

## Renewed interest in powder diffraction data indexing

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### *Powder diffraction / Indexing software / Benchmarks*

**Abstract.** Recently released powder indexing programs are reviewed and placed in competition with the established programs (ITO, TREOR, DICVOL, etc.) through a series of problems selected among previously unindexed ICDD entries designated as “high quality”. Benchmarks are provided for testing indexing programs, based on the bethanechol chloride powder diffraction data. Applying these benchmarks leads to a classification (with respect to this specific example) of indexing programs as they face progressively more difficult situations. High data quality and the user experience to obtain it are concluded to remain the best way to indexing success, given that nearly all programs produce excellent results with excellent data. Lack of attention to data quality, even if followed by use of the most efficient programs, will usually lead to failure. It is demonstrated how not restricting oneself to a single indexing program can considerably increase the chances of success.

### Introduction

*Ab initio* structure determination by powder diffractometry (SDPD) is more and more widely used for the characterization of all sorts of compounds (>1000 structures solved in the past 20 years), including pharmaceuticals and even proteins. Indexing is the first step which has to be successfully passed through. Depending on the importance of the problem, researchers may consider the use of synchrotron radiation, but the first contact with a sample is usually made via conventional laboratory X-ray powder diffraction. Now that the International Centre for Diffraction Data (ICDD) has accommodated powder patterns calculated from inorganic (ICSD: Inorganic Crystal Structure Database), organic and organometallic (CSD: Cambridge Structural Database) crystal data of atomic coordinates, a negative search-match against the PDF allows one in principle to infer an unknown crystal structure. If not one good quality single crystal is available, the crystallographer then faces the problem to first index the powder data. Why

indexing is still a non-routine process, why a number of new indexing computer programs have appeared in recent years, how the old and new programs perform and what recommendations can be made about indexing today – these are the principal questions addressed in this review article. “Powder indexing works beautifully on good data, but with poor data it will usually not work at all”, this 24-year-old warning from Robin Shirley [1] will be re-examined, with the intention of fixing more precisely a modern definition of “poor data”, the issue being how far recent indexing software developments have really extended our capacities. In other words, can one really get away with recording powder data less carefully than in the past, and conversely, is it now possible to solve more complex problems from data of comparable accuracy than previously? Can indexing tasks now be done successfully in a press-button fashion by a technician uneducated in crystallography?

### Three classic indexing programs

Examining the citation index (ISI – Web of Science) shows that three programs are traditionally selected by the powder diffraction community for indexing purposes: ITO [2], TREOR [3] and DICVOL [4] (references to previous versions are given in these papers). The citation numbers of these three papers are an order of magnitude higher than those for any other publications about indexing programs (753, 834 and 540 citations in the periods 1975–2004, 1986–2004 and 1992–2004 for ITO, TREOR and DICVOL, respectively). These three classic programs are integrated with seven others in the Crysfire suite [5]. More complete historical reviews and description of the basic principles behind the indexing crystallographic problem can be found in Ref. [6–8], so will not be reproduced here. Details will be given only about the most recent programs.

### Some recent indexing programs

Despite the full availability of these above individual programs (the source codes have circulated freely) and of the Crysfire package, which acts as an expert system for

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users inexperienced in indexing, there is a renewed interest in trying to improve our indexing capability. The TREOR program was recently updated (N-TREOR [9]) and some new facilities are being implemented in DICVOL (tolerance with respect to spurious lines, etc.). In addition to these evolutionary developments, several new programs have also been developed and are briefly described below.

### AUTOX

This algorithm [10] is part of a program suite VMRIA for the analysis of spectra of nuclear reactions. The indexing problem is described as a fitting of diffraction reflections by their analytical formulae; the initial unit cell parameters are found by a Monte-Carlo method and the fitting procedure refines them and selects the appropriate *hkl*s. The best-fitted pattern in a series of such refinements is taken as the solution of the indexing problem for the given symmetry, phase(s) and parameter region.

AUTOX strengths reflect the niche which it is intended to cover:

1. Applicability not only to angular distributions, but also to time of flight data, where first reflections are often not recorded.
2. Extension to the case of multiphase samples.
3. Wide openness of the algorithm control to the user's manual guidance.

An additional goal is to gather experience in using modern programming technologies such as visual object-oriented ones (in particular, Delphi).

However:

1. AUTOX is oriented mainly to an experienced user and calls for training;
2. The algorithm's general form leads on average to longer run times in simple cases than for more heuristic algorithms.

### EFLECH/INDEX

EFLECH [11] is an automatic peak-hunting/refinement program. In its most useful mode, it starts from an empty set of peaks, selecting automatically the degree of a background polynomial and using the ray-traced fundamental parameter peak profile model of the program BGMN. It then searches for the "best set of peaks and background polynomials". As a bonus, EFLECH writes a full covariance matrix of all of its peak parameters to the output file. INDEX uses this error information for calculating a more detailed figure of merit. INDEX uses a random search. For searching cubic down to monoclinic, it generates random cell parameter values (parameter space search mode). For triclinic, it searches in index space instead by randomly selecting 6 reflections and setting 6 random *hkl* triplets to this selection. EFLECH/INDEX is a pair of programs tuned each to work best with the other. Hence it is impossible to run INDEX on ICDD data sheets, since it requires the raw powder profile.

### GAIN

This program [12] considers the raw data: the powder diffraction profile itself. The quality of a given set of cell parameters is determined from the  $R_{wp}$  factor, obtained following a Le Bail-type fit [13] of the intensity profile. A genetic algorithm is used to explore the  $R_{wp}$  ( $a, b, c, \alpha, \beta, \gamma$ ) hypersurface. Only simple tetragonal and orthorhombic cases (cell parameters  $< 6 \text{ \AA}$ ) have so far been reported. These demonstrate the potential success of this approach, when computer speed has more dramatically increased.

### Hmap

Hmap [5, 8] uses two new figures of merit, Pr which contains the joint probability of a particular fit between observed pattern and model, and Ir, the "indexedness" of that pattern, reported as a (non-integral) effective number of indexed lines. Both Pr and Ir have the valuable property of being relatively transparent to unexplained lines, routinely disregarding 10 or more impurity lines. In non-pathological cases, there is thus a reasonable hope, for example, of indexing both components of a 50:50 mixture of unknown low-symmetry phases, even with laboratory data, assumed to be of good modern quality. Hmap does not perform full ab initio indexing unaided, but (like Mmap and LOSH) takes a 4-parameter SIW basis set found previously, for example by LZON, as its starting point. A generalized version Peurist (still under development) will lift this restriction and use joint-probability methods to carry out complete ab initio indexing. Although these methods are tolerant of non-model features such as impurity lines, that is not the case for inaccuracy, which degrades the subset of close fits upon which they depend to identify solutions.

### Crysfire

The Crysfire suite itself [5] is a widely used multi-program indexing facility, which, from a single unified user interface and data file format, provides both a toolkit to help with the preparation and enhancement of powder diffraction peak data for use in powder indexing, and an expert system and wizard (in the Microsoft sense) to allow indexing to be carried out relatively fast and painlessly by non-specialists. Crysfire 2002 (currently in full release) supports a total of nine indexing programs: Ito12, Dicvol91, Treor90 (in their authors' unmodified binaries), Kohl, Taup, Fjzn6, Lzon, Losh (modified and recompiled) and Mmap (embedded). Crysfire 2003 (16 and 32-bit versions in limited release due to conflicts with Windows/XP) adds a further two programs to give a total of 11: McMaille (its author's Crysfire version), and Hmap (embedded) as described above. References for all programs are given in the Crysfire documentation.

For each dataset, Crysfire maintains a cumulative summary file that displays an overview of the trial solutions found by each indexing program, sorted into descending order of lines claimed to have been indexed out of the first 20, then FoM. For good data, the physically correct solution will usually appear at the top of this list, found repeatedly by different programs (or very near the top, in

the case of a sample with impurity lines in which low-merit solution(s) “indexing” all 20 lines have risen to the top due to the sorting criteria used – a situation that is easily recognized and seldom causes problems in practice). Crysfire includes tools both for self-calibration to estimate zeropoint correction and for stripping out weak lines, the latter in particular proving important in the manual stage of the bethanechol chloride benchmarks.

### McMaille

This program [14] operates in parameter space. Once a set of cell parameters is selected randomly by a Monte Carlo process, the corresponding peak positions can be calculated and the Miller indices assigned. Testing a cell proposal is made against an idealized powder profile generated from the extracted  $d$ s and  $I$ s. Using intensities improves the tolerance to impurity lines, provided that the sum of the intensity of impurity lines remains below 10–15% of the total intensity. Tolerance to zeropoint error is up to  $10.051^\circ$ . The main inconvenience of this program is long calculation times in low symmetries. A full exploration of all crystal systems in large cell parameter and volume ranges may require hours, though where the symmetry is monoclinic or above, results are usually obtained in a few minutes for the vast majority of moderately complex cases ( $V < 2000 \text{ \AA}^3$ ).

### SVD-Index

Critical to the success of this program [15] is the use of singular value decomposition (SVD) in an iterative manner for solving linear equations relating  $hkl$  values to  $d$ -spacings. SVD is applicable to cases where there are more equations than variables, as in powder indexing. Above the SVD process is a Monte Carlo approach to searching parameter space, which is thus not exhaustive. The method is relatively insensitive to impurity peaks and missing low-diffraction-angle data. The method is reported to perform well on typically noisy data with large diffractometer zero errors.

### X-Cell

In this program [16], a re-implementation of the DICVOL successive dichotomy approach is used, combined with a search for the zeropoint, and allowing for a user-defined number of unindexed reflections. The algorithm makes explicit use of systematic absences while searching for possible indexing solutions, working up from cells with low numbers of calculated reflections to cells with high numbers of reflections. No contribution to the UPPW Round Robin nor to the indexing benchmarks could be obtained for this program, despite solicitations.

## UPPW Round Robin

In order to compare the performances of indexing programs, a weekly Round Robin (UPPW = Unindexed Powder Pattern of the Week [17]) was organized by the end of 2003 (a previous Round Robin [18] had highlighted EFLECH/INDEX). The datasets were selected mainly

from those ICDD entries designated as “high quality” (Grant-in-Aid, imposing high data recording standards). Unindexed entries are accepted by ICDD only if evidence of purity is provided. The resulting series of eleven selected cases appeared representative of most problems encountered in indexing powder diffraction data: large zeropoint error, impurity lines, both these effects and also an elongated cell giving a dominant row (43-1748 and 46-1964, bethanechol chloride), a flat cell giving a dominant zone (45-1677 and 48-2476), very low-resolution data due to ill-crystallized compound (52-0231). In this last case, the raw profile was also available [19]. For bethanechol chloride, two new powder patterns were also recorded (laboratory X-ray diffractometer, synchrotron radiation).

A problem with this approach is that, as long as the structures have not yet been determined, there can be no independent demonstration that the cell proposals are correct. However, that is the same situation that one faces when starting a SDPD, needing to be convinced that the cell proposal is sufficiently probable to justify the investment of further time and effort in the structure solution. In one case at least, that ultimate proof with a complete SDPD was obtained – for bethanechol chloride [20].

## Round Robin results

For six ICDD entries from the eleven UPPWs, there was generally a consensus between the participants (applying generally AUTOX, Crysfire, McMaille, SVD-Index, and TREOR) and the most probable cells are reported in Table 1. Only one case (44-1791) presents a cell volume larger than  $2000 \text{ \AA}^3$  which may have forced users of some programs to change the default limits for obtaining the solution (McMaille for instance could not find the result in automated mode but found it in manual mode).

In the cases of flat cells, the principal problem is to fix the relatively weakly determined values of the short cell parameter, and especially of its two associated cell angles (Tables 2 and 3).

In the case of  $\delta\text{-Zn}_2\text{P}_2\text{O}_7$  (52-0231), there is even more discrepancy in the results (Table 4). The cells proposed tended to be selected by the participants because their calculated density was similar to the measured one. Nevertheless, several programs are suggesting similar cells, which is surprising because the pattern quality is quite low, in this case due to the poor crystallization of the sample rather than lack of care in data measurement.

In the case of bethanechol chloride – i.e. for the two ICDD entries (43-1748 and 46-1964) – no proposed solutions were submitted within the week allowed. However, the cell was established without any difficulty when two further datasets were provided, respectively from a synchrotron source and with a modern laboratory X-ray diffractometer.

These ICDD entries were selected for examining in more detail the extent to which the various indexing programs are sensitive to data problems, reducing the weight of the problems in stages in order to see whether a correct result would have been obtained with less error (zeropoint corrected, impurity weak lines removed, or both).

**Table 1.** Typical unit-cell dimensions suggested by most indexing programs for the UPPW-selected ICDD PDF entries. The definitions for the  $M(20)$  and  $F(20)$  figures of merit (FoM) are from Ref. 21 and 22. The number of impurity lines is  $Imp$  compared to the total number of lines used for indexing.

PDF	Formula	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$	$\beta$	$\gamma$	$V$ (Å <sup>3</sup> )	$M(20)$	$F(20)$	Imp
44-1791	C <sub>26</sub> H <sub>32</sub> F <sub>2</sub> O <sub>7</sub>	11.739	13.891	15.236	90	90	90	2484.5	19	49(0.008,49)	1/30
44-1794	C <sub>18</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub>	15.644	10.090	11.814	90	106.18	90	1790.9	20	47(0.008,52)	0/36
49-2190	C <sub>14</sub> H <sub>9</sub> NO <sub>4</sub>	10.618	8.501	13.808	90	98.23	90	1233.6	20	40(0.012,43)	0/28
51-1595	K <sub>x</sub> (Al <sub>x</sub> Si <sub>1-x</sub> )O <sub>2</sub> · H <sub>2</sub> O	7.473	18.379	13.964	90	99.39	90	1883.3	21	46(0.008,53)	0/25
51-1948	C <sub>16</sub> H <sub>26</sub> O <sub>5</sub>	10.502	13.896	11.158	90	90	90	1628.3	18	29(0.010,71)	0/25
53-1910	C <sub>8</sub> H <sub>13</sub> MgNO <sub>6</sub>	18.411	8.913	8.373	90	90	90	1374.0	14	19(0.009,108)	0/24

**Table 2.** Unit-cell dimensions suggested by users of different programs for the ICDD PDF entry 45-1677 (first flat cell, probably orthorhombic). There were two different TREOR users.

Program	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$	$\beta$	$\gamma$	$V$ (Å <sup>3</sup> )	$n$	$M(n)$	$F(n)$ or Chi2
TREOR(1)	16.672	14.956	4.763	90	90	90	1187.7	14	14	25(0.021, 28)
TREOR(2)	14.968	16.669	4.775	90	90.32	90	1191.3	18	12	24(0.017, 45)
AUTOX	4.758	14.991	16.692	90	90	90	1190.6	21		8.93
McMaille	14.995	16.675	4.772	90	90	90	1193.2	20	20	45(0.011, 40)

### Bethanechol chloride benchmarks

The two ICDD entries 43-1748 and 46-1964 were the subject of the following tests, in all cases using the 20 first lines, or the first 20 lines with  $I \geq 5\%$  ( $II_{\max}$ ):

- A – indexing the raw data (possibly after finding the zeroshift using an internal system, if any).
- B – indexing the data with  $I \geq 5\%$  ( $II_{\max}$ ). Most experienced powder diffractionists give a second chance to the data after removing the lowest intensity peaks which risk being due to impurities.
- C – indexing data corrected for zeroshift.
- D – indexing data corrected for zeroshift and having  $I \geq 5\%$  ( $II_{\max}$ ).

To these  $2 \times 4$  tests (to be made on the two ICDD entries) are added two further and considerably easier tests:

- E – indexing the new laboratory X-ray data
- F – indexing the synchrotron data

There turn out to be 8 impurity lines among the first 26 lines in PDF entry 43-1748, and 3 impurity lines among the first 35 lines in PDF entry 46-1964. Moreover, both patterns have a surprisingly large zeropoint error that is close to  $-0.10(2\theta)^\circ$ . The difficulty level thus decreases

from tests A to F. The programs' default values should preferably be applied in all crystal symmetries, or at least with maximum cell parameters of 20 Å and  $V_{\max} = 2000 \text{ Å}^3$  in monoclinic symmetry. These conditions probably correspond to more than 50% of the crystal structures stored in the ICSD and CSD databases. Where applicable, the runs in manual mode could be restricted to a monoclinic search in the 800–1200 Å<sup>3</sup> volume range, and 5–20 Å cell parameters.

Summarized results for these benchmarks are reported as follows. A score of 1 for the A, B, C, D, E or F tests means that the correct cell was found in first FoM position among the proposals. Such a score means that the program may well produce good results in inexperienced hands (if that score was obtained from a run with default values). A score of 0 means that the correct cell is mixed with incorrect ones and is not at the head of the list but is among the first ten. In that case, an expert may still succeed in locating the correct cell among the garbage, but this can require much more additional work. A score of  $-1$  means that the correct cell was not found at all, or at least not among the first ten proposals. An overall score will be calculated in the range  $\pm 20$ . A global score of 20 would indicate an excellent program which should give excellent results, even in inexperienced hands, while one

**Table 3.** Unit-cell dimensions suggested by users of different programs for the ICDD PDF entry 48-2476 (second flat cell, probably monoclinic or triclinic).

Program	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$	$\beta$	$\gamma$	$V$ (Å <sup>3</sup> )	$n$	$M(n)$	$F(n)$
TREOR(1)	14.652	4.270	10.660	90	96.42	90	662.8	20	19	39(0.013, 40)
TREOR(2)	14.668	3.755	10.658	90	96.41	90	583.0	20	35	69(0.008, 37)
DICVOL	29.274	6.244	21.288	90	96.52	90	3865.8	24	8	26(0.015, 61)
McMaille	16.664	?	10.651	?	96.30	?	?	20	40	72(0.009, 31) <sup>a</sup>
SVD-Index	4.180	10.695	14.694	83.92	93.65	85.44	649.3			49.49 <sup>b</sup>
AUTOX	14.651	3.754	10.659	90	96.40	90	582.5			

a: if  $b = 3.21$  (Å), which is, however, uncertain

b: Goodness of Fit

**Table 4.** Unit-cell dimensions suggested by different programs for the ICDD PDF entry 52-0231 (low resolution data, due to poor crystallization). FoM are not provided, being generally too low to be informative.

Program	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\alpha$	$\beta$	$\gamma$	<i>V</i> (Å <sup>3</sup> )
TREOR	9.201	12.347	4.747	90	95.47	90	536.5
EFLECH/INDEX <sup>a</sup>	5.467	5.960	9.436	92.54	100.43	113.32	275.4
SVD-Index <sup>b</sup>	4.784	5.978	9.189	89.65	95.55	81.44	258.9
AUTOX	9.205	6.145	4.750	90	95.54	90	267.4
	9.200	6.157	9.484	90	95.61	90	534.7
McMaille	9.208	6.158	9.495	90	95.54	90	535.9
	6.946	6.771	5.890	97.30	86.61	93.66	273.9
Crysfire 2003 <sup>c</sup>	6.215	9.493	5.717	93.23	105.60	103.07	314.0

a: Output of the Le Bail fit using BGMN [23], one solution among other ones.

b: Unambiguous solution not found, one of the best results from multiple Pawley [24] refinements using TOPAS.

c: Best of many possible solutions: considered uncertain, but indexes all 21 lines with FoM (M1) = 14.9.

close to zero would indicate a rather more average program by current standards, at least on these particular rather difficult tests.

The results are reported in Table 5. The benchmark data are listed in Table 6. A problem however is that programs requiring the raw powder diffraction profile (like EFLECH/INDEX and GAIN) cannot be tested against

these benchmarks. Unfortunately, participation from X-Cell and SVD-Index could not be obtained, limiting the interest of the Table 5 results. The four first rows in Table 5 present the individual results for ITO, DICVOL, TREOR and McMaille. Row 5 provides the best results selected from these four programs. Row 6 presents the best results of all applications, now including the best re-

**Table 5.** Results for the bethanechol chloride benchmarks. See text for the A, B, C, D, E and F definitions. Programs were run either in default (def) or manual (man) modes. Scores can be -1 (cell not found), 0 (cell found but not in first FoM position, though among the first ten – the order being given as a subscript: e.g. 0<sub>6</sub>) and 1 (cell found in first position, 1V meaning first position in a list sorted according to the increasing volume). The row labelled “first 4” gives the best results from the above rows including ITO13, DICVOL91, TREOR90 and McMaille when executed outside Crysfire. This shows the advantage in not restricting oneself to a single indexing program – underlined by the success of the Crysfire suite with its many supported programs (rows below the Crysfire 2003 row). Apart from one McMaille run using the Crysfire defaults, none of the successful Crysfire runs took more than a minute, and most were under 10 seconds. Below the Crysfire 2003 row are the results of the individual programs in Crysfire. The “Best” row is the combination of all best results. ITO12 and ITO13 are functionally identical, differing only in their interfaces, so presumably ITO12 could also have indexed dataset E in manual mode, if suitably directed. Similarly the different TREOR90 results reflect differences in the manual commands chosen and differences in attempts to correct for zeropoint error.

Program	A <sup>a</sup> def-man		A <sup>b</sup> def-man		B <sup>a</sup> def-man		B <sup>b</sup> def-man		C <sup>a</sup> def-man		C <sup>b</sup> def-man		D <sup>a</sup> def-man		D <sup>b</sup> def-man		E <sup>c</sup> def-man		F <sup>d</sup> def-man		Global note
ITO13	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	+1	+1	+1	-14
DICVOL91	-1	-1	-1	-1	-1	-1	-1	+1	-1	-1	-1	-1	-1	-1	-1	+1	+1	+1	+1	+1	-8
TREOR90	-1	-1	-1	-1	-1	-1	+1	+1	-1	-1	-1	-1	-1	-1	+1	+1	+1	+1	+1	+1	-4
McMaille	-1	0 <sub>6</sub>	+1V	+1	+1V	+1	-1	+1	-1	-1	-1	+1	-1	+1	-1	+1	+1	+1	+1	+1	+5
First 4	-1	0 <sub>6</sub>	+1V	+1	+1V	+1	+1	+1	-1	-1	-1	+1	-1	+1	+1	+1	+1	+1	+1	+1	+9
<b>Best of all</b>	<b>-1</b>	<b>+1</b>	<b>+1V</b>	<b>+1</b>	<b>+1V</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>-1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+1</b>	<b>+12</b>
Crysfire 2003	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	+1	+1	+1	+1	+1	+1	+6
TAUP	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	+1	0
KOHL	-1	-1	-1	0	-1	-1	-1	0	-1	-1	-1	0	-1	-1	+1	+1	+1	+1	+1	+1	-5
TREOR90	-1	-1	-1	-1	-1	-1	-1	+1	-1	-1	-1	+1	-1	-1	-1	+1	-1	-1	+1	+1	-8
DICVOL91	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	+1	+1	+1	+1	-12
McMaille(*)	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	+1	+1	+1	+1	-12
LOSH	na	-1	na	-1	na	-1	na	-1	na	-1	na	-1	na	-1	na	+1	na	+1	na	+1	-14
Mmap	na	-1	na	-1	na	-1	na	-1	na	-1	na	-1	na	-1	na	+1	na	+1	na	+1	-14
Hmap	na	-1	na	-1	na	-1	na	-1	na	-1	na	-1	na	-1	na	0	na	+1	na	+1	-15
FJZN	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	+1	+1	-16
ITO12	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	+1	+1	-16
LZON	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-20

a: ICDD PDF entry 43-1748,  $\lambda = 1.5418$  Å

b: ICDD PDF entry 46-1964,  $\lambda = 1.5418$  Å

c: Conventional X-ray data,  $\lambda = 1.54056$  Å

d: Synchrotron data,  $\lambda = 0.6995$  Å

na = not applicable, there is only a manual mode (taken as -1 when calculating the totals)

(\*) Crysfire does not yet support McMaille properly in manual mode.

A <sup>a</sup>	A <sup>b</sup>	B <sup>a</sup>	B <sup>b</sup>	C <sup>a</sup>	C <sup>b</sup>	D <sup>a</sup>	D <sup>b</sup>	E <sup>c</sup>	F <sup>d</sup>
6.238	6.690	6.712	13.601	6.138	6.590	6.612	13.501	10.765	4.887
6.712	9.417	13.171	14.757	6.612	9.317	13.071	14.657	13.522	6.139
9.403	10.849	13.584	15.492	9.303	10.749	13.484	15.392	14.690	6.664
13.171	13.135	14.882	16.463	13.071	13.035	14.782	16.363	15.398	6.989
13.584	13.601	15.498	17.419	13.484	13.501	15.398	17.319	16.336	7.403
14.483	14.757	16.528	18.925	14.383	14.657	16.428	18.825	16.453	7.460
14.882	15.492	17.430	19.730	14.782	15.392	17.330	19.630	17.312	7.850
15.498	16.463	18.928	20.131	15.398	16.363	18.828	20.031	18.828	8.531
16.528	17.419	19.808	20.841	16.428	17.319	19.708	20.741	19.699	8.921
17.430	18.925	20.148	22.508	17.330	18.825	20.048	22.408	20.031	9.062
18.534	19.730	20.852	23.224	18.434	19.630	20.752	23.124	20.752	9.251
18.928	20.131	22.539	23.614	18.828	20.031	22.439	23.514	21.641	9.386
19.808	20.841	23.680	23.979	19.708	20.741	23.580	23.879	22.414	9.781
20.148	21.722	23.982	25.085	20.048	21.622	23.882	24.985	22.788	10.136
20.852	22.508	25.088	25.650	20.752	22.408	24.988	25.550	23.152	10.300
21.852	23.224	25.844	26.796	21.752	23.124	25.744	26.696	23.528	10.468
22.331	23.614	26.556	27.407	22.231	23.514	26.456	27.307	23.872	10.634
22.539	23.979	27.412	28.262	22.439	23.879	27.312	28.162	24.970	10.783
23.252	25.085	28.272	29.724	23.152	24.985	28.172	29.624	25.365	11.280
23.680	25.650	29.786	31.220	23.580	25.550	29.686	31.120	25.549	11.450

a: ICDD PDF entry 43-1748,  $\lambda = 1.5418 \text{ \AA}$

b: ICDD PDF entry 46-1964,  $\lambda = 1.5418 \text{ \AA}$

c: laboratory X-ray data,  $\lambda = 1.54056 \text{ \AA}$

d: synchrotron data,  $\lambda = 0.6995 \text{ \AA}$

**Table 6.** Indexing benchmarks. Several sets of twenty peak positions ( $2\theta$ )° from various bethanechol chloride powder diffraction data. See text for the A, B, C, D, E and F definitions. Programs can be tested by loading these 20 peak positions and running in default and manual modes. For those programs needing intensities, these are available at the UPPW web site <http://sdpd.univ-lemans.fr/uppw/benchmarks/>

sults from Crysfire which are presented in row 7. The next rows present the results of the individual programs as they were executed within Crysfire. This presentation reflects the fact that Crysfire does not always apply the same default and manual conditions as those which were used separately for ITO, DICVOL and TREOR and McMaille (first 4 rows of table 5) and cannot yet support the McMaille manual mode nor exploit some special features of McMaille, such as reporting the most probable cells not only according to the best figures of merit but also by increasing volume. Table 5 is planned to be extended as further results are received and made available on the Internet. Though there is no flat-cell (dominant zone) problem in these selected benchmarks, some programs may nevertheless encounter difficulties due to the fact that the bethanechol chloride  $b$  parameter is substantially larger than  $a$  and  $c$  (dominant row). The best FoM was reported from the use of the synchrotron data:  $M(20) = 197$ ,  $F20 = 1080$  (0.0006, 32), the cell being monoclinic with  $a = 8.875$  (Å),  $b = 16.408$  (Å),  $c = 7.137$  (Å), and  $\beta = 93.84$  (°),  $V = 1036.9$  (Å<sup>3</sup>), space group  $P2_1/n$ .

One conclusion from these benchmark tests is that some of the recent indexing programs do seem more robust against zeroshift error, and also against data inaccuracy and impurity lines, and do indeed offer more chances to index poor data than some previous classic programs. However, different benchmarks that presented other problems (e.g. flat cell = dominant zone) would have revealed different strengths, so these results should not be taken as providing an absolute rank order, but rather as underlining the dangers of habitually using only one pro-

gram (particularly if listed in Table 5 with a low global score).

Special conditions of the benchmark runs with the various programs:

### ITO13

**Default mode:** blank parameter cards, giving only the wavelength.

**Manual mode:** some parameters are varied manually, primarily the tolerance (*TOLG*) on the match between calculated and observed two thetas. Solutions indexing up to only 10 lines were tolerated (*PRNTLN*=10.).

### DICVOL91

**Default mode:** typically lines 3, 4 and 5 in the entry data are filled with zeros, specifying only the wavelength.

**Manual mode:** the absolute error on each observed line is taken larger than the default value (i.e.  $>0.03^\circ$ , in most case  $0.05^\circ$  was selected) and the cell parameters and volume ranges were specified.

### TREOR90

**Default mode:** the parameter cards are reduced to *MONO*=130.0, *WAVE*=1.5418, *CHOICE*=3,

**Manual mode:** more instructions are added such as *NIX*=10, *IDIV*=0, *MONOSET*=7, *D2*=0.0006, *D1*=0.0003 (or *D2*=0.0002, *D1*=0.0001 for the synchrotron data), so that there are 10 tolerated unindexed lines.

## McMaille

**Default mode:** 3 unindexed lines maximum are tolerated. All symmetries examined. Maximum cell parameters and volumes are respectively 20 Å, 2000 Å<sup>3</sup> (monoclinic) and 1000 Å<sup>3</sup> (triclinic). There is no internal system able to find the zeropoint automatically.

**Manual mode:** 8 unindexed lines are tolerated, successive runs are made, the solution being found in a monoclinic run with volume range 800–1200 Å<sup>3</sup>, and 5–20 Å cell parameters.

## Crysfire

**Default mode:** Crysfire's "all default" route provides defaults for the various indexing programs as described in its user guide [5]. Typically  $V_{\max}$  is 6000 Å<sup>3</sup> and, where applicable, the number of unindexed lines is set to zero.

**Manual mode:** Interventions were limited to those available from Crysfire's interactive commands and menus. EDit and Strip were used to exclude the 10 and 4 weakest lines from A1 and A2 respectively. Where applicable,  $V_{\max} = 1200$  and unindexed lines = 1. D2Theta was set to 0.05 or 0.06, if not already the default. The basis sets for LOSH, Mmap and Hmap used in datasets D2, E and F (already indexed by default runs of KOHL, DICVOL, etc.) were taken from previous runs of LZON or KOHL.

## Recommendations, hints and tips

There is nothing really new here. The finding that some programs may be relatively tolerant to some kinds of errors should not be regarded as an incitement to reduce one's efforts to obtain the best possible powder pattern. Data quality remains the more important factor in indexing, and great care should still be invested in recording the powder pattern. Obtaining both the highest resolution and the highest accuracy should be the primary aim, since in general all programs are likely to yield an obvious solution with high FoM for such data.

Self-calibration for zershift estimation can help, but remains an uncertain process in inexperienced hands. It is highly recommended to use a reference compound mixed with the sample. The risk with this procedure is to miss some (vital) lines for indexing due to fortuitous overlapping. There is also the possibility of correctly aligning the diffractometer and checking the adjustment with appropriate standard reference materials (particularly those suited to the low angle region), which is especially suitable in Debye-Scherrer arrangements. This too becomes risky with the widely used Bragg-Brentano geometry, where the diffracting part of a sample has some thickness because of the X-ray penetration depth, so that the real mean diffracting plane is not the surface of the sample unless the absorption is very high. For this reason, a reference compound mixed with the sample should have a similar absorption to that of the sample. The fact that the two ICDD Grant-in-Aid entries of the same compound, bethanechol chloride, came to present similar large zershifts would be consistent with a systematic specimen-displace-

ment error of this kind. Preferred orientation may also have contributed to the problems with these datasets, plus the presence of a residual impurity or perhaps a second polymorph.

Removing low intensity peaks should not be done routinely, but is worth trying if no obvious result is obtained from the complete dataset.

It could be argued that novice users with poor or mediocre data will not have much success with structure solution and refinement from such data either, even if they do find the correct cell. Nevertheless, the final recommendation is still to complete the task by confirming the cell with a crystal structure determination. Failing that, at least a satisfactory whole-profile fitting with cell constraint (either by the Pawley or Le Bail methods) would provide more confidence that the cell is correct (unless the FoM is already very high). This would also help establish the space group before proceeding to the solution step, either by using the extracted  $|F_{\text{obs}}|$  and using Direct or Patterson or direct-space methods, or by a direct-space approach using the raw powder pattern. Such a structure-free but cell-constrained approach allows one to obtain initial values for the cell and profile-shape parameters that can be used either in a direct-space solution or in the final Rietveld refinement.

## Conclusion

Can an indexing task be carried out successfully in a press-button fashion by a powder diffractionist not fully educated in crystallography, through using the most modern indexing programs? The answer is no, or at least, not yet and only sometimes. Of course many programs will propose plausible solutions, but judging the quality of those solutions remains a task for a well-trained crystallographer. Because of the time that can be wasted in trying to solve a structure from powder data if the cell is wrong, extreme attention needs to be focused on the indexing problem. Applying the present benchmarks led to a classification (although specific to multiple data sets of one particular compound) of indexing programs as they faced progressively more difficult situations. However, data quality and user experience for recording excellent data are still concluded to be the surest way to success, rather than applying the latest programs to slackly measured data, given that any program is likely to produce excellent results with excellent data. Perhaps the main conclusion from this study is that, compared even with one of the newest programs, the chances of success remain greatly increased by trying as many different indexing programs as possible.

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## Note added in proof

At the time of correcting the proofs of this paper, the details about the new DICVOL04 were published [25].

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