feature is viewable at the site.



Filenames	Normalization
C:\temp\D_per1.dat	10
C:\temp\d_per2.dat	5
C:\temp\d_per3.dat	1.0
	1.0
	1.0
	1.0
	1.0
	1.0
	1.0
	1.0

Fig 7: *Screen shot of Nita Dragoe's Powder v4 interface for merging multiple diffraction data sets, with the option of inputting a monitor/normalization value for each diffractogram.*

New Chekcell with Density / Z / Molecular Volume Explorer

A new feature in Jean Laugier and Bernard Bochu's Chekcell powder indexing helper tool is the addition of a Density / Z / Molecular Volume Explorer. Users can output for all trial cells, ranges of i) Z, ii) Density, iii) expected molecular volume and iv) the ratio of molecular volume over the trial cell volumes. Chekcell allows you to enter a molecular formula and save it for later use. While the default non-hydrogen atom volume is 18Å^3,

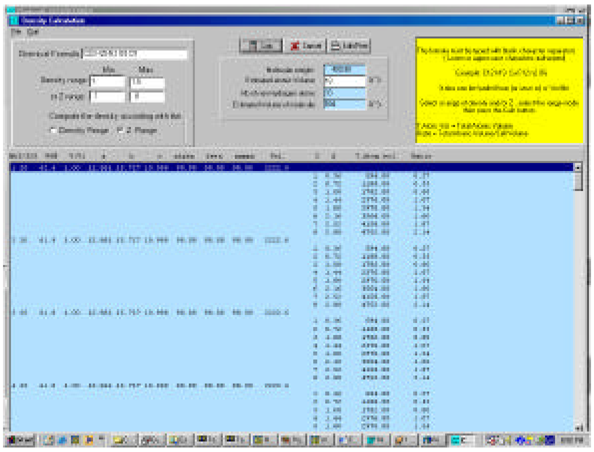


Fig 8: *Screen image of Chekcell running the Density / Z / Molecular Volume explorer on powder diffraction data of Tetracycline hydrochloride. In the above screen image, Chekcell is outputting the relevant densities, molecular volumes and ratios for Z values of 1 to 8.*

While good as another tool to explore trial cells, if combined with a density measuring device (such as a Berman Density Balance for precision density measurements), this option can assist in difficult cases of powder indexing and structure solution (Berman, American Mineralogist (24) 1939, 434-440). Knowing the measured density is much better than guessing it.

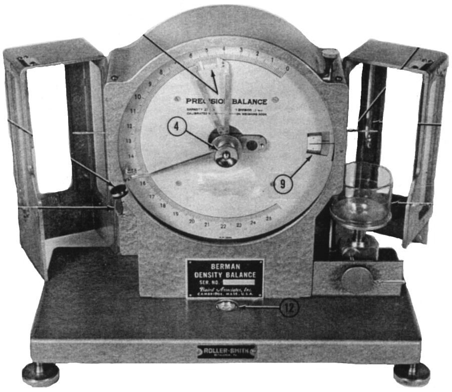


Fig 9: *Photograph of a Berman density balance for precision density measurement. (image courtesy of Richard J. Staples of Harvard University, Cambridge, Massachusetts, USA)*

Rietveld Software Updates (as of late June2002):

Hugo Rietveld website:
http://home.wxs.nl/~rietv025/
BGMN (20th June 2002)
http://www.bgmn.de/
DBWS (22nd February 2000)
http://www.physics.gatech.edu/downloads/young/download_dbws.html
Debvin (25th May 2001)
ftp://ftp.cc.uniud.it/DEBVIN/
GSAS (28th March 2002)
ftp://ftp.lanl.gov/public/gsas/
EXPGUI (29th March 2002)

http://www.ncnr.nist.gov/programs/crystallography/
Jana (18th June 2002)
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) (18th June 2002)
http://www.ing.unitn.it/~luttero/maud/
Prodd (3rd April 2001)
http://www.ccp14.ac.uk/ccp/web-mirrors/prodd/~jpw22/
Profil (24th May 2001)
ftp://img.cryst.bbk.ac.uk/pdpl/
Rietan 2000 (GPL'd) (6th March 2002)
http://homepage.mac.com/fujioizumi/rietan/angle_dispersive/angle_dispersive.html
Winplotr/Fullprof (17th June 2002)
http://www-llb.cea.fr/winplotr/winplotr.htm
ftp://bali.saclay.cea.fr/pub/divers/fullprof.2k/
Winmprof (21st June 2001)
http://lpec.univ-lemans.fr/WinMProf/
XND (2nd May 2002)
http://www-cristallo.polycnrs-gre.fr/xnd/xnd.html
ftp://old-labs.polycnrs-gre.fr/pub/xnd/

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/).

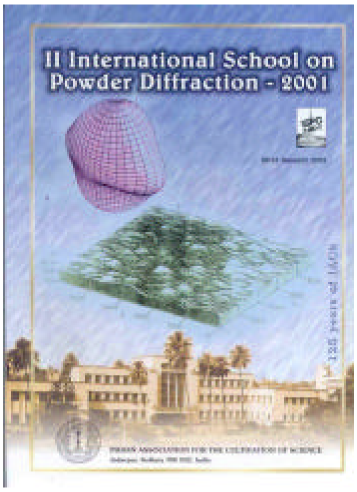
Summary lists of some software available via the EPSRC funded CCP14 website:

"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/

MEETING AND SCHOOL REPORTS

ISPD 2001" – the 2nd International School on Powder Diffraction, Calcutta (India), 20-23.1.2002



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The Second International School on Powder Diffraction (ISPD 2001) was held recently, from 20-23 January 2002, at the Indian Association for the Cultivation of Science (IACS), Jadavpur, Calcutta. The choice of venue was appropriate as this event formed part of the year-long celebration for 125 years of the IACS, the first Asian Institute to embark on teaching and research programs in science, producing amongst its scholars such an eminent scientist as C V Raman himself. This important meeting is unique in its character in this sub-continent and was initiated in October 1998 under the sponsorship and active support of the International Union of Crystallography. S. P. Sen Gupta, Professor and former Head of the Department of Materials Science of IACS, the Convener-Secretary of this meeting, is an active Member from India in the Commission on Powder Diffraction of the IUCr and also organized the first School in Calcutta in 1998. Proceedings of both the Schools have been published by Allied Publishers, New Delhi.

About 150 scientists, young and senior, from India and abroad (France, Germany, Hungary, Singapore, Vietnam and Bangladesh) participated in the school. They interacted through lectures, computer sessions and poster sessions. The most recent developments in the field in the form of basic formulations and applications have been presented in the School by eminent speakers like Tamas Ungar (Hungary), Gert Kruger (South Africa), Jürg Bergmann and Reinhard Kleeberg (Germany). Daniel Louër (France) and Gert Nolze (Germany) could not be present but their lecture materials have been published in the Proceedings which will greatly benefit the participants.

Dr. Krishan Lal (Director of the National Physical Laboratory, New Delhi) gave the Key-note Lecture on surface and interface studies in microelectronic devices and Dr. S. K. Sikka, Associate Director of BARC, Trombay presented the high pressure research work done at the Bhabha Atomic Research Centre. Neutron diffraction studies were highlighted by Dr Siruguri of IUC-DAEF, Mumbai. Prof. Milan Sanyal and his co-workers of Saha Institute of Nuclear Physics, Calcutta presented the basic understanding and applications of surface and interface structures of multi-layered films using grazing incidence X-ray diffraction methods. Professor T.N. Guru Row of the Indian Institute of Science, Bangalore, dealt in his article with ab initio structure determination from powder data, a major breakthrough when single crystals are unobtainable. Professors Kruger and Ungar presented the basic concepts of powder diffraction and its applications in recent problems of materials science. In a technical presentation, Dr. Stefanovic from Philips Singapore highlighted the recent developments in detector technology that revolutionized commercial powder diffractometers.

Interactive computer tutorial sessions (coordinated by Dr. Partha Chatterjee) of three to four hours duration on each of three days were participated in with great enthusiasm by eighty participants. Breaking up into several small groups, they were given demonstrations on how to handle a wide spectrum of programs. Ample opportunities for applying the new software to their own problems existed and were actively used by the eager participants.

A colourful inaugural session included fascinating items such as the garlanding of guests and the lighting of a conference lamp. In the evenings participants were treated to a classical dance cultural programme and a dinner at the Lake Rowing Club. The school was sponsored by a number of funding agencies and commercial sponsors. All participants agreed that the school was a great success and that it achieved its purpose of educating a new generation of young scientists about the new developments in powder diffraction.

Participants in front of the IACS Main Building

A lunch-time discussion involving Professor Sen Gupta (right)and some of the invited lecturers (from left around the table: Sikka, Ungar, Chatterjee, Kleeberg, Kruger, the Bergmanns)

Workshop on Practical Structure Solution from Powder Diffraction Data prior to ACA 2002, San Antonio, Texas, USA, Saturday 25th May 2002

Lachlan Cranswick, CCP14 Project, School of Crystallography, Birkbeck University of London, Malet Street, London, WC1E 7HX, UK. E-mail: l.m.d.cranswick@dl.ac.uk

Organised by Joseph Reibenspies and Sean Ouyang of Texas A&M University, plus Alexandre Yokochi of Oregon State University; and with the emphasis on live tutorials, the one day ACA 2002 powder symposium held at the Hyatt Regency Hotel in San Antonio Texas gave an overview of what is possible for people to achieve with both freely available and commercial crystallography software. Tutorials based on the talks are still available on the web at the TAMU Department of Chemistry website at http://www.chem.tamu.edu/xray/powder/powder.html. The reviewer apologises in advance for variable quality of the following photos which were taken in “no-flash”mode.

After an introduction by Joe Reibenspies, Lachlan Cranswick from the EPSRC-funded CCP14 project at the Birkbeck University of London, UK, gave an overview of available software for solving structures from powder diffraction, ranging from the conversion of raw data into useful formats, up to photorealistic rendering of the solved structure. Ranting was also heard about Variable Count Time (VCT) data collection as being something those performing powder diffraction should take an interest in.

Robin Shirley from the University of Surrey, UK gave live demonstrations of the new Crysfire 2002 powder indexing suite, and the Chekcell powder indexing helper tool. He also explained why some indexing programs apparently succeed more easily than others under a certain set of circumstances.

Fig 1: *Robin Shirley after his presentation*

Damodara M. Poojary then elaborated about conventional structure solution of structures from powder diffraction data using direct method and Patterson methods. Many of these methods have made the Texas A&M group a powerhouse of solving structures from powder diffraction data.

Fig 2: *Damodara M. Poojary*

Damodara's talk was followed by a demonstration of the new Accelrys Reflex Plus software as given by Max Petersen. Starting from scratch, with peak fitting and powder indexing, the solving of a structure could be achieved well within the workshop time restraints.

Fig 3: *Max Petersen presenting the Accelrys Reflex Plus software.*

Fig 4: *Joseph Reibenspies aerodynamically optimised presentation strategy.*

Joseph Reibenspies then proceeded to give his happy experiences of using Cheng Dong's PowderX for evaluating and indexing powder diffraction data. This was followed by his personal experiences of using the EXPO direct methods software for solving structures from powder data.

Arriving from the ESRF Synchrotron in Grenoble, France, Vincent Favre-Nicolin then gave a live demonstration of the FOX software for solving structures. While suffering the slings and arrows of the dark side of MS-Windows (instead of his preferred Linux), Vincent emphasised the features in FOX not found in other software which make it highly suitable for solving inorganic and mineral structures. As FOX is GPL'd software, it is also freely available, not only as executables, but also with source code that others can modify and expand on if they wish.

Fig 5: *Pondering penguin power? Vincent Favre-Nicolin after his FOX presentation.*

Brian Toby from NIST, Gaithersburg, Maryland, USA, gave a talk and demonstration of GSAS and EXPGUI for Rietveld refinement of structures from powder diffraction data. He also showed several additions to EXPGUI that add to the set of functions that add extra power to those using GSAS for Rietveld refinement.

Fig 6: *Brian Toby during his GSAS and EPGUI demonstrations, showing considerable Jedi skills by his skilful wielding of the symposium light-sabre.*

Using the Topas Rietveld program, Arnt Kern of Bruker AXS, Germany, showed that solving structures of the future and performing a Rietveld refinement might be one and the same by setting all atoms near 0,0,0. Arnt showed more complicated problems where Topas succeeded by applying simulated annealing and/or energy minimization.

Fig 7: *Arnt Kern controlling Topas during his symposium presentation.*

The final presentation was from Carmello Giacovazzo of Bari University, Italy, using the latest EXPO 2002. Structures that failed to solve during Joe Reibenspies' demonstration using EXPO 99, succeeded to solve with EXPO 2002.

Fig 8: *Despite Joe Reibenspies' formidable gaze, crystallographic Paparazzi manage to snap this shot of Carmello Giacovazzo during the overhead tranparencies part of his EXPO 2002 presentation.*

ACA 2002 Solving Structures by Powder Diffraction Symposium, San Antonio, Texas, USA, Tuesday 28th May 2002

Lachlan Cranswick, CCP14 Project, School of Crystallography, Birkbeck University of London, Malet Street, London, WC1E 7HX, UK. E-mail: l.m.d.cranswick@dl.ac.uk

Organised by Professor Abraham Clearfield of Texas A&M University, USA, a solid session of talks was organised (with no official time-out for afternoon tea). Abstracts of the session are still visible at http://www.hwi.buffalo.edu/ACA/ACA02/abstracts/STR01.html. Again, the reviewer apologises in advance for variable quality of the following photos, which were taken in "no-flash"mode.

Lachlan Cranswick from the CCP14 project, Birkbeck University of London, UK, (with Robin Shirley of Surrey University, UK in a reassuring supporting role), gave an overview of powder indexing history, peak profiling and the use of the latest Crysfire 2002 and Chekcell powder indexing helper tool. This included elaboration of the new Mmap facility in Crysfire 2002 for examining powder indexing solution space in two dimensional maps.

Fig 1: *Abraham Clearfield introduces the session*

Carmelo Giacovazzo from Bari University, Italy presented the latest on "Expo200~~1~~2: The New Features". Carmelo showed the power of combining the latest in direct methods algorithms with chemical crystallographic information.

Fig 2: *Carmelo Giacovazzo and Abraham Clearfield.*

Hideo Toraya from Nagoya Institute of Technology, Japan, concentrated on the structure solution of inorganic materials from powder diffraction data using direct-space methods.

With an emphasis on solving calcium silicates and calcium aluminium silicates from powder diffraction data, mention was made of the new DSS Monte Carlo software authored by Hideo.

Fig 3: *Hideo Toraya*

Differential Evolution was the main subject for Maryjane Tremayne of University of Birmingham, UK; and how it can be applied to solve organic structures from powder diffraction data. Examples of its application were shown by emphasising its use in helping solve families of polymorph structures where single crystals could not be grown in all cases.

Fig 4: *Maryjane Tremayne*

Assisting industrial requirements, using state of the art structure solving techniques, combined with good crystallographic intuition, was the intent of Jim Kaduk of BP Chemicals, Naperville, Illinois, USA. Jim focussed on the structure solution of aromatic carboxylate salts, using all tricks of the trade that can be found and applied.

Fig 5: *Jim Kaduk*

John Parise of State University of New York, Stony Brook, USA, elaborated on the possibilities behind crystal structure determination and refinement from high-pressure powder diffraction data. While outlining the technology used to achieve these high pressures, their advantages and pitfalls were also discussed.

Fig 6: *Abraham Clearfield (left) and John Parise (right)*

In the afternoon, John Parise took over the chair from Abraham Clearfield; after which Camden Hubbard of Oak Ridge National Laboratory, Tennessee, USA (and current Chairman of the International Centre of Diffraction Data in Newtown Square, Pennsylvania, USA) elaborated on the possibilities of using the ICDD database to assist in structure solution from powder data. This was closely followed by Bill David of the Rutherford Appleton Laboratory, Oxfordshire, UK showing the latest features and algorithms in the Dash software and its application in the solving of relatively complex organics, organic salts and organometallics.

Fig 7: *Camden Hubbard (left) and Bill David (right)*

Chris Gilmore of the University of Glasgow, Scotland discussed the algorithms and application of Maximum Entropy and Maximum Likelihood on powder diffraction data in defining envelopes. The interpretation of contour maps derived from these techniques was also elaborated on by using examples ranging from small organics through to powder diffraction data collected on proteins.

Fig 8: *Chris Gilmore (left), Abraham Clearfield (seated) and John Parise (right)*

Peter Stephens of State University of New York, Stony Brook, USA, discussed the options of the open source PSSP software for solving organic structures from powder diffraction data. Peter encouraged anyone who was interested and motivated in trying to solve organics from powder data to try it out.

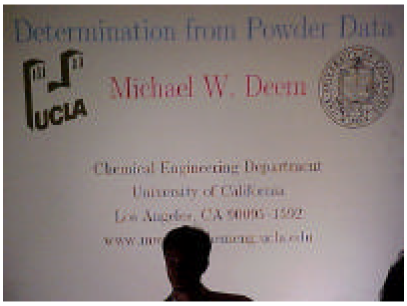
Fig 9: *Peter Stephens, also showing the power and flexibility of his table assisted laser pointer technique.*

Rob Grothe from the Howard Hughes Medical Institute, Los Angelos, California, USA presented work on the use of area detector for collecting data in the solving of amyloid-forming peptide structures from powder diffraction. Much use is made from getting the most out of the preferred orientation of the samples.

Fig 11: *Rob Grothe (left) and Joe Reibenspies (right)*

Finally, Peter Stephens presented Bob von Dreele's talk on Proteins and Synchrotron X-ray Powder Diffraction (Los Alamos Laboratory, New Mexico, USA). He showed the power of GSAS in using stereochemical restraints and powder data to solve a previously unknown protein crystal structure. Examples were also shown of the features visible in difference electron density maps in being able to identify the position and orientation of the bound ligand in some of the proteins studied.

The changing algorithms in the GPL'd ZEFSA II for solving zeolite structures from powder data was discussed by Michael Deem of UCLA, Los Angelos, California, USA. The power of biased Monte Carlo combined with parallel tempering has resulted in the ZEFSA II software being able to solve all relevant zeolite structure types, with the implication that it should be able to handle any novel zeolite structure types encountered in future.



Determination from Powder Data

Michael W. Deem

UCLA

Chemical Engineering Department
University of California
Los Angeles, CA 90095-1592

Fig 10: *Harking back to a simpler time, before life was cheapened by heartless metal machines (and Microsoft Powerpoint), Michael Deem (in silhouette) presents his talk via overhead film noir transparencies.*

Professor X-ray Ted does AXAA 2002, University of Newcastle, New South Wales, Australia, 11th to 15th February 2002

By Professor X-ray Ted (laboratory icon), University of Bearuit, Melbourne, Australia

Being of a horticultural bent, I have been known to do odd jobs in the woods. However, work occasionally calls on my attendance at distinguished gatherings; the latest being the Australian X-ray Analytical Association (AXAA) Schools and Conference. This was held at the University of Newcastle (north of Sydney), New South Wales, Australia from 11 to 15 February, 2002.

Fig 1: *Professor X-ray Ted during the AXAA 2002 Conference Dinner*

Apparently, following 4 days of XRD/XRF schools and conference talks, showing some of the latest methods and vendor hardware, there was the conference dinner - after which my professorial memory becomes even more vague. Was it all just an alcohol sodden dream?.

Fig 2: *Professor X-ray Ted with Cam Hubbard and Brian O'Connor during the AXAA 2002 Conference Dinner*

Fig 3: *Professor X-ray Ted sees a mentoring opportunity and shares his much noted words of wisdom. Prof. Ted also wishes to point out that, despite appearances, all interactions were of a purely professional nature!*

No! As a picture tells a thousand words, following are some photographs of the more important parts of the conference. Not surprisingly to those in the know, all contain me, taken by the local X-ray analytical Paparazzi-who are forever relentless in stalking my very person

Fig 4: Still standing! (well maybe sitting): *Professor X-ray Ted at the AXAA 2002 Conference Dinner*

Fig 5: *Professor X-ray Ted hob-nobbing it with the crystallographic nobility prior to the AXAA 2002 conference. In this photo, he converses with the famed Count Geiger-Müller.*

WHAT’S ON

The following web-site contains an up-to-date and semi-exhaustive list of conference and workshops in crystallography and related areas.
http://www.iucr.org/cww-top/mtg.date.html

1st – 6th September 2002
IMA2002 - International Mineralogical Association
Edinburgh International Conference Centre
Edinburgh, Scotland
Web: http://www.minersoc.org/IMA2002
E-mail: ima-abstracts@minersoc.org

4th – 7th September 2002
40th European High-Pressure Research Group Meeting
David Hume Tower, Edinburgh, Scotland
Web: http://www.ph.ed.ac.uk/EHPRG-40/
E-mail: EHPRG-40@ph.ed.ac.uk

2nd – 5th November 2002
USTHB, Algerian Crystallography Congress
Algiers, Algeria
Web: http://www.iucr.org/cww-top/mtg.date.html
E-mail: alcris@usthb.dz

8th – 12th December 2002
The Second Pharmaceutical Powder X-ray Diffraction Symposium PPXRD-2
Best Western Concordville Hotel and Conference Center, Concordville, Pennsylvania, USA
Web: http://www.icdd.com/ppxrd/
E-mail: ppxrd@icdd.com

4th – 15th June 2003
International School of Crystallography: High Pressure Crystallography
Erice, Sicily, Italy
Web:http://www.geomin.unibo.it/orgv/erice/highpres.htm
E-mail: paola.spadon@unipd.it

26th – 31st July 2003
American Crystallographic Association Annual Meeting, ACA 2003
Northern Kentucky Convention Center,
Cincinnati, Ohio, USA
Web: http://www.hwi.buffalo.edu/ACA/
E-mail: jeanette.krause@uc.edu

4th – 8th August 2003
Denver X-ray Conference
Denver, Colorado, U.S.A
Web: http://www.dxcicdd.com/03/
E-mail: webmaster@icdd.com

10th – 13th August 2003
AsCA'03/Crystal-23 : Asian Crystallographic Association and the Society for Crystallographers in Australia and New Zealand (SCANZ)
Cable Beach Club resort, Broome, W.A Australia,
Web: http://www.crystal.uwa.edu.au/CrystalsDownUnder/
E-mail: srh@crystal.uwa.edu.au

24th – 30th August 2003
21st European Crystallographic Meeting
International Conference Center, Durban, South Africa
Web: http://www.ecm21-africa.co.za/
E-mail: jboeyens@postino.up.ac.za

31st August – 4th September 2003
XIX Conference on Applied Crystallography
Krakow, Poland
Web: http://crystallography.us.edu.pl
E-mail: dana@us.edu.pl

4th – 7th September 2003
Summer School on Polycrystalline Structure Determination by Direct Methods
Krakow, Poland
Web:http://www.us.edu.pl/univwersytet/konferencje/2003/cac/tekst/index.shtml
E-mail: dana@us.edu.pl

2nd – 5th September 2004
9th European Powder Diffraction Conference (EPDIC 9)
Charles University in Prague, Prague, Czech Republic
Web: http://www.xray.cz/epdic
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Call for contributions to the next CPD Newsletter (No 28)

The next issue of the CPD Newsletter will be edited by *Paolo Scardi*, to appear in December 2002. Paolo 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 28 (addresses are given below)

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