TRENDS IN STRUCTURE DETERMINATION BY POWDER DIFFRACTOMETRY

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Abstract

Techniques for solving structures from powder diffraction data have considerably evolved during the last 10 years. Tendencies are deduced from an exhaustive review of the SDPD-Database, a bibliography extending over more than 300 experimental cases. Last year, it was said that the Rietveld method allowed refining structures more complex than we could determine solely from powder data. Recent advances show that we can now locate molecules more complex than we could refine without constraints.

1. Introduction

During the past 10 years, the number of structure determinations by powder diffractometry (SDPD) increased from 28 to more than 300. A commented bibliography (the SDPD-Database), available on Internet [1], allows drawing some conclusions on current tendencies. Quantity is not quality, so that you may not consider that the leading methods deduced from the following statistics are really representative of the ways people can best solve their problems. Nevertheless, many methods and softwares listed below have proven their efficiency for succeeding in the various steps of the process of solving structures from powder diffraction data routinely. “Routine” means, in the author opinion, that the job can be done by any crystallographer in any lab in the world, not only by the method inventors. There was no reason that major trends in crystallography would not have affected the SDPD sub-discipline. One irreversible tendency is that normal human brains are no longer able to realize the calculations needed for a non-trivial structure determination. More and more fast and powerful computers do the job. Fortunately, humans having not found limit in that domain continue to conceive new software as well as hardware. A trend in SDPD is thus clearly the emergence of sophisticated methods that would not have been applicable if the power of cheap computers had not increased so much. How many times (at least, as found in the SDPD-Database) some methods and softwares were applied to experimental cases will be given along the text, under parentheses. Note that several methods for solving one particular step may have been used in the same study.

2. Statistics on productivity, peoples, reviews

If we consider the UCl_3 structure determination by Zachariasen [2] as the first work of this kind, it appears that 1998 is the SDPD jubilee. Uranium and plutonium-based compounds were the subject of three other publications [3-5], till 1968. We waited 1977 for the first modern SDPD by Berg and Werner [6], making use of computers for indexing (TREOR), applying the Patterson method to 120 integrated intensities (Guinier-Hägg film), locating 2 heavy (Mo) atoms, completing and refining the structure by successive Rietveld refinement and Fourier calculations. According to the SDPD-Database [1], up to 1987, only 27 publications coped with structure determination by powder diffractometry. The annual production in this early stage was ranging episodically from 0 to 4 papers maximum. During the year 1988, a peak occurred with 12 papers, and then the annual production was more or less stable till 1992 showing a new expansion corresponding to 29 publications. The yearly production oscillated then, with 22, 40, 55, 34 and finally 46 papers in 1997. These publication numbers correspond to slightly more structures determined (Fig. 1). The jubilee coincides with exceeding 300 structure determinations (at least 318 structures described in 295 papers). These numbers are underestimated because some trivial (including many structure determinations based on isotypism) and pre-Rietveld structures were not included in the SDPD-Database.

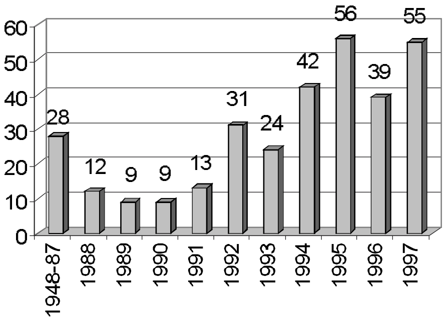

Fig. 1
Structures determined by powder diffractometry

As many as 570 peoples are authors or co-authors of these 295 papers. Among them, 170 have co-authored 2 papers minimum, 41 have co-authored at least 5 papers, and 17 at least 10 papers. These contributions attest for an increasing professionalism and give an idea of the mass of researchers motivated by solving structures in the absence of a suitable single crystal. The two leaders (Clearfield and Poojary) have solved together 33 previously unknown structures. Obviously, SDPD was and remains hot topic since now 10 years. It is hard to say if the two abrupt variations in publication numbers (1988 and 1992) have some team-leader precise detonators. Possibly, following the Werner [7-11], Rossel [12], Noläng [13], Raveau [14-16], Smith [17] and Clearfield [18-19] early series of SDPDs, the 1988 peak could be due to a new series of papers published then in *Nature* by Cheetham [20-21]. Popularity and temperature of SDPD can be also measured by the number of review papers already published on the subject (33 references are gathered in the database, of which only a selection is proposed here [22-44]). These reviews may provide different colors of SDPD, according to the authors main specialties. Solving metallo-organic phosphates [43], metal hydrides [35, 42], zeolites [27], coordination compounds [44] (...) crystal structures with conventional X-ray sources [24, 33], synchrotron [30, 31, 37] and neutron data [28], by direct method [41], Monte

Carlo [40] or other methods do have some peculiarities. None of the previous reviews gave the exhaustive list of references available at their publication date, although it was much shorter than now. A complete list of references on experimental works, methods and softwares would be larger than 500 and will not be given here. The reader will find them in the SDPD-Database, including works involving structure redeterminations for the purpose of feasibility demonstration (20 publications listed in the SDPD-D). The most famous of these already known (AK) compounds is cimetidine [45], $C_{10}H_{16}N_6S$, having long been given as the example of what could be done from synchrotron data (1991), with 17 non-hydrogen atoms located by direct methods. This limit was attained in cases of previously unknown structures since, even from conventional X-ray data, though it was not much outperformed.

3. More statistics on periodicals, compounds, crystal systems, instruments

The 295 papers are distributed in 51 periodicals of which 18 have published more than 5 SDPD, and 9 have published more than 10 SDPD. Two journals are largely heading : the Journal of Solid State Chemistry and the European Journal of Solid State and Inorganic Chemistry, with 67 and 32 contributions, respectively. This tends to indicate the main kind of problem solved by powder diffraction, up to now. Indeed, only 31 organic, 63 organometallic and 8 polymers have been the subject of a SDPD. This may be considered as abnormal because of the almost reversed organic/inorganic 4/1 ratio in the Cambridge Structure Database (CSD) and in the Inorganic Crystal Structure Database (ICSD, excluding compounds with C-C bonds). Most of the 216 inorganic phases are oxides (159), the remaining being mainly halides (43) and intermetallics (12). Oxides based on tetrahedra building units represent 90 compounds with 73 in the group of phosphates, sulfates and arsenates, and 17 silicates. The next well-identified group are nitrates (12) studied mainly by Louër 's group. Why these compounds are special candidates for a SDPD is an interesting question. Most of them were obtained from syntheses involving hydrothermal process at medium temperatures, unfavorable to the growing of sufficiently large single crystal, or dehydration leading to unavoidable fragmentation. It is not risky to predict that the future will very probably see the reversal of this current 1/4 ratio in order to fit the 4/1 proportion of organic/inorganic compounds observed in the CSD/ICSD databanks. Arguments in this sense will be given.

All crystal systems were the subject of SDPD, the monoclinic and orthorhombic systems being the more generally studied with 42.5 and 29.7%, respectively (Fig. 2). The crystal system repar-

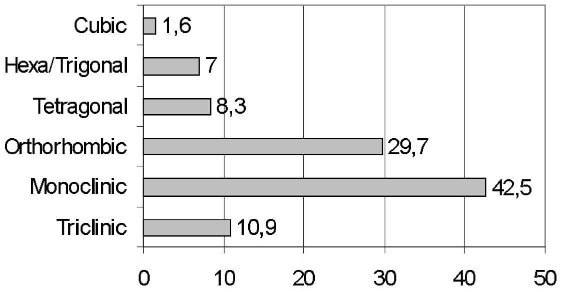

Fig. 2 - Crystal systems (%)

tition for these modern powder studies does not seem to differ from single crystal studies.

Instruments selected for these SDPD are traditionally located at either neutron reactors (65) or at synchrotron radiation sources (64), or are in-laboratory conventional X-ray diffractometers with (94) or without (143) incident beam monochromator. Graphite reflected beam monochromator allows the study of samples containing 3d element with a copper X-ray tube. Monochromatic conventional X-ray is obviously reserved to non-fluorescent samples (containing either light or very heavy elements, or both of them). However, if the use of Peltier-cooled solid-state detectors is generalized, this distinction could vanish. The Figure 3 shows the repartition of instrument use by year. In fact these numbers do no reflect the possible joint use of 2 or 3 of these instruments. Neutrons were used scarcely alone (22), many neutron cases correspond to studies of liquid-solid state phase transitions at low temperature (Fitch and Cockcroft, [46-55]), or to deuterium and lithium-based compounds. Obviously, the most complex structures will soon be solved from synchrotron data. We should first agree on what is a complex structure and define complexity criteria. Anyway, conventional X-rays have not really been outperformed yet by synchrotron radiation in quantity (237 and 64 applications, respectively) nor in quality (no real gap in complexity is observed, although it should be). These points will be treated further in this review.

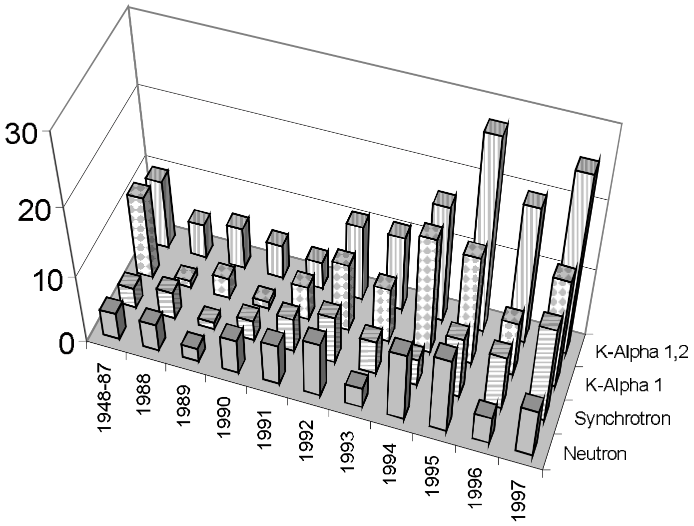

Fig. 3. Instruments

4. SDPD steps - summary

SDPD is a step by step operation where computers are essential at stages of (a) indexation, (b) structure factor extraction, (c) structure factors selection and massaging, (d) application of Patterson or direct methods, (e) model completion, and (f) Rietveld method refinement. Beside this classical approach, when initial models are known from other techniques than crystallography (molecule from NMR), stage (d) may be replaced (d') by using methods that try to find an optimum position for a starting model/fragment inside the cell. Testing a molecule location is realized by comparison of the corresponding calculated diffraction data either to the extracted "$|F_{obs}|$" or to the whole (or large part of) observed powder pattern (suppressing the need of stages b and c). Only stages (a, b, c, f) are fully specific to powder diffraction methodology. Stages (d, d', e) may be realized by using single crystal softwares applied to extracted structure factors. Adapted single crystal softwares may work on the whole powder pattern instead of extracted structure factors. Moreover, some powder-specific modifications were introduced for dealing with overlapping reflections.

4.1 Indexation

Automatic indexing is not actually a very innovative field. Three main well known programs traditionally occupy the market : TREOR (111 applications to SDPD), ITO (90) and DICVOL (42). The next most applied technique is electron diffraction (11). Difficulties to index powder patterns of which you are not even sure than they represent a pure phase has discouraged many people to determine structures from powder data, in spite of the extreme efficiency of the above programs. Recommendation is to use all of them. DICVOL is exhaustive in its search, but does not tolerate unindexed reflections, which could be due to an impurity in weak proportion. In principle one cannot go further if this essential step is not fulfilled successfully, so that we have here undoubtedly a well established trend (but see structure determination from packing considerations below, at the d' stage).

4.2 Structure factors extraction

At heroic times, structure factor extraction by hand was not rare (cutting peaks on the recording paper by using scissors, and weighting them), or more sophisticated, by using a planimeter. In a quite early (1971) systematic approximate method for the determination of structure factors from a powder diffractogram, the profile shapes were described as triangles. The method was applied to the solution of the structure of metavariscite (AK) [56]. Nowadays, mainly the Pawley (43), Le Bail (134) or Rudolf and Clearfield (20) methods realize this stage. A trend is that the two first methods are used also in order to check the correctness of cells proposed at stage (a), rather than using the classical cell parameter refinement from estimated reflection positions. The space group proposition is now also generally checked at this stage. Possibly due to a better stability and faster execution, the Le Bail method (LB) dominated over the last 6 years (Fig. 4).

Although the method (P) was described in 1981 [57], the first application to an experimental case occured in 1987 [58]. The LB method was mainly used by the author and co-workers during 4 years (ARIT Software) [59-72], although also soon available at the

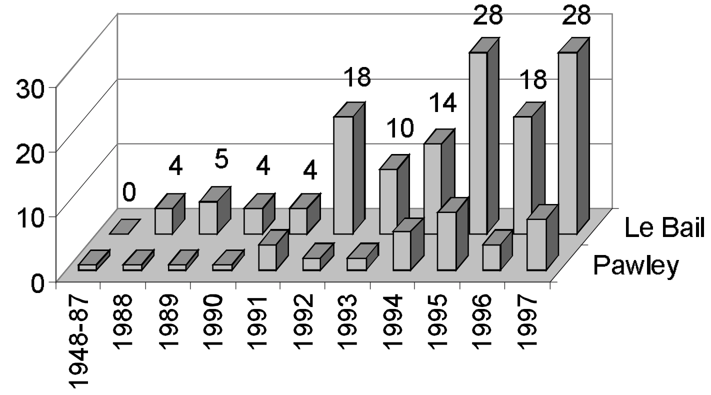

Fig. 4. Structure factors extraction : Pawley and Le Bail methods

ILL, introduced into the FULLPROF software [73] and disclosed at the Powder Diffraction satellite meeting of the IUCr XVth Congress [74]. The abrupt increase of the SDPD application number in 1992 (13 →31) coincides with the availability of this method in a series of Rietveld softwares (compare Figures 4 and 1), including GSAS, MPROF and some unnamed ones gathered as "LBM". One is thus tempted to attribute a part of the merit in the 1992 increase in SDPD applications to the LB method availability, with 18/31 of those year applications. These applications included some remarkable works like $Ga_2(HPO_3)_3{\cdot}4H_2O$ [75] with 29 independent atoms, the most complex at this date, and from this point of view ; τ-AlF_3 [76] with a completely new and unexpected structure built exclusively from corner sharing octahedra.

Both P and LB methods allow whole powder pattern fitting with cell constraint. The difference comes from the consideration of intensities as independent refinable parameters (P) or not (LB). Thus, extracting 1000 reflections by the P method imposes 1000 parameters to be added to the usual (Rietveld) profile parameters. In the LB method, the structure factors are extracted by iterating the Rietveld decomposition formula giving the so-called "$|F_{obs}|$" which are used for estimating the Bragg R_B as well as the R_F reliability factors. Starting structure factors are constrained to be identical. This relation with the Rietveld method explains the easy introduction of the LB method in numerous Rietveld codes. Those principles applied in the P and LB methods were thus adopted by many softwares, the main of which are listed in Figure 5, giving the number of applications for each of them, as found in the SDPD-Database.

Alternative is to use softwares extracting structure factors without cell constraint. The most popular is MLE (Maximum Likelihood Estimation) from Rudolf and Clearfield. On the Figure 6, PD is meaning Pattern Decomposition, and corresponds to 15 publications, which were not providing the name of the softwares, but explicitly indicated the method for obtaining integrated intensities. To be noted is the low score of POWLS (one application), a program proposed in the past for the so-called two-stage alternative to the Rietveld method. Discussions on the P and LB methods, including comparisons of their respective efficiencies were published [41, 77-81]. Improvements were proposed including either a Bayesian approach that tackles the problem of highly correlated positive and negative intensities in the P method [82] or another stabilization algorithm [83]. The current rate of use of the P and LB methods and of related algorithms does not indicate any tendency to abandon them, on the contrary.

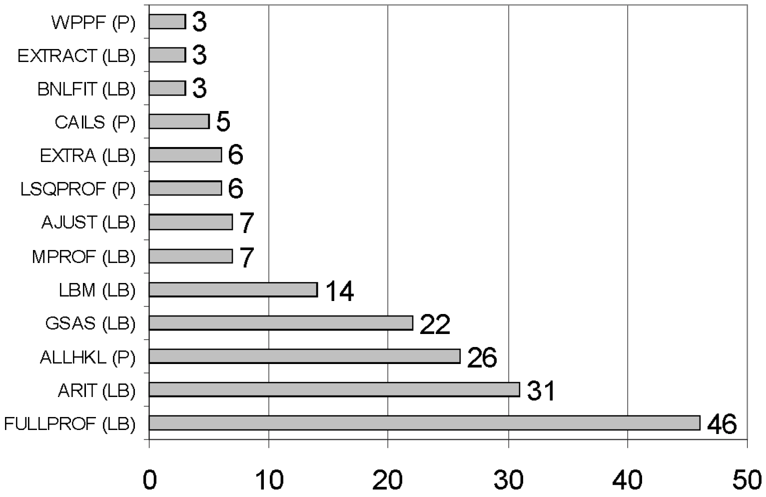

Fig. 5. Softwares for structure factors extraction with cell constraints (P = Pawley, LB = Le Bail)

4.3 Structure factors selection, treatment of overlapping reflections

Many variants exist at this stage. Either the whole data set (in 141 experimental cases) is used or a selected set of unambiguously indexed reflections (80) is reserved for the next (d) step. At this step, the problem of the intensity repartition among reflections, which are more or less overlapping, is considered. No need to say that you can hardly expect to obtain the correct intensity estimation of the exactly overlapping reflections. The default output of the P and LB methods is the equipartition (but see later comments about the GSAS program implementing a variant of the LB method, and note the tendency of the P method to produce negative intensities when the slack constraints are not used appropriately). Alternatively, the data may be further modified, after extraction, by methods trying to extrapolate knowledge from a selected set of non-overlapping reflections

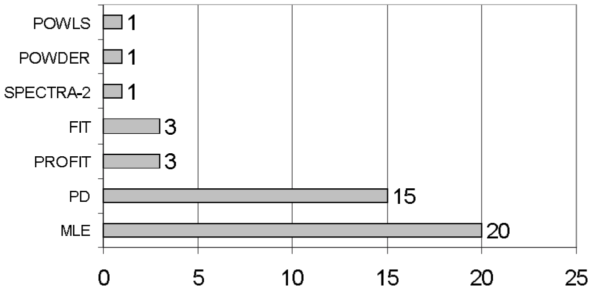

Fig. 6. Softwares for structure factors extraction without cell constraints

in order to discriminate and change the intensity repartition between those more or less overlapping reflections. Many artifices were used, including for instance giving a random repartition of intensity instead of equipartition, or using the expected positivity of the Patterson map. David [84] based his estimates on the entropy maximization of an $|F|^2$ Patterson function. Use of Patterson map is also made in the FIPS (Fast Iterative Patterson Squaring) method [85]. In the DOREES program [86], the approach is based on the triplet and quartet relations from direct methods and the theory of the Patterson function. In the direct methods SIRPOW program [87-88], a special treatment is reserved to the more or less overlapping reflections. Texture was also used as an intensity-separating ‘device’ [89] in an attempt at partial elimination of the problem of overlapping reflections. A probabilistic method was integrated with the LB algorithm [90]. Finally, Patterson informations are also used in reference [91]. The simplest approach is the preparation of a series of data sets from which reflections having a neighboring one at less than $\delta(2\theta)$ (with $\delta = 0.01°$, 0.02°, 0.03°..., or fractions of the FWHM varying from 0.1 to 0.5) are excluded. Direct methods are then applied to these reduced data sets (with a limit corresponding to 50% maximum of the hkl excluded), or Patterson methods (up to 80-90% of the reflections can be excluded if 1 or 2 heavy atoms maximum are to be located). All these methods may enhance the success rate for structure solution. Nevertheless, a comparison of the efficiency of these approaches is lacking. The SDPDRR (Structure Determination by Powder Diffractometry Round Robin) [92] could draw some conclusions on this point. Anyway, it seems that in almost half of the SDPDs (141 cases), the whole extracted “$|F_{obs}|$” data set, with equipartition, led to the success without any data massaging.

4.4 Solving the structure by direct or Patterson methods

For this more than essential SDPD step, authors have simply adopted the general trend in structure determination from single crystal data, by using Patterson (104 cases) and direct methods (149 cases), including their most recent improvements. For instance, the new SHELXS-97 includes phase annealing direct methods and new developments in Patterson interpretation. SHELX programs are used in well over than 50% of small molecule structure determinations from single crystal data as well as from powder data (versions SHELX-76, SHELXS-86 or 97). The main softwares used for Patterson and direct methods are shown in the Figure 7.

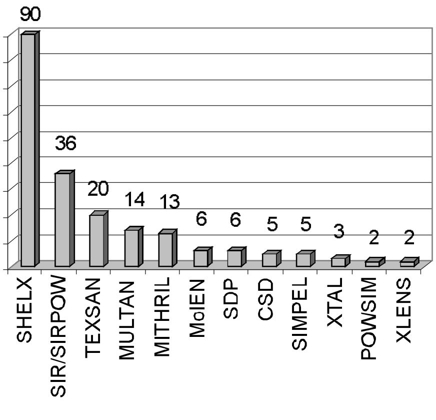

Fig. 7. Softwares for Patterson and direct methods

It should be realized that in many cases, only one or two heavy atoms had to be located for obtaining a partial model allowing to start refinements, the location of the remaining atoms being then obtained by Fourier difference syntheses. There are 99 of these simplest cases in the SDPD-Database. In 17 of them, the heavy atom is zirconium. Other frequent occurrences are for lanthanides (7 cases), U and Bi (6 for each of them), Ba, Mo, Pd (4), Ag, Tl (3). Solving these rather trivial structures was even possible by Patterson method applied to a very limited range of data : 30 or 40 intensities may suffice, obtained from those reflections unambiguously indexed of which the integrated intensities can be extracted by the old generation of profile fitting softwares without cell constraint (POWLS, PROFIT, MLE...). In the years 1948-87, Patterson method dominated the direct methods with a ratio 16/6. Since 1988, the tendency is reversed with a ratio 79/139. The SDPD-Database contains 18 structures guessed from some convergent informations (for instance there could be 4 Pt atoms occupying obviously only one possible special position with all fixed coordinates). Model building methods concern the 51 remaining structures in the Figure 8. With single crystal data, estimated standard deviations of structure factors are used by most Patterson and direct method softwares only in order to exclude reflections with a limit generally set to $|F_{obs}| < 2\,\sigma(|F_{obs}|)$. The LB method is reputed for not providing correct esds. I recommend to avoid any "$|F_{obs}|$" elimination based on esds, whatever the method used for structure factors extraction, this would exclude the very important information (for direct methods) contained in weak reflections.

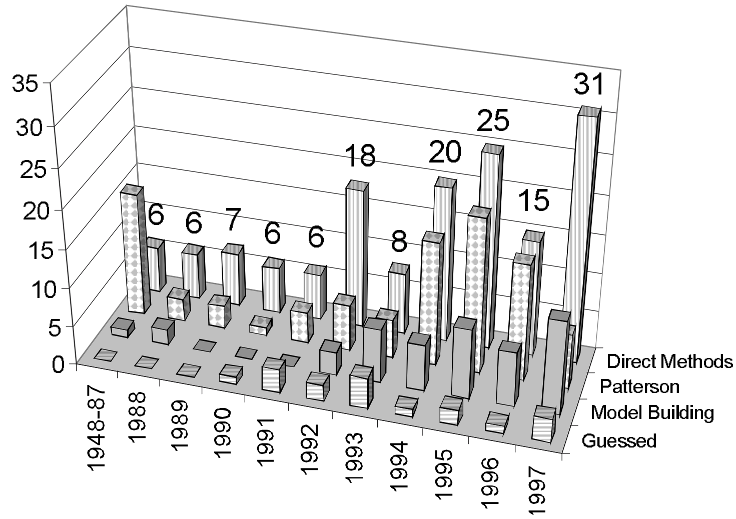

Fig. 8 Methods for structure solution

Recent review articles on direct methods applied to powder data may be found [41, 93]. Use of Patterson and direct methods rules for an alternative to the equipartitionning of the overlapping reflections was already discussed at the previous paragraph. The dominant position, in this field, of the program SIRPOW is clear on Figure 7, however application of conventional direct and Patterson methods for single crystal data are still heading (SHELX, and to a lesser extent, TEXSAN, MULTAN, MITHRILL...). Other special adaptation of direct methods for solving structures from powder diffraction data were proposed, namely a multisolution method of phase determination by combined maximization of entropy and likelihood (program MICE) [94-99], dividing data in two sets (overlapping and non-overlapping). It was scarcely used for the determination of unknown structures, up to now [100 - 101]. Special adaptations of the Patterson method were applied, using maximum entropy Patterson maps [102] and symmetry minimum function [103 - 104], and a tangent formula was derived from Patterson-function arguments [105]. Aspects of structure determination from powder data using anomalous scattering were considered [106-109], requiring access to synchrotron radiation and recording at multiple wavelengths. Application to direct methods of the early finding of preferred orientation was examined [110]. Direct determination of polymer crystal structures from fibre and powder X-ray data was considered [111]. A weighting scheme lowering the probability of phase relations for intensities of overlapping reflections was introduced in the optimal symbolic addition program SIMPEL88 [112]. But no trend is obvious, for this step, that the classical approach (i.e. using directly softwares developed for single crystal data) will be soon removed from its dominant position by some clearly more efficient approach.

4.5 Model building (MB), locating fragments of known or guessed geometry

When standard methods fail (Patterson and direct methods), the alternative is to build a model and to locate it in the cell. This could be either a simple or a formidable task, depending on the existence or not of prior informations. Locating fragments of known geometry was long ago used in single crystal studies of organic compounds. Prior information may consist in the whole connectivity scheme of a molecule from NMR data. On the other hand, inorganic phases allow also some guess when the basic structural units are known or obvious (tetrahedra, octahedra...) and moreover if the connectivity of these units is evident (for instance exclusive corner sharing of [SiO_4] tetrahedra in compounds having basically SiO_2 formula, like in zeolites). It is in this (d') stage that the last ten years of SDPD were particularly innovative. No less than 20 new methods or transposition of existing (single crystal or molecular modelling) methods recently emerged for solving structures from powder data. The list, as found in titles of recent papers, is reviewed below, but the reader should keep in mind that the present author has never used any of them ! Some methods have evolved and improved over the years. This (d') sub-topic is quite hot because pharmaceutical or other economically important compounds are potentially involved. Is model building/locating specific to powder diffraction? Absolutely not, one could apply these methods also to single crystal data set, of course. A total of 51 cases were found in this category in the SDPD-Database, since 1988. A tendency to expansion is obvious, with 12 cases in 1997. The basic difficulty in these approaches is in fact to define the starting model ; most of those model-location methods have a role to play only when this difficulty has been solved. We are between prior chemical knowledge and full model prediction.

1- Early studies. In pioneering works, models were guessed (more or less) from convergent evidences. Once models are built, they can be optimized by various means like the distance least squares program () [113] or some energy minimization tools. It is not always easy to understand how the models were built before being optimized in some works classified in this MB category [46, 114]. Packing considerations on the heavy atoms were used to solve the structure of two lanthanum palladium oxides [115]. The 4 SDPD cited above were published before 1988 and are the first ones in this category. Many of the subsequent approaches of this kind cannot be easily summarized, here is an example for a metal-substituted aluminum phosphate catalyst [116] which was “solved on the basis of evidence garnered from high-resolution electron microscopy, electron diffraction, and other methods including energy minimization”..."A consideration of possible frameworks of appropriate dimensions and with the observed size and spatial distribution of unidimensional, large-pore channels suggests a trial structure with idealized symmetry Cmcm". In this case, DLS and METAPOCS programs [117] were used for the model optimization. Numerous other SDPD succeeded by this kind of model building [118-126], for which the optimization of the starting models was derived either from the above programs or from MNDO calculations [129], or CERIUS [130], or THEO, or INSIGHT-II [131].

2- Model location without energy minimization. When an initial model is selected, which should be sufficiently large for leading to calculated structure factors or Patterson map or phases evaluation near of the observed ones, then the only problem is to locate this initial model into the cell. The PATSEE program [132] is an old SHELX companion. It was applied to powder diffraction data [133-134]. The program requires extracted structure factors and attempts to combine the merits of both Patterson and direct methods in order to position a fragment of known geometry in the unit cell. Random rotations may concern one fragment and the program allows one torsional degree of freedom. The random translation search may locate up to two independent fragments of any size. Early works in this model-location category consisted in the brute force : searching for a molecular position and orientation following a systematic grid search, as in the cases of solid CF_3I [53], $CFCl_3$ [55], or RS-camphor [135]. Sometimes, retaining a proposition before trying a Rietveld refinement was based on interatomic distances criteria : i.e. packing considerations. The ROTSEARCH program [136-137] allows rotation and translation Patterson searches, checked against extracted intensities. It was applied to the solution of zeolite and organic compounds [138-140]. A recent version (ROTS96 [141]) was able to locate 3 independent molecules in $C_{16}H_{22}N_6$ [142]. P-RISCON is a real-space scavenger program [143] capable of setting an initial rigid model by refining the fractional coordinates of its center of mass and its angular orientation, using extracted intensities for checking [144-146]. A search for the model position may also be found in the structure determination of $C_{60}Br_{24}(Br_2)_2$ [147]. More sophisticated approaches in optimization of known fragment location include simulated annealing or the related Monte Carlo (MC) algorithm. The MC efficiency was demonstrated by the determination of known [148-151] as well as unknown [149, 152-158] structures using programs assessing the suitability of the model location on the basis of the agreement with the experimental diffraction data (no need to extract structure factors). Variants have incorporated restrained relaxation of the molecular geometry or a high degree of molecular flexibility or were said to be generalized (OCTOPUS96 and OCTOPUS97 programs). Do not forget that the model has to be known when dealing with these methods. Even more sophisticated, maybe, are methods applying simulated annealing, possibly through a genetic algorithm

(GA), because a set of internal coordinates defines the geometry of the molecule (the conformation), allowing torsional angles to vary (in addition to the usual external degree of freedom defining position and orientation). The use of GA was developed independently by two teams and applied either to already known [159-160] (program "GAP") or unknown compounds [161-162]. Testing the agreement between the postulated structure and the experimental diffraction data was either on extracted structure factors (using the Pawley method) or on the full powder pattern (program "GAPSS").

3- Model location from crystal packing considerations. Computational methods, which predict possible crystal structures on the basis of the molecular structures, were applied to powder data [163]. Even more, the A modification of guanylhydrazone structure could be determined without knowledge of the lattice parameters and crystal system. For a packing-based structure determination, indexing is not essential, however it is very useful in reducing the amount of computations by restricting the packing to a limited number of space groups. Nevertheless, the powder pattern remains essential for a confirmation of the model, of course. An inconvenience of this method is that the whole molecular structure should be known otherwise packing consideration would not apply. In this category, but using the prior knowledge of cell dimension and spacegroup, may be classified various methods for computer prediction of molecule location (still without the need of intensities), by packing energy calculation [164] (on AK samples) ; computational chemistry techniques [165-167] (3 AK samples, one with previously large R = 20% powder result) ; minimization of the crystal-lattice potential energy calculated with semi-empirical atom-atom potentials [168] using the PMC program [169]. Finally, the systematic ranking of all potential packing arrangements on the basis of lattice energies was shown to be efficient on AK samples [170].

4- *Ab initio* prediction. Most experts believe that crystal structure prediction from a given combination of elements is still a faraway goal. Easier, prediction by simulated annealing starting from unit cell dimensions and content has progressed for simple systems [171-172]. The more complex structures are predicted when the prior knowledge of symmetry is added [173].

To be classified as hybrid approaches or new concepts are the combination of chemical information and powder diffraction data in an automated structure determination procedure for zeolites (Fourier recycling with a specialized topology search) [174-175] and the use of a pe-

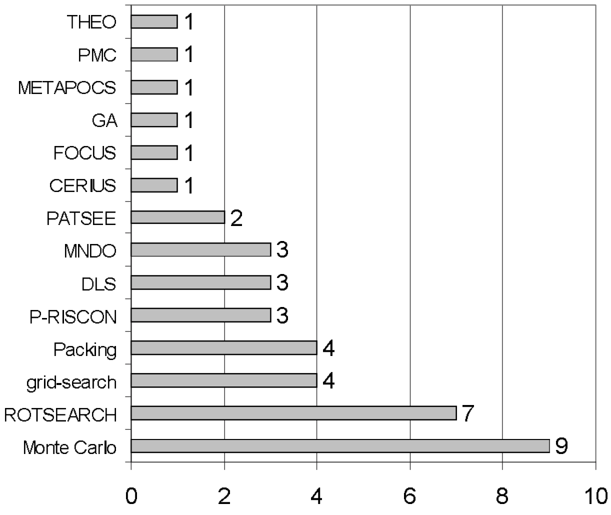

Fig. 9. Model building/location, softwares and methods

riodic nodal surface calculated from a few strong, low-index reflections to facilitate structure solution [176]. A summary of these 51 applications of model building-location methods to unknown structure is shown in Figure 9.

The dominant trend is given by Monte Carlo and Patterson-search methods. These programs for molecule location are seldom in the public domain. However, they are quite recent and could be methods for the future. Most of them are specifically designed for organic compounds and they cannot be applied if at least a large part of the structure is not already known. Trends are in adding flexibility to the starting models. The use of genetic algorithm appears currently to be the most sophisticated approach, giving freedom to non-rigid molecule parts. Anyway, the impact of these methods on the routine analysis is small. Some methods were applied to the solution of AK structures [177] and still not to any unknown one. Each of the above method is claimed to possess advantages that are considered as inconveniences by others. For instance : avoiding structure factor extraction is times to times considered as being an advantage because the use of the full pattern overcomes overlapping problems ; working on extracted structure factors is considered as an advantage for speed ; those predicting the position of molecules without the need of intensities at all find this an advantage (although few people will trust such results alone) ; those working on molecule packing underline that they even do not need the cell parameters (anyway, they always make a Rietveld final refinement). Finally, some current sophisticated model location approaches are no more than the old good “trial and error” process, modernized for making high numbers of trials in small times.

4.5 Structure completion

Structure completion is usually performed by Fourier syntheses applied to “$|F_{obs}|$” provided by the Rietveld decomposition formula. Few users (147) are really explicit on softwares used to realize this step. Not many Rietveld softwares are able to give a Fourier synthesis as output. GSAS and XRS-82 are part of them; this explains their presence in the Figure 10. The great majority of the other softwares are directly issued from single crystal packages. Again SHELX dominates (SHELX-76, -93 or -97, or -TL). When a big molecule is located from 100 or 300 reflections, and the structure is rigid-body refined, or is refined with many restraints up to $R_B < 5\%$, then it is normal that Fourier difference synthesis does not reveal any residual. Sometimes, Fourier syntheses remain also silent with large R_B value, so that one may have to guess the position and nature of a few last atoms. Using software like DLS-76 or softwares allowing holes location or making use of maximum entropy [178] possibly help the guess.

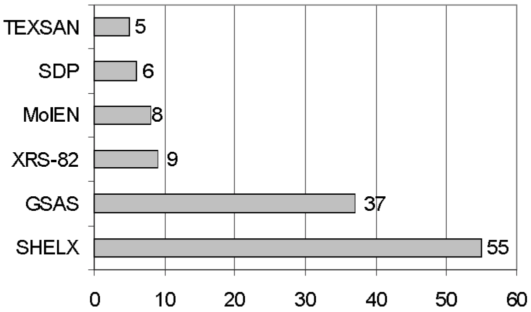

Fig. 10. Softwares for Fourier syntheses

4.6 Final Rietveld refinement

GSAS (with 84 applications) and FULLPROF (57) programs dominate the Rietveld [179-180] refinement last stage, as shown in Figure 11. Five other softwares totalize more than 6 applications, and 20 softwares (whose names are not reported here) were applied 1 to 5 times. In 12 cases, there was no Rietveld refinement at all, the final least squares being realized on the integrated intensities by using single crystal softwares. At the structure factor extraction stage, the GSAS/FULLPROF ratio was reversed (22/46 instead of 84/57 here), this point merits some explanation. The LB method is supposed to iterate the Rietveld decomposition formula starting from a set of all identical |F| values, and this is achieved in many Rietveld softwares including FULLPROF. Another approach is used by GSAS, that consists in generating the initial |F|s from intensities corresponding to a dummy atom, the position of which depends on the user decision. Using an atom in general position is highly recommended, because the LB method may encounter difficulties to change null structure factors (they will stay at zero after each iteration unless an additional process changes their value). Anyway, the exactly overlapping reflections will keep an intensity ratio equal to that generated by the dummy atom. The equipartition of strictly overlapping reflections is therefore not respected. This may be the reason of this GSAS/FULPROFF ratio reversal, and possibly instabilities when patterns including the K alpha doublet are processed with GSAS.

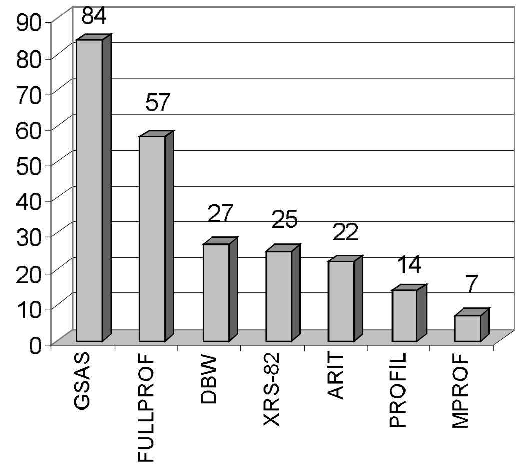

Fig. 11. Softwares for final Rietveld refinement

You should have the last improvements incorporated in your Rietveld program for dealing with strong asymmetry, or preferred orientation or anisotropic line broadening. Developers compete for updating their programs. The tendency to undertake large structures leads to the need of efficient programs including soft constraints and rigid-body refinement. Trends are to deal with more and more complex structures using low-resolution data. The results will be of poor quality, with large estimated standard deviations on atomic coordinates, dubious interatomic distances (the fact that they are constrained will not be a sufficient reason for trusting them).

5. Complexity

There is a perpetual race for the publication of the most complex structure ever determined from powder diffraction data. Each time the maximum number of independent atoms is overcome, those words occur in the paper introduction “X is the most complex structure ever solved from SDPD”. Things are not so simple that the complexity would be the total number of independent atoms. Moreover, the attainable complexity level is not just defined by the structures already determined. The current maximum complexity should be defined by the most complex structures determined by using the lowest resolution. For instance, finding 10 independent atoms by the direct methods with a pattern showing minimum FWHM as large as 0.25° (2θ), extending at least up to 100°, for a wavelength ~1.5 Å, is possible (sample 1 of the SDPD Round Robin [92]). Then, you can extend proportionally this proposition to synchrotron data with 0.05° FWHM and obtain that solving a 50 atoms structure should be feasible as well, or a 250 atoms structure if the minimum FWHM was lower than 0.01° (as obtained recently at ESRF). Nevertheless, does complexity is currently increasing ? Not really, the world of SDPD is concerned by moderately complex structures. The maximum of atoms simultaneously located by direct methods is not larger than 18. The total number of independent atoms is near of 60. On the other hand, rarely more than one independent molecule was located by model-building non-conventional methods (d’). For organic compounds, the trend is to use geometrical restraints in the final refinement. A kind of limit has been attained recently for $C_{16}H_{22}N_6$ with 70 atomic coordinates rigid-body-refined from 104 reflections for 3 independent molecules located by Patterson search [142]. Confidence in crystal structure accuracy depends on the reflection/parameter ratio which is admittedly ≥10 when single crystal data are involved and should be ≥ 20 when powder data are concerned (due to overlapping). One could doubt about some details of the structure when this ratio is not much larger than 1. Modifying torsion angles would be of little influence on the final fit. Locating hydrogen atoms could not be seriously undertaken.

The SDPD-Database sorts compounds according to 4 complexity criteria :

C1 = Number of independent atoms in the asymmetric unit.

N_c = Number of refined atomic coordinates at the final stage.

C2 = Number of independent atoms in the initial model (Patterson or direct methods).

C3 = Number of independent fragments located by model building techniques.

Looking at Figure 12, showing the variation of the maximum and mean C1 values during the last 10 years, one is tempted to conclude that the complexity of structures, which can be determined from SDPD, is slightly increasing. The maximum C1 values are still below the number of atoms that one may expect to refine by the Rietveld method. This number depends on the instrumental resolution for a well-crystallized compound. From synchrotron data with FWHM ~ 0.03°(2θ), extending over 120°, 4000 hkl could be “half-resolved”, allowing the refinement of 400 atomic coordinates, corresponding to more than 130 atoms in general position.

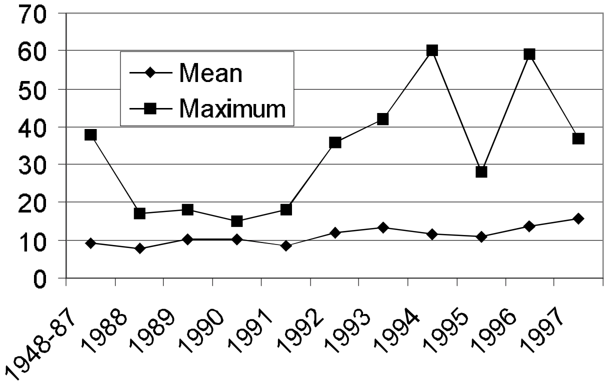

Fig. 12. Complexity criterion C1 : Number of independent atoms

The number of refined atomic coordinates (Nc) is a complexity criterion giving similar results as C1 (Figure 13). The mean Nc value in 1997 (45.6) is almost twice the value observed in the 1948-87 period (23.5). These C1 and Nc tendencies need to be confirmed in 10 years. Anyway, this evolution is really expected because of increasing instrumental resolution at synchrotron sources (FWHM as low as 0.01° 2θ was attained at ESRF) and also in laboratories (FWHM as low as 0.04° 2θ is produced by using variable slits).

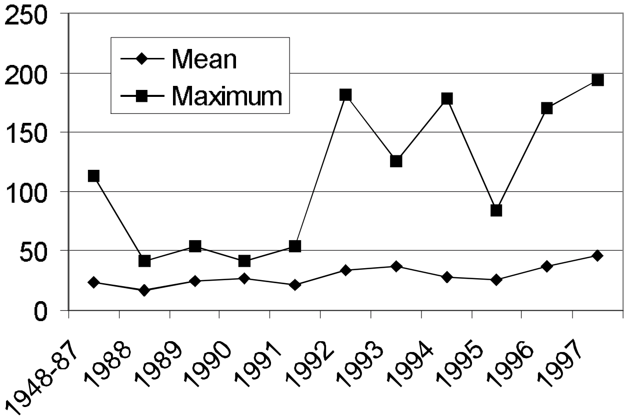

Fig. 13. Nc complexity criterion : Number of refined coordinates

From the C2 criterion, the mean (noted M1) number of located atoms was calculated and reported on Figure 14 along years. A partial mean (noted M2) was also reported, excluding the 99 structures for which 1 or 2 atoms were found to represent a sufficient starting model. In fact, only the maximum shows a tendency to increase.

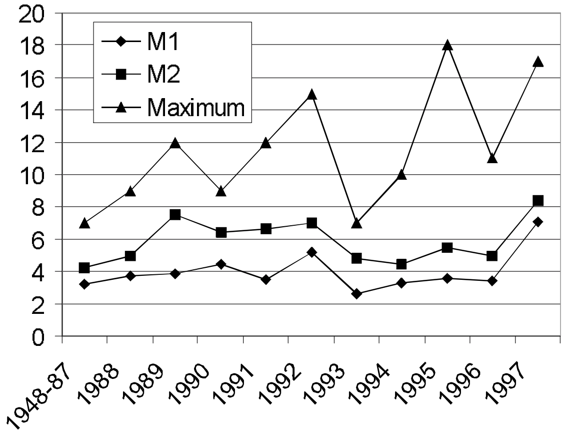

Fig. 14. C2 complexity criterion : Number of atoms located by Patterson or direct methods

The C3 criterion was considered to be applicable to methods locating molecules or fragments. Trial and error process used in trying to locate one or several heavy atoms were discarded. Only 26 unknown structures were determined since 1993 corresponding to the C3 criterion, so that statistics are hardly possible. Building proteins from molecules will need the ability to locate simultaneously much more fragments than is possible at present.

6. Accuracy

When no single crystal is available, it is hardly possible to have an idea of the accuracy of a structure determination solely from powder diffraction data. However, as a general rule, we know that accuracy will always be lower than if the same structure had been determined from single crystal data. The many SDPD from AK (already known) compounds have produced a set of interesting references for comparison. Very probably a trend is that AK compounds will continue to be used as test samples for new methods. Care to keep common sense will be necessary. Credibility of structures should not increase when the data/parameters ratio decreases. IUCr tends to make difficulties for publishing single crystal data when this ratio is less than 10, and R-values larger than 5%. Overlapping problems obviously should lead to a revision of these limits for SDPD.

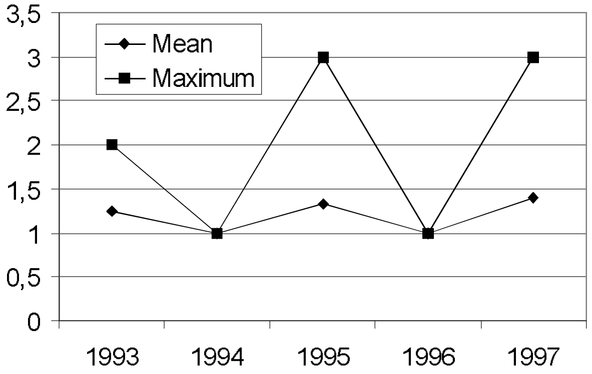

Fig. 15. C3 complexity criterion : Number of independent molecules or fragments simultaneously located

7. Conclusion

SDPD created a need for the development of specific methods or for adapting single crystal techniques. Many methods are even common to both powder and single crystal data without any need for adaptation. There is not so much difference between crystallographers either trying to cope with bad single crystal data or facing powder diffraction data. A cleavage is apparent between the unknowns for which it will be possible to guess a molecule or a sufficiently large fragment (or several ones) and those for which no sufficient prior information will be available. In the latter case, the *ab initio* methods will continue to be applied (Patterson and direct methods). In the former case, not necessarily restricted to powder problems, various simulated annealing approaches have yet proven their ability. The definition of a “previously unknown” compound is different for inorganic and organic compounds. In most cases, the molecular structure is available for the latter, and only the position and orientation in the cell is unknown.

Some time ago, it was stated that we were unable to determine structures as large as those we could refine by the Rietveld method. The new paradox is that we can locate now molecules in much bigger cells than we could refine without constraints. Due to resistance to change, habits listed in the present review have chances to survive and give us the tendencies for the years to come. A few softwares dominate each step of the SDPD whole process, they will probably extend their domination unless more efficient ones appear. Not all softwares are in the public domain so that some methods are the exclusivity of developers or teams repeating structure determinations by their own way. SDPD will not expand faster before a largest distribution of these new softwares. Alternative should be remembered as well : structure determination from very small single crystal [181] and structure determination from electron diffraction [182]. The former possibility comes in laboratories with imaging plate data recording, or at synchrotron radiation sources for crystal size as low as 20 µm (single crystal data for sample 2 of the SDPD Round Robin were obtained from a 40x30x20 µm selected from the “powder”). A trend is even that many of the first SDPD can now be compared to single crystal studies (the way to obtain a single crystal was found later). The last trend will be that overlapping peaks in powder diffractometry will continue to overlap, forever.

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