

# Powder pattern indexing with the dichotomy method

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The efficiency of the successive dichotomy method for powder diffraction pattern indexing [Louër & Louër (1972). *J. Appl. Cryst.* **5**, 271–275] has been proved over more than 30 years of usage. Features implemented in the new version of the computer program *DICVOL04* include (i) a tolerance to the presence of impurity (or inaccurately measured) diffraction lines, (ii) a refinement of the ‘zero-point’ position, (iii) a reviewing of all input lines from the solution found from, generally, the first 20 lines, (iv) a cell analysis, based on the concept of the reduced cell, to identify equivalent monoclinic and triclinic solutions, and (v) an optional analysis of input powder data to detect the presence of a significant ‘zero-point’ offset. New search strategies have also been introduced, *e.g.* each crystal system is scanned separately, within the input volume limits, to limit the risk of missing a solution characterized by a metric lattice singularity. The default values in the input file have been extended to 25 Å for the linear parameters and 2500 Å<sup>3</sup> for the cell volume. The search is carried out exhaustively within the input parameter limits and the absolute error on peak position measurements. Many tests with data from the literature and from powder data of pharmaceutical materials, collected with the capillary technique and laboratory monochromatic X-rays, have been performed with a high success rate, covering all crystal symmetries from cubic to triclinic. Some examples reported as ‘difficult’ cases are also discussed. Additionally, a few recommendations for the correct practice of powder pattern indexing are reported.

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## 1. Introduction

*Ab initio* powder pattern indexing is a major application of the powder diffraction method. It consists of finding the unit-cell parameters from the radial *d*-spacing data available in a diffraction pattern. The success of this geometrical three-dimensional reconstruction of the lattice from indexing procedures depends on both data precision and the *d*-spacing information that can be recovered from the collected data. Among modern methods used for powder pattern indexing (for recent reviews, see, for example, Langford & Louër, 1996; Werner, 2002), the efficiency of the successive dichotomy method (Louër & Louër, 1972), has been proved through the indexing of hundreds of powder diffraction patterns, including powder patterns used in our group for subsequent *ab initio* structure determinations. The method has also been found to be useful in the context of physical form screening within the pharmaceutical industry (Florence *et al.*, 2003). The method was first applied for indexing powder diffraction patterns of materials with an orthorhombic or higher symmetry lattice

(Louër & Louër, 1972). With the continuous development of computer technology, the successive dichotomy principle was applied later to monoclinic and triclinic lattices (Louër & Vargas, 1982; Boultif & Louër, 1991), from which resulted the computer program *DICVOL91*. The dichotomy algorithm is based on an exhaustive search of solutions, working in the parameter space through crystal systems in decreasing order of symmetry. Although the selection of the input parameters (*e.g.* limits on cell parameters and volume, choice of the crystal system, choice of the absolute error on input peak positions, *etc.*) offers a flexibility to the user, indexing practices have revealed the need for more options. Such additional facilities have been implemented in the new version of the successive dichotomy program, namely *DICVOL04*, described in this study. They include a tolerance for (unindexed) spurious diffraction lines, the refinement of the ‘zero-point’ of the powder data together with the cell parameters, an *a priori* inspection of input data to evaluate a significant ‘zero-point’ error in the measured data, and new specific strategies, such as an automatic review of all available (input) data from the solution(s) found from the first (generally 20) lines, the use of the reduced-cell concept to detect equivalent solutions in

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monoclinic and triclinic lattices, and a separate exploration, within the input cell-volume limits, of each crystal system. All these aspects are discussed in the present study and the results of many tests are reported.

## 2. The dichotomy method

*Ab initio* powder diffraction pattern indexing is based on the use of the quadratic forms obtained by squaring the reciprocal-lattice vectors  $\mathbf{d}^*$  ( $= h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ ):

$$Q_i = h_i^2 Q_A + k_i^2 Q_B + l_i^2 Q_C + h_i k_i Q_D + k_i l_i Q_E + l_i h_i Q_F, \quad (1)$$

where  $Q_i = 1/d_i^2$ ,  $Q_A = \mathbf{a}^{*2}$ ,  $Q_B = \mathbf{b}^{*2}$ ,  $Q_C = \mathbf{c}^{*2}$ ,  $Q_D = 2\mathbf{a}^* \cdot \mathbf{b}^*$ ,  $Q_E = 2\mathbf{b}^* \cdot \mathbf{c}^*$  and  $Q_F = 2\mathbf{c}^* \cdot \mathbf{a}^*$ ,  $d_i$  being the direct spacing and  $h_i k_i l_i$  the Miller indices of the  $i$ th diffraction line;  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  are the unknown vectors of the reciprocal lattice. The solution to the problem cannot be solved by ordinary algebra since the number of equations (*i.e.* number  $N$  of triplets  $h_i k_i l_i$ ) is always smaller than the number of unknowns (*i.e.*  $n$  parameters,  $n = 6$  for triclinic, 4 for monoclinic, ..., 1 for cubic lattices, and  $N$  sets of three indices  $h_i k_i l_i$ ).

The solution to equation (1) can be obtained with a successive dichotomy procedure, the principle of which has been described by Louër & Louër (1972) for crystal systems down to orthorhombic, and later for the monoclinic and triclinic cases (Louër & Vargas, 1982; Boulitif & Louër, 1991). In this approach, the right-hand side of equation (1) is considered as a parametrical function  $f(\mathbf{m}, \mathbf{x})$ , where  $\mathbf{x}$  is a vector formed by the  $n$  cell constants (three linear and three angular parameters in the general triclinic case) and  $\mathbf{m}$  is a vector with three components ( $h, k, l$ ). Consider an  $n$ -dimensional domain  $D$  defined as follows:

$$D = [x_1^1, x_1^2] \times [x_2^1, x_2^2] \times \dots \times [x_n^1, x_n^2]. \quad (2)$$

If for all vectors  $\mathbf{m}$ , in a particular set  $M$ ,  $f$  is continuous in  $D$ , the following implication occurs whatever a vector  $\mathbf{m}^0$  of  $M$ :

$$\mathbf{x} \in D \rightarrow f(\mathbf{m}^0, \mathbf{x}) \in [f_{\min}^0, f_{\max}^0], \quad (3)$$

where  $f_{\min}^0$  and  $f_{\max}^0$  are the minimum and maximum bounds of  $f$  in the domain  $D$ . The converse of implication (3) allows one to find the unknowns  $\mathbf{x}$  and  $\mathbf{m}^j$  from the discrete set of values  $y_1, y_2, \dots, y_N$  corresponding to  $f(\mathbf{m}^1, \mathbf{x}), f(\mathbf{m}^2, \mathbf{x}), \dots, f(\mathbf{m}^N, \mathbf{x})$ . For the powder pattern indexing problem, the set  $M$  is sufficiently small to be scanned within a reasonable computing time. If for a particular initial domain  $D$ ,

$$\exists y_i \in \{y_1, y_2, \dots, y_N\} / \forall \mathbf{m}^k \in M, y_i \notin [f_{\min}^k, f_{\max}^k], \quad (4)$$

no solution  $\mathbf{x}$  is found, the domain is eliminated and a new domain, obtained by increment, is generated. On the contrary, if a solution can exist in  $D$ , the domain is further explored by bisecting each domain side  $[x_i^1, x_i^2]$ , so that the  $n$ -dimensional domain  $D$  is divided into  $2^n$  sub-domains. Each sub-domain is thus analysed as before and any sub-domain that cannot contain a solution is eliminated. This dichotomy process is repeated six times in all. At the end of the procedure, the sub-domains define the cell constants at intervals of 0.00625 Å and 0.0781° for initial step lengths of 0.4 Å and 5° for the linear

and angular parameters, respectively, and the  $hkl$  indices are stored for a subsequent least-squares refinement of cell parameters.

In this algorithm, the absolute error of measured data (*i.e.*  $2\theta$  diffraction angles) is considered without any re-evaluation during the numerical calculations. Moreover, the search of solutions is carried out systematically within the solution space defined by the input parameter limits. These two points mean that the solutions are searched exhaustively in the  $n$ -dimensional parameter space. It can also be noted that, if no solution is found within the input parameter limits and selected crystal systems, the information can be used to extend the input limits on parameters without re-investigating the already scanned volume space.

The mathematical details concerning the bounds  $f_{\min}^0$  and  $f_{\max}^0$  of  $f$  in domains  $D$ , *i.e.* the limits  $Q_-(hkl)$  and  $Q_+(hkl)$  for the indexing problem, have been reported elsewhere for crystal lattices down to orthorhombic (Louër & Louër, 1972), monoclinic and triclinic (Boulitif & Louër, 1991, including the appendix deposited as supplementary material No. SUP 54279). It must be noted that the dichotomy strategy consists of searching the solution(s) with the smallest cell volume(s) according to the universal crystallographic convention, *i.e.* 'the smallest repeat unit for which its delineating vectors are parallel to, or coincide with, important symmetry directions in the lattice' (Ladd & Palmer, 1993). This definition fits well with the definition of the figure of merit (FoM)  $M_{20}$  ( $= Q_{20}/2\langle\Delta Q\rangle N_{\text{calc}}$ ) introduced by de Wolff (1968) for assessing the reliability of a unit cell derived from powder diffraction data. Indeed,  $M_{20}$  combines two concepts, forming the denominator of the formula, namely data accuracy reflected by the agreement between  $Q_{\text{io}}^{\text{obs}}$  and  $Q_{\text{ic}}^{\text{calc}}$  ( $\langle\Delta Q\rangle$ ) and the idea of small cell volume  $V$  through  $N_{\text{calc}}$ , the number of theoretical lines until the 20th observed line (*e.g.*  $N_{\text{calc}} \simeq 4\pi V_{\text{tric}}/3d^3$  for a triclinic lattice). The successive dichotomy algorithm is applied successively to each crystal system, starting from the cubic side of the symmetry sequence.

## 3. New features

The options implemented in the new version of the successive dichotomy indexing program, *DICVOL04*, are as follows.

### 3.1. The zero-angle offset

High-quality powder data are required to ensure a correct pattern indexing. A common source of error in data collected with a conventional X-ray source combined with Bragg–Brentano optics is the presence of the so-called 'zero-point' error. With a significant 'zero-point' shift, *e.g.* 0.05° ( $2\theta$ ), the risk of missing the indexing solution is increased. If, by chance, the solution is found, it will be characterized by a dramatic decrease of the figures of merit (Louër, 1992). Consequently, it can be difficult to identify the correct unit cell among several solutions with low figures of merit. In practice, the overall 'zero-point' error has often been considered, for low angles, as one mixed error resulting from the true zero-point error and

**Table 1**

Examples of equivalent solutions found by *DICVOL91* for piracetam I ( $V = 724.2 \text{ \AA}^3$ ,  $M_{20} = 43$ ) (ICDD PDF No. 45-1997) and  $\alpha$ -ZnMoO<sub>4</sub> ( $V = 520.2 \text{ \AA}^3$ ,  $M_{20} = 68$ ) [National Bureau of Standards (US) (1963–1985), §21, p. 132] together with their reduced forms (RC).

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)
Piracetam form I						
Cell 1	8.101 (2)	13.411 (2)	6.750 (1)		99.02 (2)	
RC	6.750	13.411	8.101	90.00	99.02	90.00
Cell 2	9.698 (2)	13.411 (2)	6.750 (2)		124.43 (2)	
RC	6.750	13.411	8.100	90.00	99.02	90.00
$\alpha$ -ZnMoO <sub>4</sub>						
Cell 1	12.040 (3)	8.371 (2)	6.965 (1)	78.29 (2)	112.01 (2)	126.91 (2)
RC	6.965	8.371	9.695	96.76	106.87	101.71
Cell 2	11.428 (2)	8.372 (2)	6.965 (1)	101.72 (2)	112.39 (2)	120.60 (2)
RC	6.965	8.372	9.694	96.76	106.87	101.72

the specimen-surface displacement (SSD), *i.e.*  $\Delta(2\theta) = -(2s/R) \cos \theta$ , where  $s$  is the SSD and  $R$  is the goniometer radius [*e.g.*  $\Delta(2\theta) = 0.04^\circ$  at  $30^\circ$  ( $2\theta$ ) for  $s = 0.1$  mm and  $R = 250$  mm].

According to the magnitude of the zero-angle offset, two approaches are proposed in *DICVOL04*.

(i) For small shifts ( $< \sim 0.03^\circ 2\theta$ ), the indexing solution must be found without any particular problem. An option to refine a zero offset in the  $2\theta$  scale together with the least-squares refinement of cell parameters is proposed to the user. Its favourable effect will be to improve significantly the figures of merit and to avoid a bias in the unit-cell constants (see below Table 2).

(ii) If the shift is significant ( $\sim 0.10^\circ 2\theta$ ), the reflection-pair method (Dong *et al.*, 1999) can give an estimate of the zero origin. This option is proposed for an *a priori* analysis of the input data, to be applied before embarking on the indexing process. The method is based on the search of subsets of reflections with different orders using equations derived by Dong *et al.* (equation 6 of Dong *et al.*, 1999). If more than one reflection pair is detected, the ‘zero shift’ is then averaged. A serious problem arises if a reflection pair is incorrectly indexed (*i.e.* the lines are not a pair of reflections with different orders). The calculation can then provide an incorrect origin-shift correction, which can have an opposite sign with respect to the result from the other reflection pair. Therefore, a second category of reflection pairs, corresponding to an opposite-sign averaged zero correction, has to be considered. The probability that one category of reflection pairs is the best one is directly related to the number of subsets contained in each category. In *DICVOL04*, this is admitted as soon as the difference between subsets in both categories is equal to or greater than 2. If it is not verified, the search of indexing solutions is carried out for the two possible cases. It should be noted that such an approach is not unambiguous and, consequently, a careful check of the setup adjustment, prior to data collection, must be preferred to the use of this *a priori* error evaluation.

The efficiency of this option has been demonstrated with the powder data of monoclinic barium titanate hydrate (Louër *et al.*, 1990), with a cell volume of  $2596 \text{ \AA}^3$ . The powder data are indexed [ $M_{20} = 51$ ,  $F_{20} = 171$  (0.0037, 32)] by *DICVOL04*, using the default limit values except for the maximum volume,

which is extended to  $3000 \text{ \AA}^3$ . With a zero-point error of  $0.20^\circ$  ( $2\theta$ ) artificially added to the entered data, no solution is found in 7 s, which shows the sensitivity of pattern indexing to a zero-angle offset. Using the *a priori* zero-origin evaluation, only one category of reflection pairs is found, the zero error is satisfactorily corrected, and *DICVOL04* proposes the solution in 3 s.

### 3.2. Cell analysis

A current problem with powder pattern indexing is the multiple solutions that can be generated. In particular, with monoclinic and triclinic lattices, equivalent solutions having different cell parameters are often found. A powerful analysis of such cells can be based on the reduced-cell concept, which has been reviewed in detail by Azároff & Burger (1958) and discussed by many authors (see, for example, Santoro & Mighell, 1970; Mighell, 2001). It consists of a cell built on the shortest three noncoplanar lattice parameters and it can be right (all angular parameters  $< 90^\circ$ ) or left (all angular parameters  $\geq 90^\circ$ ). The main characteristic of the reduced cell is that it is unique for a given lattice, so that it is a useful tool to determine whether two cells represent the same lattice. It has been found particularly useful in crystallographic database work (Mighell, 2001) and, also, in calculating standard cells from the reporting of crystalline materials, as carried out by the computer program *NBS\*AIDS83* (Mighell *et al.*, 1981). The two examples given in Table 1, indexed with *DICVOL91*, illustrate the benefit of the reduced-cell concept to identify equivalent solutions. In both examples, the reduced cells show that the two cells found by *DICVOL91* are equivalent. In *DICVOL04*, a systematic reduced-cell analysis is carried out for monoclinic and triclinic cells. If equivalent solutions are detected, only one of them (together with its reduced form) is listed in the output file.

### 3.3. Review of the entire powder data

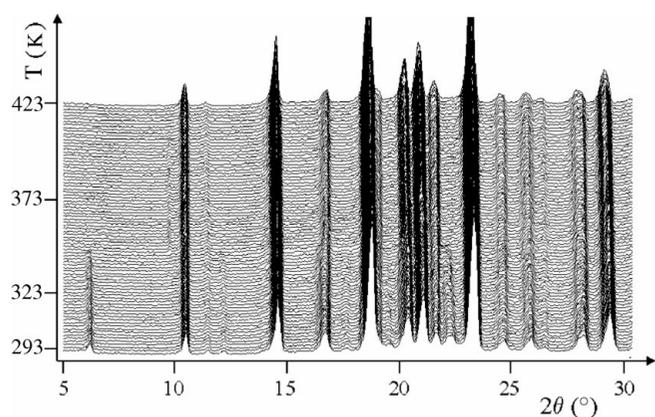
The search of indexing solutions is currently based on a limited number of lines, typically the first 20 lines in the pattern (or more than 20 lines if there is a dominant zone, *i.e.* one axis is significantly shorter than the other two). In fact, there is no absolute criterion to validate an indexing result, except a subsequent successful *ab initio* structure determination from the powder diffraction data. However, there are conditions that must be (ideally) satisfied for a correct solution, such as high FoMs and, also, the (accurately measured) density of the material should lead to an integral number of chemical formulae in the unit cell. Additionally, an obvious important condition to satisfy is the indexing of all available observed powder data from the unit-cell parameters of the solution. This reviewing process is carried out systematically in *DICVOL04* as soon as a solution has been found. In this process, the unit-cell parameters are refined again from all input data, new FoMs are calculated and unindexed lines, within the input angular error limit(s), are displayed. Moreover, this evaluation process is a helpful stage for the derivation of possible space groups from the inspection of the *hkl*

indices of the observed diffraction lines. It should be noted here that, if the full trace of the powder pattern is available, another useful complementary check of cell validity is the use of a pattern-matching approach (combined with a zoom facility), e.g. the iterative Le Bail algorithm (Le Bail *et al.*, 1988), in which a full pattern fitting is carried out using peak positions constrained by the found cell parameters. Such pattern matching refinement is implemented in the Rietveld program *FULLPROF* (Rodriguez-Carvajal, 1990) available in the software *WinPLOTR* (Roisnel & Rodriguez-Carvajal, 2001), in which major indexing programs can also be used in connection with an automatic peak search.

### 3.4. Unindexed diffraction lines

In the context of the dichotomy algorithm, unindexed diffraction lines can arise from two origins: (i) spurious lines due to the presence of a second (or more) crystalline phase(s) in the sample and (ii) errors of peak measurements greater than the absolute error  $|\Delta(2\theta)|$  of data input to the program. No direct facility was provided in *DICVOL91* for such cases. Indeed, in the case of expected spurious lines, the recommended practice was, in a first run of the program, to omit low-intensity lines or to start pattern indexing with a small number  $N$  of (independent) diffraction lines and, then, to follow the behaviour of solution(s) FoMs when progressively increasing  $N$  up to 20, by discarding lines for which a sudden significant decrease of the FoM is observed. For imprecise peak positions, the user had the possibility to change individual error bounds. The presence of imprecise data could also be detected by looking at the number of iterations at each dichotomy level listed in the output file, e.g. no solution at the last level, whereas a non-zero number exists at the preceding level, could be an indication that the input absolute error was possibly too strictly estimated (at least for some lines). Although such a practical strategy is still possible with *DICVOL04*, a new facility has been introduced to tolerate a limited number (to

be decided by the user) of unindexed lines among the data used for the indexing search. It should be noted that such an option must be used with caution, since it seriously increases the risk of generating additional (erroneous) mathematical solutions and of missing the correct one. Moreover, if unindexed lines are accepted, they should always be explained from chemical (e.g. materials used for the synthesis, sample stability, etc.) or physical (polymorphism, phase transformation, etc.) reasons. Since pattern indexing cannot be considered as a trivial operation, it is recommended to use additional analytical methods for the detection of impurity lines, such as a powerful search-match algorithm (see, for example, Caussin *et al.*, 1988) to identify the origin of spurious lines. Another practice can be, if applicable, the study of the thermal behaviour with temperature-dependent powder diffraction to detect a mixture of phases. This is illustrated by the diffraction data of a tablet of the pharmaceutical compound Advil. The temperature-dependent diffraction plot in Fig. 1, obtained with an INEL detector using Cu  $K\alpha_1$  radiation and a semi-focusing diffraction geometry, clearly shows that the initial sample contains, at least, two phases. Indeed, some low-intensity lines vanish at  $\sim 343$  K, while the intensities of others remain stable until 423 K. If the 'spurious' lines (less abundant phase) are omitted in the precise data set input in *DICVOL91*, the correct orthorhombic solution is found. With *DICVOL04*, the orthorhombic solution is found with an impurity tolerance of seven lines among the first 21 lines (Fig. 2). The reviewing of the entered 28 lines revealed the presence of eight spurious lines in the complete data set. This unit cell corresponds to that of  $\beta$ -D-mannitol [PDF File No. 22-1797; International Centre for Diffraction Data (ICDD), 2003]. The unindexed



**Figure 1** Temperature-dependent X-ray diffraction plot of an Advil tablet displaying the presence of two phases at room temperature (counting time per pattern 1800 s, heating rate  $8 \text{ K h}^{-1}$ ). The diffraction lines (e.g.  $6.10^\circ$ ,  $12.21^\circ$ , shoulder at  $16.62^\circ$ ,  $22.36^\circ$   $2\theta$ ) of the minor phase (ibuprofen) vanish at  $\sim 343$  K.

```

      O R T H O R H O M B I C   S Y S T E M
DIRECT PARAMETERS :  A= 16.88152 B=  8.66729 C=  5.54299 VOL=
811.03
STANDARD DEVIATIONS :    0.00239    0.00134    0.00088
REFINED ZERO-POINT SHIFT : 0.0241 deg. 2-theta

   H   K   L   DOBS   DCAL   DOBS-DCAL  2TH.OBS  2TH.CAL  DIF.2TH.
(  1   0   0) 14.48441 *****          6.097          -0.891
  2   0   0   8.46262  8.46019  0.00244  10.445  10.448  -0.003
  1   1   0   7.72737  7.72663  0.00075  11.442  11.443  -0.001
(  1   1   0)  7.24005 *****          12.215          -0.772
  2   1   0   6.05607  6.05694 -0.00087  14.615  14.613  0.002
(  1   0   1)  5.33004 *****          16.619          0.178
  1   0   1   5.27240  5.27387 -0.00147  16.802  16.797  0.005
(  1   0   1)  5.01193 *****          17.682          -0.885
  3   1   0   4.72480  4.72571 -0.00091  18.766  18.762  0.004
  0   1   1   4.67396  4.67558 -0.00162  18.972  18.965  0.007
  2   0   1   4.63883  4.63905 -0.00022  19.117  19.116  0.001
(  1   1   1)  4.54650 *****          19.509          0.176
  1   1   1   4.50897  4.50614  0.00282  19.673  19.685  -0.012
(  0   2   0)  4.39380 *****          20.194          0.259
  0   2   0   4.33895  4.33870  0.00025  20.452  20.453  -0.001
  4   0   0   4.22555  4.22517  0.00038  21.007  21.009  -0.002
  1   2   0   4.20202  4.20228 -0.00026  21.126  21.125  0.001
  2   1   1   4.09047  4.09056 -0.00009  21.709  21.709  0.000
(  3   0   1)  3.97283 *****          22.360          0.113
  4   1   0   3.79808  3.79830 -0.00023  23.403  23.402  0.001
  3   1   1   3.59720  3.59696  0.00023  24.730  24.732  -0.002

* NUMBER OF LINES
.- LINES INPUT      = 21
.- LINES INDEXED   = 14
.- LINES CALCULATED = 19
* FIGURES OF MERIT
  1.- M( 14) = 143.3
  2.- F( 14) = 242.1(0.0030, 19)
    
```

**Figure 2** Output list of the indexing of the powder data of an Advil tablet with seven spurious lines among the first 21 lines. The solution corresponds to the unit cell of  $\beta$ -D-mannitol.

lines have been explained by the *SOCABIM* search-match software (Caussin *et al.*, 1988). They correspond to the more intense lines of the powder data of ibuprofen (PDF File No. 32-1723).

This example illustrates the efficiency of *DICVOL04* with respect to spurious lines. Nevertheless, a successful indexing should not mask the risk of missing the correct solution if too many unindexed lines are tolerated. The power of this option is probably more useful for data sets in which, for some reason (*e.g.* lines with low intensity, shoulder, *etc.*), one or a few input peak positions have been measured with a lower precision with respect to the input absolute error  $\Delta(2\theta)$  of the peak positions. For example, with the data of sodium germanium phosphate [National Bureau of Standards (US), 1984, §20, p. 84] and an input error of  $\pm 0.02^\circ$  ( $2\theta$ ) of the peak positions, the correct hexagonal cell [ $a = 8.0912$  (8),  $c = 21.528$  (4) Å,  $M_{19} = 31$ ,  $F_{19} = 41$  (0.0078, 60)] is found with the acceptance of one unindexed line among the first 20 lines. This fifth line ( $26.784^\circ$   $2\theta$ , relative intensity 1), presents a discrepancy of  $-0.038^\circ$  ( $2\theta$ ) with respect to the position calculated from the refined parameters, which exceeds the input absolute error. With the tolerance of one spurious line, the problem is solved. (In this particular case, another possibility for finding the solution would be to enter an overall error of  $\pm 0.03^\circ$   $2\theta$  of input peak positions.)

## 4. The indexing program and applications

### 4.1. Program features

The program *DICVOL04*, written in Fortran77, is the successor of *P1* and *P2* (Louër & Louër, 1972), *DICVOL* (Louër & Vargas, 1982) and *DICVOL91* (Boultif & Louër, 1991). The parameters under user control are (i) the number of lines  $N$  used for solution search, the  $d$ -spacing unit, the choice of crystal lattices, (ii) the limits on linear parameters (default maximum value 25 Å), cell volume (default 2500 Å<sup>3</sup>) and  $\beta$  angle for monoclinic lattices (default 130°), (iii) the wavelength (default Cu  $K\alpha_1$  radiation) and, optionally, the density, its estimated absolute error and molecular weight, (iv) the estimated absolute error of peak positions (in  $^\circ$   $2\theta$ ) (default 0.03° for Cu  $K\alpha_1$  radiation), the minimum FoM  $M_N$ , the tolerance for unindexed lines, an indicator for *a priori* data analysis (zero-error evaluation) and an indicator for 'zero-point' refinement, and (v) all diffraction powder data available (an option allows the user to enter specific estimated errors for each individual line). As already noted, the search is exhaustive within the selected input limits. The scan of parameters is carried out from minimum values calculated from the input data, according to limits reported by Louër & Louër (1972, Table 1 therein) and completed by Louër & Vargas (1982). If a minimum value cannot be derived from the input data, *e.g.* the smallest parameter of an orthorhombic cell, it has been fixed to 2.5 Å in the program. As described by Boultif & Louër (1991), the strategy used for triclinic lattices differs slightly, since the search is faster if  $hkl$  combinations are attributed to the first two lines. Limited to 14 independent  $hkl$  combinations

in *DICVOL91*, subroutines have been added to cover additional cases, *i.e.* (100, 210), (100, 2 $\bar{1}$ 0), (100, 012) and related cases obtained by permutation. Moreover, the constraints on  $hkl$  have been extended, *i.e.* ( $h + k + l$ ) lower than 6 for the first five lines and lower than 9 for the other lines, instead of 3 and 6, respectively, in *DICVOL91*. The scanning of the volume space is carried out to reveal first solutions with smallest cell volumes. This is facilitated by the use of a space partition by volume shells of 400 Å<sup>3</sup>, in the general case, or by volume domains [ $V_-$ ,  $V_+$ ] defined from the density and its related absolute error if they are known (see Louër & Vargas, 1982). The search of indexing solutions begins from the cubic end of the symmetry sequence. In order to avoid missing solutions characterized by geometrical ambiguities, each crystal system is explored independently up to the maximum input volume, unless a solution has been found with a higher symmetry. If so, the maximum value is replaced by the volume of the unit cell found and the search continues.

### 4.2. Lattice metric singularities

Mighell & Santoro (1975) have discussed in detail geometrical ambiguities, called lattice metric singularities, which can occur in some indexing cases. According to Mighell (2000) 'a lattice metric singularity occurs when unit cells defining two (or more) lattices yield the identical set of unique calculated  $d$ -spacing'. Such singularities can often be easily detected from simple relationships between the lattice parameters of the two cells and particular cell-volume ratios. Typical lattice metric singularities are as follow.

(i) Hexagonal-orthorhombic: a hexagonal pattern (cell parameters  $a_H$  and  $c_H$ ) can be indexed with an orthorhombic unit cell having the parameters  $a_H/2$ ,  $(a_H\sqrt{3}/2)$  and  $c_H$  and a cell volume half that of the hexagonal cell (Louër & Louër, 1972; Louër, 1992).

(ii) Cubic tetragonal-orthorhombic: any powder pattern indexed with a body-centred cubic cell (volume  $V$ ) can also be indexed in terms of a tetragonal cell ( $V/4$ ) or orthorhombic cells ( $2V/3$  or  $V/8$ ) (Mighell & Santoro, 1975).

(iii) Rhombohedral-monoclinic: a pattern indexed with a rhombohedral cell (volume  $V$ ) can also be indexed with a monoclinic cell ( $V/2$ ) (Mighell, 2000). With *DICVOL04* this case is transformed into a hexagonal cell ( $3V$ ), orthorhombic ( $3V/2$ ) and monoclinic ( $V/2$ ) subcells.

The strategy used in *DICVOL04* is well suited to these mathematical ambiguities, since they generate subcells with lower symmetry. The search strategy based on crystal lattices analysed separately, in a decreasing order of symmetry, and looking for smaller unit-cell volumes, must display all solutions (if needed).

### 4.3. Short and long axes

Difficult indexing cases are often related to the presence of one axis that is significantly shorter or greater than the other two. The short-axis case gives rise to dominant zones, namely the first consecutive lines are indexed with a common zero index. As already discussed elsewhere (Louër, 1992), the

**Table 2**Powder diffraction pattern indexing of pharmaceutical materials [ $\Delta(2\theta) = \pm 0.03^\circ$ ]. $M_{20}$ : FoM obtained with 'zero-shift' refinement;  $M'_{20}$ : FoM without 'zero' offset refinement; Z-s: refined 'zero shift' ( $^\circ 2\theta$ );  $N_{\text{imp}}$ : number of spurious lines.

Name	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ ( $^\circ$ )	Z-s	$M_{20}$	$M'_{20}$	$N_{\text{imp}}$	Time (s)
Barbital sodium	12.134 (2)	11.961 (2)	6.728 (1)		-0.028	69	50	0	<1
Phenacetin	13.327 (2)	9.611 (2)	7.737 (1)	104.05 (2)	-0.029	56	33	0	2
Theophylline	24.555 (2)	8.4756 (9)	3.8204 (3)		-0.029	97	41	0	<1
Sulfaguanidine	24.578 (6)	5.5419 (9)	7.506 (1)	90.44 (2)	-0.020	49	34	0	2
Aspirin	11.432 (5)	6.592 (3)	11.3400 (7)	95.64 (4)	-0.036	25	23	3	21
Urea (tetragonal)	5.6401 (2)		4.6958 (2)		-0.026	235	145	0	<1
Piracetam I	8.1090 (6)	13.4242 (7)	6.7585 (4)	99.016 (7)	-0.007	158	146	0	2

successive dichotomy method is not highly sensitive to this situation, except if the number of lines with a common zero index approaches the number  $N$  of lines selected for the solution search stage (e.g. for  $\text{ZnOHNO}_3 \cdot \text{H}_2\text{O}$ , the first 14 lines of the powder data have  $k = 0$ ; ICDD PDF No. 47-0965). Of course, if such a situation occurs,  $N$  must be increased in order to stabilize the search procedure. The automatic reviewing of the complete input data set should be helpful to deal with these cases. The longer-axis case is generally detected by the first consecutive lines with different orders of one line (e.g.  $0k0$  reflections only). A representative example is the powder pattern of  $N$ -(*p*-tolyl)dodecylsulfonamide, in which the first five lines are  $h00$  reflections (Rajeswaran *et al.*, 2002, Fig. 3 therein). If such a situation is detected, the number of lines  $N$  for searching the solution should also be increased accordingly.

#### 4.4. Data quality

Although new facilities to deal with measurement errors have been implemented in *DICVOL04*, it should be remembered here that having high-quality data is a major requirement for indexing powder diffraction patterns, as clearly stated long ago by de Wolff (1957), who claimed that 'the indexing problem would be quite an easy puzzle if errors of measurement did not exist'. Many aspects of error effects have been discussed elsewhere, as well as recommendations to help with the adjustment/control of parafocusing powder diffractometers before collecting data for pattern indexing (Louër, 1992; Louër & Langford, 1988). Errors associated with inadequate sample preparation can be significant, e.g. transparency errors. For low-absorbing materials, such as organics, a thin sample layer deposited on a zero-background sample holder must be used to obtain precise peak positions. With modern powder diffractometers using a conventional X-ray source, errors of peak measurements lower than  $0.02^\circ$  ( $2\theta$ ) can be obtained routinely. Obviously, with synchrotron X-rays a considerably higher precision is obtained, with the immediate consequence of indexing solutions with higher figures of merit, compared with those obtained from data collected with a conventional X-ray source (Cernik & Louër, 1993). A representative example reported by these authors is the indexing of the powder data of triclinic zirconium hydroxide nitrate with the FoMs ( $M_{20}/F_{20}$ ) 54/112 (0.0058, 30) and 295/635

(0.0012, 26) from data collected with  $\text{Cu K}\alpha_1$  and synchrotron X-ray (1.4039 Å) radiation, respectively.

#### 5. Program tests

Indexing of a large number of accurate powder diffraction data has been carried out with *DICVOL04* with a very high success rate. Tests have been performed with a Dell Latitude D800 laptop equipped with an Intel Pentium M processor running at 1.7 GHz. For an objective evaluation of

the efficiency of the program, various data sources have been chosen (unless it is specified, the default values were used in the input data file).

(i) Monograph No. 25, §20 [National Bureau of Standards (US), 1984]. In §20, experimental powder diffraction data are reported for 71 substances, including 9 cubic, 10 tetragonal, 18 hexagonal, 16 orthorhombic and 18 monoclinic patterns. The indexing tests were carried out with an absolute error of peak positions of  $0.02^\circ$  ( $2\theta$ ) and the search was carried out from cubic to orthorhombic lattices for compounds with orthorhombic and higher symmetry, and from cubic to monoclinic lattices for monoclinic materials. All powder diffraction patterns have been indexed successfully. The average CPU time for searches down to orthorhombic was 0.4 s. It was 6.9 s for monoclinic examples (minimum 1 s for  $\text{NaSbF}_4$ , maximum 60 s for  $\text{Eu}_2\text{O}_3$ ).

(ii) Triclinic patterns [National Bureau of Standards (US), 1963–1985]. The 21 sections of Monograph No. 25 contain 29 powder diffraction patterns of triclinic substances. An error of  $\pm 0.02^\circ$  ( $2\theta$ ) was applied to all peak positions, except for the powder data of  $\text{Na}_3\text{MgH}(\text{PO}_4)_2$  (§21, p. 117), for which an error of  $\pm 0.03^\circ$  ( $2\theta$ ) was selected. For two cases there was tolerance for one spurious line (§3, p. 45; §16, p. 26). All patterns were indexed successfully with *DICVOL04*. The CPU times for these triclinic powder data were less than 2 s for ten data sets, in the ranges 2–60 s for six examples and 60–360 s for ten examples. The last three cases were indexed in 1215 s (§15, p. 48), 3307 s (§16, p. 122) and 3770 s (§15, p. 47).

(iii) Pharmaceutical materials. Although precise peak positions with conventional X-ray sources are generally obtained with the Bragg–Brentano optics, this reflection geometry is not appropriate for low-absorbing materials, unless thin deposits are used. If the Debye–Scherrer optics is used, the precision of peak positions used for indexing is generally lower. If specimen absorption and axial divergence effects are neglected, the angular error is then related to the respective displacements  $x$  and  $y$  of the capillary from the centre of the goniometer, i.e.  $\Delta 2\theta = (x \sin 2\theta - y \cos 2\theta)/R$ . Though its variation is not constant, the extra degree of freedom in the least-squares refinement of lattice parameters, in the form of a 'zero-shift' variable in *DICVOL04*, leads to a significant improvement of the FoMs of indexing solutions. This is illustrated by the indexing of powder diffraction data of 'as received' pharmaceutical compounds, collected with

**Table 3**

Examples reported as 'difficult' cases indexed with *DICVOL04*.

S: crystal system. *N*: number of lines used for indexing search.  $N_{\text{imp}}$ : tolerance for unindexed lines. *AP*: *a priori* search for zero offset ( $^{\circ} 2\theta$ ). *M*: de Wolff FoM. Time: CPU time (s). Changes in default parameter limits are indicated [ $\Delta$  is the absolute error on peak positions ( $^{\circ} 2\theta$ )] as well as comments on particular results (e.g. solution instability). CPU times were evaluated according to the protocol as follows: for examples down to orthorhombic symmetry, cubic, tetragonal (T), hexagonal (H) and orthorhombic (O) systems are scanned; for examples with monoclinic (M) symmetry, higher-symmetry systems are also scanned; for triclinic examples, only the triclinic (Tric) system is scanned.

	S	N	$N_{\text{imp}}$	AP	$M_N - N_{\text{imp}}$	Time	Parameter limits/comment
(i) From Neumann (2003)							
Compound, No.							
Fluoroapatite, 2	H	20	0	–	288	<1	
<i>p</i> -Methoxybenzoic acid, 11	M	20	0	–	28	2	
$\alpha$ - <i>l</i> -Glutamic acid, 12	O	23	4	–	40	<1	
Akermite, 13	T	20	0	–	58	<1	
4-Nitrophenylhexylurethane, 16	M	15	0	–	48	3	
( <i>E</i> )-2-(4,6-Difluoroindan-1-ylidene)acetamide I, 17	M	20	3	–	42	14	
( <i>E</i> )-2-(4,6-Difluoroindan-1-ylidene)acetamide II, 18	Tric	23	0	0.10	22	103	Unstable, No. of solutions > 30
( <i>E</i> )-2-(4,6-Difluoroindan-1-ylidene)acetamide III, 19	M	21	0	0.04	22	4	
Octane, 20	Tric	21	3	–	63	131	V/2 with respect to reported cell†
Pentadecane, 21	Tric	20	1	0.007	17	1766	Orders 200 and 400 omitted‡
Nonane, 22	O	20	2	–	15	<1	$\Delta = 0.02$ , <i>a</i> , <i>b</i> , $c_{\text{max}} = 45 \text{ \AA}$
Aigh ( $\alpha$ phase), 23	Tric	21	3	–	18	2	
Indigo ( $\alpha$ phase), 24	M	21	1	–	11	7	$\Delta = 0.05\text{§}$
(ii) From Coelho (2003)							
Example 1	T	20	0	–	34	<1	
Example 2	H	38	0	–	2	44	H only, $\Delta = 0.004$ , <i>a</i> , <i>b</i> , $c_{\text{max}} = 85 \text{ \AA}$ , $V_{\text{max}} = 500\,000 \text{ \AA}^3$
Example 3	O	20	0	–	16	<1	
Example 4	M	20	0	–	56	2	
Example 5	M	20	0	–	38	2	
Example 6	M	20	0	–	52	3	
Example 7	M	20	3	–	13	9	$\Delta = 0.05\text{¶}$
Example 8	Tric	20	0	–	33	1	
Example 9	Tric	20	0	–	38	<1	
Example 10	Tric	20	2	–	12	6	$\Delta = 0.01$
Example 11	Tric	26	0	–	31	244	$\Delta = 0.01$ , <i>a</i> , <i>b</i> , $c_{\text{max}} = 45 \text{ \AA}$
Example 12	Tric	30	0	–	13	3	Tric $\Delta = 0.01$ , <i>a</i> , <i>b</i> , $c_{\text{max}} = 55 \text{ \AA}$ , $V_{\text{max}} = 3000 \text{ \AA}^3$

† Cell parameters found by *DICVOL04* are  $a = 10.962$  (3),  $b = 4.661$  (1),  $c = 4.0822$  (9)  $\text{\AA}$ ,  $\alpha = 74.86$  (2),  $\beta = 96.69$  (2),  $\gamma = 95.13$  (3) $^{\circ}$ ,  $V = 199.6 \text{ \AA}^3$  (RC  $a = 4.082$ ,  $b = 4.661$ ,  $c = 10.962 \text{ \AA}$ ,  $\alpha = 84.87$ ,  $\beta = 83.31$ ,  $\gamma = 74.86^{\circ}$ ). The results of data evaluation with *NBS\* AIDS83* of the reported data and cell parameters are:  $a = 4.094$  (5),  $b = 9.34$  (1),  $c = 11.48$  (2)  $\text{\AA}$ ,  $\alpha = 71.3$  (1),  $\beta = 89.7$  (1),  $\gamma = 105.4$  (1) $^{\circ}$ ,  $V = 399.1 \text{ \AA}^3$  [ $M_{19} = 7$ ,  $F_{20} = 9$  (0.038, 56), rejecting angular differences greater than  $0.2^{\circ}$  ( $2\theta$ )]. ‡ The least-squares refinement with *NBS\* AIDS83* of reported observed data [ $a = 4.090$  (2),  $b = 4.628$  (3),  $c = 24.864$  (2)  $\text{\AA}$ ,  $\alpha = 97.16$  (4),  $\beta = 90.484$  (5),  $\gamma = 75.08$  (4) $^{\circ}$ ,  $M_{20} = 14$ ,  $F_{25} = 20$  (0.020, 61)] shows the low precision of some measured peak positions, e.g. angular discrepancies between observed and calculated positions are  $-0.018^{\circ}$ ,  $0.033^{\circ}$ ,  $0.015^{\circ}$ ,  $0.046^{\circ}$  ( $2\theta$ ) for the 001, 002, 004 and 006 lines, respectively. § Data evaluation with *NBS\* AIDS83* gives  $M_{20} = 7$  and  $F_{21} = 10$  (0.031, 69), with four angular differences exceeding  $0.05^{\circ}$  ( $2\theta$ ). ¶ Data evaluation with *NBS\* AIDS83* indicates three unindexed reflections and two angular differences exceeding  $0.1^{\circ}$  ( $2\theta$ ) [ $M_{19} = 16$ ,  $F_{20} = 31$  (0.015, 42), rejecting angular differences greater than  $0.2^{\circ}$  ( $2\theta$ )].

Debye–Scherrer optics, using a monochromatic Cu  $K\alpha_1$  radiation and a step length of  $0.025^{\circ}$  ( $2\theta$ ) (data have been deposited with the ICDD). All patterns were successfully indexed with satisfactory figures of merit. The results are listed in Table 2.

(iv) 'Difficult' cases. In recent papers (Neumann, 2003; Coelho, 2003), some powder diffraction data have been reported as 'difficult' cases to index. These examples have been considered here as tests for *DICVOL04*.

Neumann (2003) has reported the results of powder pattern indexing with various indexing programs, including his program based on the Louër & Louër successive dichotomy method. Among the 24 diffraction data sets, he claims that *DICVOL91* failed for 13 of them. No spurious lines in the input data being tolerated by *DICVOL91*, the failure was evidently to be expected for seven of the data sets. For at least two examples, the author clearly used the default values in the input file of the program, which is not correct practice for expected difficult cases. Hexagonal fluoroapatite (compound No. 2) is a typical case of lattice metric singularity, discussed

above and elsewhere (Louër, 1992). For monoclinic indigo (compound No. 24), the reported  $\beta$  value is  $130.15^{\circ}$ , whereas the default maximum  $\beta$  value in *DICVOL91* is  $125^{\circ}$ . Extending  $\beta_{\text{max}}$  to  $135^{\circ}$ , together with an absolute error of  $0.06^{\circ}$  ( $2\theta$ ) for peak positions, the reported cell and, even better, the equivalent cell  $a = 10.91$  (1),  $b = 5.829$  (6),  $c = 9.824$  (8)  $\text{\AA}$ ,  $\beta = 107.62$  (6) $^{\circ}$  [ $M_{21} = 6.5$ ,  $F_{21} = 10$  (0.030, 70)] are found in 6 s. These 13 data sets have been used as tests of *DICVOL04*. They have been indexed successfully. Details and comments are given in Table 3.

Powder diffraction data reported recently by Coelho (2003) for 12 examples have also been input in *DICVOL04*. These data sets have been successfully indexed (Table 3).

## 6. Concluding remarks

Powder pattern indexing with the successive dichotomy algorithm (Louër & Louër, 1972) has been investigated through new facilities implemented in the program *DICVOL04*. The tolerance for unindexed diffraction lines is efficient, both for

impurity lines and lines measured with a smaller precision, the identification of equivalent cells with the reduced cell concept is convenient for low symmetry unit cells, and the program can deal with a 'zero' offset of a few hundredths of a degree. The various tests reported in this study show that the success rate is high, provided that data have been measured precisely and that the user's decisions about input limits on cell parameters and volume, on the absolute error(s) of peak positions and the minimum accepted FoM are correctly estimated. Powder pattern indexing is one of the most exacting applications of the powder diffraction method. This is clearly due to the nature of the mathematical problem, in which a three-dimensional object must be reconstructed from one-dimensional data. It is well known that the errors in the data seriously perturb such an operation. The successive dichotomy method offers the possibility of an exhaustive search. The immensity of the mathematical problem prescribes the use of filters to orient the search to the tree-type approach. These filters relate to the quality of data, *i.e.* measurement errors, and to the physical problem, *i.e.* finding the smallest unit cell describing the true lattice of the material. They are both combined in the de Wolff figure of merit, which acts as an additional filter. However, in spite of the efficiency of the filters, data peculiarities can sometimes baffle the strategy employed. Solutions being valid within the error bounds and the selected constraints, one must always be aware that changing the input limits can orient differently the progress of the search.

Finally, checks on the validity of the solutions must always be carried out. They include the reviewing of all discrete data available, the use of a pattern-matching method for a visual inspection of fit quality, the use of observed density to check whether a solution corresponds to an integer number of chemical formula in the cell, and structure determination if applicable. Additional information can also be used as a help to validate the solution, such as empirical rules reported for classes of compounds, *e.g.* the hydrate-formula equivalent volume  $V_{\text{eq}} (= V/Z)$  varies linearly with the number of water molecules (Leclaire & Monier, 1982) and an estimate of the cell volume  $V_{\text{eq}} (\simeq 18n)$  of organic materials can be derived from the number  $n$  of C, N and O atoms in a given unit cell (Kempster & Lipson, 1972). All these precautionary notes on validity checks can save time if a subsequent structure determination is undertaken.

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