Dicvol06

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Program for the Automatic Indexing of Powder Diffraction Patterns
by the
Successive Dichotomy Method.

Reference for this program:

A. Boultif & D. Louer, J. Appl. Cryst. 37, 724-731, 2004

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Input Data File

Input data for Dicvol06 program follow the next considerations:

Line 1

String defining the Title (free format)

Line 2

N, ITYPE, JC, JT, JH, JO, JM, JTR

where

N	Number of lines used for searching solutions
ITYPE	Spacing Data type 1 = θ Bragg angle in degrees 2 = 2θ angle in degrees 3 = d-spacing in angstrom unit 4 = Q specified in Q-units as E+04/D**2.
JC	0/1 Cubic system is NOT TESTED (0) / TESTED (1)
JT	0/1 Tetragonal system is NOT TESTED (0) / TESTED (1)
JH	0/1 Hexagonal system is NOT TESTED (0) / TESTED (1)
JO	0/1 Orthorhombic system is NOT TESTED (0) / TESTED (1)
JM	0/1 Monoclinic system is NOT TESTED (0) / TESTED (1)
JTR	0/1 Triclinic system is NOT TESTED (0) / TESTED (1)

Line 3

AMAX, BMAX, CMAX, VOLMIN, VOLMAX, BEMIN, BEMAX

where

AMAX	Maximum value of unit cell dimension **a**, in angstroms. If AMAX= 0.0 then default= 25. 0 Å
BMAX	Maximum value of unit cell dimension **b**, in angstroms. If BMAX= 0.0 then default= 25. 0 Å
CMAX	Maximum value of unit cell dimension **c**, in angstroms. If CMAX= 0.0 then default= 25. 0 Å
VOLMIN	Minimum volume for unit cells in $Å^3$
VOLMAX	Maximum volume for unit cells in $Å^3$
BEMIN	Minimum β angle for monoclinic cells in degrees. If BEMIN= 0.0 then default= 90.0º
BEMAX	Maximum β angle for monoclinic cells in degrees. If BEMAX= 0.0 then default= 125.0º

Line 4

WAVE, POIMOL, DENS, DELDEN

where

WAVE	Wavelength in Angstroms (Default=0.0 If Cu $K\alpha_1$)
POIMOL	Molecular weight of one formula unit in a.m.u. (Default =0.0 if formula weight not known)
DENS	Measured density in $g.cm^{-3}$. (Default =0.0 if density not known)
DELDEN	bsolute error in measured density. (Default =0.0 if density not known)

Line 5

EPS, FOM, N_IMP, ZERO_S, ZERO_REF, OPTION

where

EPS	= 0.0	The absolute error on each observed line is taken to 0.03°. 2θ (default value) whatever the spacing data type (ITYPE).
	= 1.0	The absolute error on each observed line is input individually from Line 6, after the observed 'd(i)' on the same line, according to the spacing data unit (e.g. 18.678 0.018 in $2\theta°$).
	0.0 < EPS < 1.0	The absolute error is taken as a constant (= EPS) in $2\theta°$, whatever spacing data type (ITYPE) (e.g. 0.02, which will apply to all input lines).
FOM		Lower figure of merit M(n) required for printed solution(s) (Default=0.0 M(n)=10.0).
N_IMP		Maximum number of impurity/spurious lines accepted among the first N lines (N_IMP takes into account both impurity lines and peak positions out of the input absolute angular error EPS). If N_IMP < 0 the search starts with zero impurity lines, then, it continues with one impurity line, and so on until N_IMP impurity lines is reached.
ZERO_S		A priori search for a zero-point error in input data
	= 0	No Search
	= 1	Search
		If ZERO_S ne 0 or 1, then ZERO_S represents a known zero correction (e.g. -0.10) in $2\theta°$.
ZERO_REF	= 0	No 'Zero-Point' Least-squares refinement
	= 1	'Zero-Point' Least-squares refinement
OPTION	= 0	Dicvol04 option (optimized strategy search with decreasing cell volumes).
	= 1	Option with extended (exhaustive) search in volume domains containing mathematical solution(s) (longer cpu times). If OPTION is omitted, default is Dicvol04

Line 6 ....

D(I) [,EPSIL(I)]

where

D(I)	Value describing the observed position of line 'i' according to spacing unit ITYPE.
EPSIL(I)	Only if EPS=1.0 : absolute error for D(I), according to ITYPE.

[If EPS= 0.0 or EPS is a constant not equal to 1.0 (e.g. 0.02), only D(I) are required].

There are 6 to 6+N_TOTAL lines containing the data.

Note:

- If ITYPE=1,2,4 the values of D(i) and EPSIL(i) must be preferably (though it is not mandatory) listed in increasing order.
- If ITYPE=3 they must be preferably listed in decreasing order.

Output Files

Dicvol06 generates two output files:

- A file containing the solutions as found by the program (also seen on the display when Dicvol06 is running).
- A second file with the same name and the extension ***.ord***, in which all (mathematical) solutions are ranked according to their De Wolff fom.

Using Dicvol06

Use as input data all available diffraction lines (N_TOTAL). Only the first N (eg 20) lines will be used for the search of solutions. These solutions are subsequently used automatically for reviewing all N_TOTAL input data. The impurity tolerance N_IMP is related only to the N lines used for searching solution(s) (of course, other unindexed lines can be found among the extra input lines in the reviewing process).

Be careful in using the impurity tolerance: spurious lines increases the risk to miss the correct solution!

- With good quality data, OPTION = 0 (i.e. Dicvol04) is recommended.
- The option ***extended (exhaustive) search*** (OPTION =1), can be useful in cases of
    a) unstable cases, i.e. many solutions are found in a small range of cell volumes,
    b) expected diffraction lines are missing among the first input lines,
    c) low quality data,
    d) significant number of impurity lines, etc.

If a solution is found in a volume shell, the search is exhaustive within this shell. thus, the search is not extended to the next volume shell (for the symmetry being analysed). if needed, the user can run again Dicvol06, for selected lattice systems, taking the higher volume value of the already analysed volume shell as VOLMIN in the new input parameters set.

Generally, runs with OPTION =1 take longer CPU times and the number of mathematical solutions is greater (it has been limited to the first 100 found solutions in the Dicvol06 output file). By acting on the input FOM (greater FOM in Line 5) solutions with lowest FOMs can be rejected).
Be careful: as soon as 100 solutions are found the calculation stops.

Dicvol06 offers the possibility to analyse your input data for the presence of a zero-point error. The method employed can suggest more than one or two solutions (due to uncertainty in searching harmonic diffraction lines). This option is to be used prior the indexing process. Please, as far as possible avoid the use of this facility by ensuring the quality of your collected data!

Usual 'zero-point' errors (if not too big) are generally corrected by the least-squares refinement of the 'zero-point' parameter ZERO_REF, together with the refinement of cell parameters. ZERO_REF is, in fact, an extra degree of freedom in the refinement. it includes all systematic measurement errors from different origin, e.g. zero-point shift, sample-surface displacement, umbrella effect, transparency, capillary displacement, ...

Suggested strategy

It is recommended to use a two- or three-stages procedure (i.e. triclinic lattices should preferably be studied separately), for example:

1. search in high symmetries down to orthorhombic: *Line 2: n,itype,1,1,1,1,0,0*
2. search in monoclinic symmetry: *Line 2: n,itype,0,0,0,0,1,0*
3. if necessary, search in triclinic symmetry: *Line 2 : n,itype,0,0,0,0,0,1*

Note that for solutions with Monoclinic and Triclinic symmetries the program provides the reduced cell. If various equivalent solutions are found, only one of them is listed in the output file.

Trigonal symmetry case with rhombohedral lattice: the pattern is indexed with an hexagonal lattice, having a unit cell volume three times greater.

Recommendations

- Read carefully references 1 and 6 (and 9), as well as this user's guide.
- Please, spend time to ensure the quality of your collected data (see ref. 5). With accurate data, the success rate of Dicvol06 is very high. Peak positions should be extracted with a profile fitting software. An interactive program should be preferred, since automatic extractions can miss lines (low intensity, shoulder, ...).
- With bad data, the chance to obtain the correct solution is small and the calculation can be time-consuming.
- With modern x-ray powder diffractometers (the use of monochromatic radiation is recommended), absolute errors on peak positions lower than 0.02 degrees 2θ can be routinely obtained. For indexing purposes, errors should not (ideally) exceed 0.03^{o} in 2θ. [In exceptional cases, a few lines with greater individual estimated error can be introduced in the input data. In this case, use the parameter EPS= 1, and enter individual errors after D(i) for each

line].

- With high resolution powder diffraction data (conventional or, particularly, synchrotron x-ray sources), the absolute error is usually less than 0.02º (or even 0.01º with ultra-high resolution) in 2θ; consequently, EPS=0.02 (or even EPS=0.01) is recommended; the convergence of the dichotomy procedure will be improved. However, be sure that this condition is true for all lines used as input data. (Remember that all mathematical solutions within the input limits and error bounds are found, the greater they are the greater is the number of mathematical solutions).
- N_IMP can be used in case of expected spurious lines (i.e. impurity lines, as well as observed lines out of the input error). N_IMP acts at all successive levels of the dichotomy algorithm. As soon as an indexing solution is retained, a least-squares refinement of lattice parameters is carried out. For this refinement a larger error on observed lines is considered. Then, a line rejected at the last dichotomy level can, by chance, be accepted with the refined lattice parameters. [Example of possible case: N_IMP = 0 no solution; N_IMP = 1 one solution; however, after LS refinement of the lattice parameters all N lines used for searching solutions are indexed with the refined parameters.]
- Note that the program Dicvol06 is executable from 7 lines- 8 lines if the 'zero-shift' is refined - (though it is not recommendable since LS refinement unstabilities can be expected).
- Long and short axis cases (dominant zone cases): if such cases are expected, the number N of lines used for searching the solution should, generally, be greater than 20.
- The minimum value for a linear lattice parameter has been fixed to 2.5 angstroms.
- Reliability of indexing solutions: read paragraph 8 of ref. 5 and refs 7 and 8.
- Note that with the option Dicvol04 (option =0), as soon as a solution is found, only solutions with smallest volumes will be subsequently retained. If (for some reasons!) you are not satisfied by the solution, you can run again the program with an input lower volume limit slightly greater than that of the found solution (the exhaustive search is then extended to a higher volume).
- Note that the search is exhaustive within the limits on the input data. In particular, the search is constrained by the higher and smaller bounds on parameters, volumes, selected FOM and absolute errors on peak positions. Please act on these parameters when using Dicvol06.
- A lattice metric singularity occurs when unit cells defining two lattices have an identical set of calculated d-spacings. This can be observed with high symmetry lattices (read ref. 5, sect. 4.2, and refs therein). simple relations exist between the parameters of the two cells, as well as particular cell-volume ratios. a typical case is: an hexagonal cell [a, c, volume v] can be indexed with an orthorhombic cell [parameters: a/2, a sqrt(3), c, volume v/2]. Due to the strategy used in Dicvol, based on an analysis through decreasing symmetry, all cells should be, in principle, displayed in the output file (except if a solution is rejected by the input maximum volume).
- Check on validity of an indexing result: please read ref. 5 (sect. 8)
- Possible space groups: look at the hkl conditions in the output list of the reviewing of the complete input data provided after a solution is found from the first N lines.
- Additional information on Dicvol06 should appeared in ref. 9.

References

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