

## 3. METHODOLOGY

**Table 3.4.3**

Classification of indexing methods

Method (strategy/search)	Space	Exhaustive
Zone indexing	Parameter	No
SIW heuristic	Parameter	Semi
Scan/covariance	Parameter (for cubic to monoclinic); index (for triclinic)	To monoclinic
Index heuristics	Index	Semi
Index permutation	Index	Yes
Successive dichotomy	Parameter	Yes
Grid search	Parameter	Yes
Genetic algorithms	Parameter	No
Monte Carlo	Parameter	No

made by considering whether a program works in direct or reciprocal space, or uses Bragg diffraction line positions or the whole experimental diffraction profile. Using the whole experimental diffraction profile requires a lot of computing time, but has become possible as a consequence of recent increases in the speed of computers. In the following, descriptions of the principal (default) steps of the most widely used indexing programs are given. Several non-default options are available for each program. The chances of success of the indexing step increase if more than one program is used.

## 3.4.4.1. Traditional indexing programs

## 3.4.4.1.1. ITO (Visser, 1969)

This program is based on the zone-indexing strategy and uses the Runge–Ito–de Wolff–Visser method of decomposition of the reciprocal space into zones, as described in Section 3.4.3.1.1.

The following steps are executed by the program:

- (1) The potential zones are found always using the 20 lowest Bragg angle peaks. The program does not work with fewer peaks.
- (2) All possible combinations of the six best zones (including the combination of each zone with itself) are found by searching for trial zones that share a row of common points. For every pair of such zones, the angle between them is found, thus giving a trial reciprocal lattice.
- (3) The reduction of the resulting unit cells is carried out using the Delaunay–Ito method (Pecharsky & Zavalij, 2009).
- (4) The program tries to index the first 20 lines and repeats this check after least-squares refinement of the unit-cell parameters.
- (5) The figures of merit are calculated to assess the quality of each trial unit cell and the four best lattices are provided.

*ITO* is very efficient at indexing patterns with low symmetry and is only weakly sensitive to impurity peaks, if they occur at high angles. The most frequent causes of failure are inaccuracy or incompleteness of the input data.

3.4.4.1.2. TREOR90 (Werner *et al.*, 1985)

Classified by Shirley (1980, 2003) as semi-exhaustive, *TREOR90* is based on the index-heuristics strategy (see Section 3.4.3.1.3) and uses a trial-and-error approach. It performs the following steps:

- (1) Some basis lines are selected among the experimental  $d$  values, generally from the low- $2\theta$  region of the powder diffraction pattern. Five sets of basis lines are generally sufficient for orthorhombic tests, whereas more than seven

sets may be necessary for the monoclinic system. At least 20–25 experimental  $d$  values are potentially required.

- (2) The trial unit cells in the index space are searched by varying the Miller indices that are tentatively assigned to the basis lines.
- (3) The analysis starts with cubic symmetry and, in a stepwise manner, tests for lower-symmetry crystal systems are performed. In the case of monoclinic symmetry, a special short-axis test is carried out.
- (4) The solution of the linear system in equation (3.4.8) gives the possible cell parameters. Different combinations of the basis lines are tested.
- (5) Each possible solution is checked by using the full list of experimental lines.
- (6) The quality of the trial cell parameters is mainly assessed by using the  $M_{20}$  figure of merit [see equation (3.4.4)]. An effective rule for identifying a reliable solution is  $M_{20} > 10$  and no more than one unindexed line.

The success of the program is related to the use of some suitable standard sets of parameter values (maximum unit-cell volume, maximum cell axis, tolerance of values *etc.*) arising from the accumulated experience of the authors; they can be easily changed by the user *via* suitable keywords in the input file.

## 3.4.4.1.3. DICVOL91 (Boultif &amp; Louër, 1991)

This program works in direct space (down to the monoclinic system) by using the successive-dichotomy search method (see Section 3.4.3.1.5), which was introduced for the automatic indexing of powder diffraction patterns by Louër & Louër (1972). *DICVOL91* has been defined as exhaustive by Shirley (1980, 2003). Its main steps are:

- (1) The unit-cell volume is partitioned by moving from high to low symmetry. Shells of  $400 \text{ \AA}^3$  of volume are scanned for all the symmetry systems except for triclinic; for the triclinic system the shells are based on the definition of volume proposed by Smith (1977) (see Section 3.4.3.1.5).
- (2) A search using the successive-dichotomy method, based on suitable intervals (see Section 3.4.3.1.5), is carried out. In the case of the triclinic system the general expression for  $Q(hkl)$  as function of the direct cell parameters is too complicated, and the reciprocal-space parameters in equation (3.4.2) are used for setting the intervals.
- (3) The derived cell parameters are refined using the least-squares method.
- (4) The quality of each trial unit cell is evaluated by using the  $M_N$  and  $F_N$  figures of merit (see Section 3.4.2.1).

The program is fast at performing exhaustive searches in parameter space (except for the triclinic case); on the other hand, its efficiency is strongly related to the quality of the data and to the presence of impurities (in fact, impurities are not permitted).

## 3.4.4.2. Evolved indexing programs

3.4.4.2.1. N-TREOR09 (Altomare *et al.*, 2009)

Implemented in the *EXPO* program (Altomare *et al.*, 2013) to perform the powder pattern indexing step, *N-TREOR09* is an update of *N-TREOR* (Altomare *et al.*, 2000), which in turn is an evolution of *TREOR90*, and preserves the main strategies with some changes introduced to make the program more exhaustive and powerful. In particular: