Supporting information for:

Advances in powder diffraction pattern indexing: *N-TREOR09*

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N-TREOR09 has been applied to a set of 102 test structures. For 48 of the 102 test structures *N-TREOR09* selects a unique cell (and therefore a unique value of *WRIP20*) and associates the highest $PROB_{ex}$ value to the correct extinction symbol (see Table S1). For 37 of the remaining 54 test structures *N-TREOR09* provides a short list of plausible solutions for which both M_{20} and *WRIP20* are able to recognize the correct cell. The main results are shown in Table S2.

A case of interest is considered below in more details.

NORBO_AG. This structure is one of the cases in which R_p is not able to recognize the correct monoclinic cell (a=7.606 Å, b=8.622 Å, c=8.749 Å, β =97.24°, space group $P2_1/c$). *N-TREOR09* supplies three possible solutions, shown in Table S3, together with the corresponding M_{20}, R_p, $PERC_{ind}$, $PERC_{pres}$, *WRIP20* and unit cell volume values. M_{20}, $PERC_{ind}$, $PERC_{pres}$ and *WRIP20* parameters correctly indicate the first unit cell as the correct one, while the smallest R_p value is obtained for the third one, which is a triple cell. A similar behaviour is observed for *CORUNDUM*, *CREATINE*, *LAMO*, *THIO_AG* and *ZINCITE*: for all of them the R_p parameter privileges cells that are multiple of the correct one. In agreement with our observations (see §3 of the paper), multiple cells are expected to be associated with the smallest R_p values: luckily M_{20}, $PERC_{ind}$ and $PERC_{pres}$ allow often to compensate in *WRIP20* the R_p perverse tendency.

Table S1. Subset of 48 test structures for which *N-TREOR09* selects a unique cell (and therefore a unique value of *WRIP20*) and associates the highest $PROB_{ex}$ value to the correct extinction symbol. For each test structures we give the code name and the main reference. X, S and N in parentheses mean conventional diffractometer, synchrotron and neutron data, respectively. X* is associated to conventional diffractometer data kindly provided by J. Bergmann.

Code name and reference
ALPHA (S)[1]; ALPO (S)[2] AMMONIUM (X)[3]; AMPICILLINE (S)[4]
AND1 (S)[5]; AND2 (S)[5]; BENZ (S)[6]; CAINE (X)[7]
CAMPHOR (S)[8]; CAPTO (X)[3]; CARBA (X)[3]; CARBAMA (X)[3]
CIME (S)[9]; CLOMIPRA (X)[3]; COPPER (X)[10]; DADA (S)[11]
DILTIA (X)[3]; EMT (S)[12]; EPIDOTE (X*)[13]; ETHYLB (X)[3]
FAMO (S)[14]; FORMYLUREA (S)[15]; GAPO (S)[16]; HYDROFLU (X)[3]
IBUPS (S)[17]; LASO (X)[18]; MCM-22 (S)[19]; MERCA (X)[3]
MES (X)[20]; METYL (S)[21]; NABENZO (S)[22]; NIZR (S)[23]
OTHYM (X)[24]; OXABICYCLO_185 (S)[25]; PARACETAMOL1 (X)[3]; PBS (S)[26]
PHENYLA (X)[3]; PIPERAZINE (X)[3]; PREDNI100K (S)[27]; SAPO-40 (X)[28]
SBPO (S)[29]; SIBUPROFEN (X)[3]; SGT (S)[30]; SODIUM (X)[3]
UTM1 (S)[31]; VERAPA (X)[3]; ZOPI (X)[3]; YURI (X)[32]

(1) Harris *et al*. (2001); (2) Baerlocher *et al*. (2004); (3) Florence *et al*. (2005); (4) Burley *et al*. (2006); (5) Chernyshev *et al*. (1999); (6) Williams *et al*. (1992); (7) Nowell *et al*. (2002); (8) unpubl. data by courtesy of Dr. M. Brunelli; (9) Cernik *et al*. (1991); (10) Banerjee *et al*. (2002); (11) Dadachov & Le Bail (1997); (12) Baerlocher *et al*. (1994); (13) Bergmann, (2007); (14) Shankland *et al*. (2002); (15) Arumugam *et al*. (1992); (16) Meden *et al*. (1997); (17) Shankland *et al*. (1998); (18) Lasocha & Schenk (1997); (19) Camblor *et al*. (1998); (20) Christensen *et al*. (1993); (21) Weiss *et al*. (1990); (22) http://www.fkf-mpg.de/xray/html/rietveld_refinement.html; (23) Jouanneaux *et al.* (1991*a*); (24) Kariuki *et al*. (1997); (25) Palin *et al.* (2007); (26) Christensen *et al*. (1991); (27) Nishibori *et al*. (2008); (28) Estermann *et al*. (1992); (29) Jouanneaux *et al.* (1991*b*); (30) McCusker (1988); (31) Plévert *et al*. (1999); (32) Andreev *et al*. (1997).

Table S2. Subset of 37 test structures for which both *WRIP20* and M_{20} are able to correctly recognize the solution. For each case, the code name and the true crystal system are given, together with:

- RK_{M20}: rank of the correct unit cell according to M_{20};
- $(M_{20})_{max}$: maximum value of M_{20} for the plausible unit cells;
- $RA_{M20} = (M_{20})_2/(M_{20})_1$. $(M_{20})_2$ and $(M_{20})_1$ are the M_{20} values associated with the unit cells ranked at position 2 and at position 1 by the M_{20} figure of merit, respectively. The value is not supplied when only one unit cell has been selected by *N-TREOR09*;
- $(WRIP20)_{max}$: maximum value of *WRIP20* for the plausible unit cells;
- RK_{WRIP20}: rank of the correct unit cell according to *WRIP20*;
- $RA_{WRIP20} = (WRIP20)_2/(WRIP20)_1$. $(WRIP20)_2$ and $(WRIP20)_1$ are the *WRIP20* values associated with the unit cells ranked at position 2 and at position 1 by the *WRIP20* figure of merit, respectively. The value is not supplied when only one unit cell has been selected by *N-TREOR09*;
- RK_{EX} : the rank of the correct extinction symbol according to $PROB_{ex}$;
- *CPU*: the *CPU* time (in minutes and seconds) required by the procedure on Intel Xeon 3.6 GHz Workstation;

X, X*, S and N in parentheses mean conventional diffractometer, data by courtesy of Dr. J. Bergmann, synchrotron and neutron data, respectively.

Code name	Crystal system	RK_{M20}	$(M_{20})_{max}$ (RA_{M20})	RK_{WRIP20}	$(WRIP20)_{max}$ (RA_{WRIP20})	RK_{EX}	CPU
ALDS (S)[1]	Orth.	1	19 (0.37)	1	1.0 (0.25)	1	2’ 23”
BAMO (X)[2]	Mon.	1	42 (------)	1	1.0 (------)	2	37”
Ca_3CoIrO_6 (X)[3]	Hex.	1	20 (0.75)	1	0.896 (0.35)	1	1’ 2”
CASSITERITE (X*)[4]	Tetr.	1	121 (0.14)	1	0.791 (0.35)	2	1’ 5”
CeO_2 (X)[5]	Cubic	1	267 (0.62)	1	0.918 (0.15)	1	26”
CF3BR (N)[6]	Mon.	1	21 (0.71)	1	0.909 (0.33)	1	10’ 15”
CORUNDUM (X*)[4]	Hex.	1	101 (0.56)	1	0.769 (0.70)	8	8’ 34”
CPD-Y_2O_3 (X*)[4]	Cubic	1	57 (0.63)	1	0.744 (0.49)	1	2’ 28”
CREATINE (X)[7]	Mon.	1	79 (0.65)	1	0.990 (0.61)	1	38”
CROX (X)[8]	Tricl.	1	49 (0.20)	1	1.0 (0.16)	1	51”
CUPZ (X)[9]	Orth.	1	45 (0.47)	1	0.847 (0.64)	1	9’ 15”
F1A (X)[10]	Hex.	1	17 (------)	1	0.993 (------)	6	1’ 44”
FLUORITE (X*)[4]	Cubic	1	552 (0.62)	1	0.873 (0.01)	2	16”
GYPSUM (X*)[4]	Mon.	1	26 (0.35)	1	1.0 (0.33)	6	6’ 53”
HYDRAZINE (X)[7]	Mon.	1	47 (0.28)	1	0.996 (0.38)	1	34”
K2CR2O7 (X*)[4]	Tricl.	1	21 (0.48)	1	0.973 (0.34)	1	8’ 50”
LaB_6 (X)[11]	Cubic	1	462 (0.51)	1	0.300 (0.96)	1	3’ 32”
LACTOSE (X)[7]	Mon.	1	26 (0.50)	1	1.0 (0.38)	1	1’ 59”

LAMO (S)[12]	Mon.	1	58 (0.45)	1	0.865 (0.65)	1	49”
LEV (S)[13]	Hex.	1	69 (0.58)	1	0.731 (0.42)	1	4’ 16”
MZTEEN(X)[14]	Hex.	1	27 (0.63)	1	0.865 (0.36)	5	3’ 57”
NBPO (S)[15]	Mon.	1	20 (0.85)	1	0.781 (0.31)	1	5’ 14”
NICKEL (S)[7]	Mon.	1	45 (------)	1	0.995 (------)	2	22”
NORBO_AG (S)[16]	Mon.	1	51 (0.23)	1	0.881 (0.31)	1	4’ 35”
PBSO4 (X*)[4]	Orth.	1	51 (0.33)	1	1.0 (0.35)	2	6’ 1”
PIPERIDINE_90C (S)[17]	Orth.	1	37 (0.40)	1	0.967 (0.47)	1	35”
PIPERIDINE_270C (S)[17]	Orth.	1	51 (------)	1	1.0 (------)	2	15”
QUARTZ (X*)[4]	Hex.	1	212 (0.27)	1	0.736 (0.43)	1	2’ 16”
SALBU (X)[7]	Orth.	1	30 (0.27)	1	1.0 (0.29)	1	2’ 26”
SCAMPHOR1 (S)[18]	Orth.	1	28 (0.71)	1	1.0 (0.01)	1	3’ 8”
SRRU (S)[19]	Orth.	1	49 (------)	1	1.0 (------)	37	4’ 40”
THIO_AG (S)[20]	Orth.	1	103 (0.84)	1	0.954 (0.889)	1	2’ 15”
TOLBU (X)[7]	Orth.	1	37 (0.51)	1	0.997 (0.549)	79	41”
VFI (S)[21]	Hex.	1	72 (------)	1	1.000 (------)	2	18”
VNI (S)[22]	Tetr.	1	11 (------)	1	0.997 (------)	11	2’ 28”
ZINCITE (X*)[4]	Hex.	1	241 (0.38)	1	0.954 (0.514)	1	1’ 1”
ZIRCON (X*)[4]	Tetr.	1	92 (0.25)	1	0.896 (0.220)	1	24’ 28”

(1) SDPDRR (1998); (2) Werner *et al.* (1997); (3) Unpublished data by courtesy of Dr. G. Campi; (4) diffraction data by courtesy of Dr. J. Bergmann; (5) Brauer & Gradinger (1954); (6) Jouanneaux *et al.* (1992); (7) Florence *et al*. (2005); (8) Norby *et al*. (1991); (9) Masciocchi *et al.* (1994); (10) Perez *et al*. (2000); (11) Eliseev *et al*. (1986); (12) Hibble *et al.* (1988); (13) McCusker (1993); (14) diffraction data by courtesy of Dr. W. Lasocha; (15) Zah-Letho *et al*. (1992); (16) Brunelli *et al.* (2001); (17) Mora *et al.* (2005); (18) Brunelli *et al.* (2002*a*); (19) Bushmeleva *et al*. (2006); (20) Brunelli *et al.* (2002*b*); (21) McCusker *et al.* (1991); (22) McCusker *et al.* (1996).

Table S3. *NORBO_AG*: unit cell parameters, M_{20}, R_p, $PERC_{ind}$, $PERC_{pres}$, *WRIP20* and cell volume (*VOL*) calculated by *N-TREOR09.*

Cell parameters (Å,°)	M_{20}	R_p	$PERC_{ind}$	$PERC_{pres}$	*WRIP20*	*VOL* (Å^3)
a= 8.741, b=8.620, c=7.603 β =97.2	51	0.120	0.418	0.953	0.881	568.3
a= 12.294, b=8.621, c=10.858 β =98.1	12	0.104	0.258	0.998	0.273	1139.3
a= 22.815, b=8.621, c=8.734 β =97.2	11	0.102	0.177	0.998	0.180	1704.5

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