**12.2-01**   AN ADVANCED SEARCH/MATCH SYSTEM FOR X-RAY POLYCRYSTALLINE IDENTIFICATION.   By T. C. Huang, G. L. Ayers and W. Parrish, IBM Research Laboratory, San Jose, California 95193, USA.

A comprehensive computer Search/Match system ·has been developed for rapid and precise phase identification of polycrystalline materials. It operates on a host computer or a minicomputer using a "question and answer" interactive input. Either full screen menu or line input formats arranged to minimize incorrect entries may be selected.

The data base may be a user created file, or the JCPDS which we have rearranged into four subfiles: inorganics, organics, minerals, and metals and alloys. In each subfile the frequently encountered phases are first, quality data second and the remainder last, which allows stopping at the end of any section when identification has been made. Data may be entered manually or by automatic transfer from Peak Search or Profile Fitting runs or stored data. Systematic errors may be automatically corrected by entering a few correct d's of an internal standard or a known constituent in a mixture. The error limits for matching are selectable and overlapping window limits are used. The program requires the three strongest standard reflections in the experimental range be present in the unknown. However there is an option to remove this requirement if strong preferred orientation is suspected. The chemical information option provides elements present, absent and/or groups of elements absent.

A comprehensive algorithm evaluates each match by computing a figure-of-merit (FOM) based on the matches of the d's, I's and number of reflections. The top FOM standards are listed after each section of the file is completed, and the user may end or continue the search. Interpretation is aided by interactive operations which include graphic terminal displays of the unknown pattern and the standards. The program employs previously determined W*G profile data to generate the standard patterns which appear as if run on the user's diffractometer, and are scaled to correspond to the amount of each phase in the unknown. The identified phases may be subtracted and the remainder plotted to aid in deciding to continue or end the search. This is illustrated below for a 3-mineral mixture; the unknown pattern appears above each standard and the tick marks indicate the peaks. The low right is the residue after subtracting the three standards and results from the differences between the experimental data and the standards. The system has been extensively tested on a wide variety of analyses and round robin data.
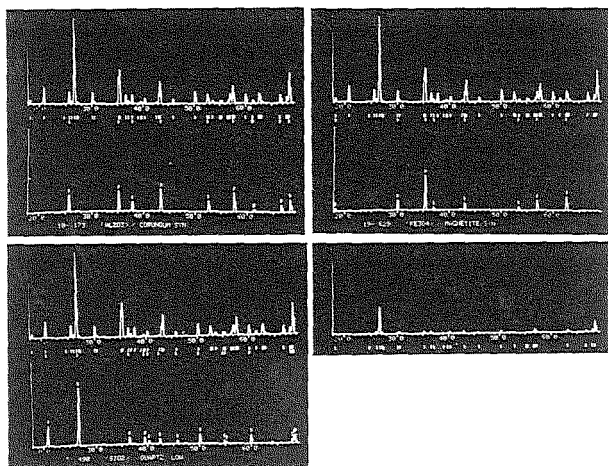
12.2-02   PROBABILITY-BASED SCORING METHOD FOR RANKING MATCHES IN X-RAY POWDER DIFFRACTION PHASE IDENTIFICATION. By W. N. Schreiner, Philips Laboratories, Briarcliff Manor, NY, R. Jenkins, Philips Electronic Instruments Inc., Mahwah, NJ.

Computer search/match programs used to identify phases of a polycrystalline material from an x-ray powder diffraction diagram have traditionally found it very difficult to compete with manual searchers, presumably because they lack the intelligence of a human being. While there is no hope of developing intelligent programs in the near future, some "algorithms" that are employed, perhaps unknowingly, by manual makers can be adapted to. the computer and improved programs result.

·One technique, which we call probability-based scoring, is based on computing event probabilities for a pattern match. The events may be "d-hits", "I-hits", loss in background, line overlap, etc.. An overall pattern match score is obtained by multiplying the event probabilities together in a maximum likelihood fashion. The method has the advantage of eliminating the so-called "windows" traditionally employed by search/match programs. To function optimally, it necessitates the separation of systematic from random errors so that the probability distributions of the events are as narrow as possible.

Probability-based scoring has been implemented in the SANDMAN (Adv. In X-Ray Anal., 24 (1981) in press) search/match/identify system which is part of the APD-3600 Automated Powder Diffractometer. (Norelco Reporter 26, 1 (1979)). It has been found to be extremely effective and has led to the development of additive (as opposed to subtractive) phase isolation. The technique will be described in detail and examples will be shown.

12.2-03   QUANTITATIVE X-RAY PHASE ANALYSIS WITHOUT STANDARDS: GENERAL CASE OF OVERLAPPING PEAKS. By L.S. Zevin, R. Shneck, Research & Development Authority, Ben-Gurion University of the Negev, Beer-Sheva, Israel and I.M. Zevin, Geological Survey of Israel.

The following expression, in matrix notation, is valid for the intensity $I_{j\ell}$ of the ℓ-th diffraction peak $(1 \leq \ell \leq n)$ in the j-th sample $(1 \leq j \leq n)$. (Assuming that $I_{j\ell}$ is corrected for absorption.)

$$[I_{j\ell}] = [X_{ji}] [K_{i\ell}] \qquad (1)$$

where X_{ji} - weight fraction of the phase i $(1 \leq i \leq n)$ in the sample j; and $K_{i\ell}$ - coefficient proportional to the intensity of the ℓ-th peak in the i-th phase. If there are no overlapping analytical peaks, the matrix $[K_{i\ell}]$ is a diagonal one; and equation (1) can be solved for all n^2 unknowns X_{ji} and n unknowns $K_{i\ell}$ if the usual condition of complete analysis is added [Zevin, J Appl. Cryst. (1977) 10, 147]:

$$\sum_{i=1}^{n} X_{ji} = 1 \qquad (2)$$

.In the case of complete overlapping (none of the values of $K_{i\ell}$ = 0), the number of unknowns $(2n^2)$ exceeds the whole number of equations (1) and (2) (n^2+n). The apparent possibility of increasing the number of significant equations by increasing the number of samples is not viable. The intensity of each diffraction peak 1 in the (n+1)th sample is simply a linear combination of the intensities I_{j1} in the previous n samples [Bezjak, Anal. Chem. (1975), 47, 790]. The only viable possibility for the phase analysis is the separation of the

peaks by the recently developed profile-fitting method
[Huang and Parrish *Ad v. X-ray Anal.* (1978), 21, 275].

In the intermediate case of partial overlapping (only
some of the values of $K_{i\ell} = 0$), the system of equations

(1) and (2) could be solved as was suggested by Majumdar
et al. [*J. Appl. Crystal* (1972) 5, 343)] for a similar
problem. The following conditions should be derived in
order to perform the phase analysis: 1) The number of
analytical peaks should be extended up to m > n.
2) For each phase at least n-1 peaks ℓ' with $K_{i\ell'} = 0$

should be found. 3) At least one phase of the remain-
ing n-1 should contribute to these ℓ' peaks. Under
these conditions the complete number of equations (1)
and (2) nm+n is equal to the number of unknowns:
n^2 of X_{ji} and n[m-(n-1)] = nm-n^2+n of K_{ij}. A least-
squares procedure for the refinement of X_{ji} and $K_{\ell i}$

should be performed if the number of samples and analy-
tical peaks exceeded the above-discussed minimal values
of n and m, respectively.

12.2-04 CORUNDUM – A REFERENCE FOR PHASE ANA-
LYSIS WITHOUT PROBLEMS? J.Zábráczky and P.Gadó
Res.Eng.& Prime Contr.Center of the Hung.Alumi-
nium Corp.,H-1389 Budapest P.O.B.128 Hungary

Corundum (α-Al_2O_3) has been adopted as a stan-
dard material for the experimental determination
of the I/I_c reference intensity ratio.Realizing
the advantages, in diffraction phase ana-
lysis, of the availability of this parameter,
recently the PDF of the JCPDS included in the
set of data published for each material – when-
ever practicable – the value of I/I_c. The app-
lication of this information is straightforward,
provided a batch of the same corundum as used
for the original determination is possessed.
Having tried some commercially offered good qua-
lity corundum samples, we found by texture
goniometer measurements that this material is
rather sensitive to [001] uni-axial preferred
orientation. The absolute intensity diffrac-
ted depends a great deal upon the way of pre-
paration (oxidation of metal or via sodium alu-
minate,temperature history,additives and sub-
sequent grinding). Kiss,A.B.& Gadó,P. (M.Kém.Fo-
lyóirat 84,289,1978) showed the effect of Na
impurities on the IR and X-ray data of corundum.
Probably any corundum will yield observations
good for analytical estimates. However,if the
accuracy stated for some reference intensity ra-
tios (± 2-3 % deviation) should be fully explo-
ited in quantitative determinations, the 5-10 %
deviations measured between the reflected inten-
sities of different corundum samples (Linde,De-
gussa,Norton,Feldmühle,Hungalu) become disturbing.
It can be concluded that further international
agreements are needed to diminish this component
of uncertainty in comparative diffraction phase
analysis.

12.3-01 THE REFINEMENT OF UNIT-CELL PARAME-
TERS FROM POWDER DIFFRACTION DATA USING STRUC-
TURE FACTORS. A.V.Chichagov, V.V.Surikov,
L.N.Ivanova, Institute of Experimental Minera-
logy, USSR Ac, Sci., Moscow District, USSR

A Fortran-Algol program for the refinement of
unit-cell parameters,using the automatic in-
dexing of experimental reflections from the
list of theoretical reflections allowing for
their weight,has been written for the BESM-6
computer. Facilities include:
1. Calculation of the θ-ordered list of theo-
retical reflections with the θ_k^c angle positi-
ons, (hkl)$_k$ indices and J_k^c intensities with
rejection of the following reflections:
a) forbidden by the space group, b) equivalent
c) deliberately forbidden, d) with the angle
positions outside the given angle range,
e) with the normalized intensities below a
given threshold value.
2. Preliminary refinement of unit-cell para-
meters through the minimization of the Δ-fun-
ction $\sum_i w_i (Sin^2\theta_i^o - Sin^2\theta_{ik}^c)^2$ by the flexi-
ble Simplex method. At each refinement step
the optimization process allows for the i-th
experimental reflection to be matched to the
ik-th theoretical reflection (hkl)$_k$ with the
maximum weight $Q_{ik} = \sum_j V_{ik} J_k^c$

j is the summation index for the theoretical
reflections that have the same angular posi-
tion but differ in their intensities). The
program allows for three types of the weight
factor:

$$V_{ik}^1 = 1 - a / \Delta\theta_{ik},$$
$$V_{ik}^2 = [1 + (\sqrt{2} - 1)(\Delta\theta_{ik}/G_i)^2]^{-2},$$
$$V_{ik}^3 = exp[-Ln2(\Delta\theta_{ik}/G_i)^2]$$

($\Delta\theta_{ik} = \theta_i^o - \theta_{ik}^c$; a is the preset constant
which determines the angular range where the
weight factor operates; if $V_{ik}^1 < 0$, the weight
is ignored; $2G_i$ is the half-width of the i-th
experimental reflection calculated from:

$(2G)^2 = m\,tg^2\theta + n\,tg\theta + \ell$ (m, n, l are gi-
ven constants)
3. The final refinement of the unit-cell para-
meters by minimizing the linearized Δ-function
for the set reflection indices obtained at
the optimization stage as well as the calcula-
tion of confidence limits and correlation co-
efficients of the parameters.
The program needs as input: the list of the
$\theta^o(2\theta^o)$, the trial parameter values, the li-
miting index values, and the information ne-
cessary for calculating the list of theoreti-
cal reflections.