

phase-pure V₆O₁₃. Our efforts here focus specifically on this problem, and subsequently on achieving controlled *chemical* lithium insertion. Phase-pure V₆O₁₃ has also been incorporated into thin-film polymer batteries, which were then cycled to facilitate *in situ* X-ray diffraction studies (transmission mode) of the corresponding *electrochemical* lithium insertion process. Structural rearrangements involved in both insertion processes are analyzed carefully and compared; observations are also made regarding the reversibility of these processes.

20.02 – Multiphase Analysis

DS-20.02.01 RECENT DEVELOPMENTS IN THE COMPUTER SEARCH/MATCHING OF MULTI-PHASE MATERIALS. By R. Jenkins, International Centre for Diffraction Data, Swarthmore, PA, U.S.A.

While most contemporary methods of qualitative analysis of multi-phase materials are still based on the classic Search/Match/Identify process developed by Hanawalt, Rinn and Frevel in the 1930's, during the past 10 years or so the Personal Computer has made a dramatic impact on the ways in which classical procedures are being implemented.

Modern search/matching procedures can conveniently be broken down into three categories - Manual Methods, Computer-Aided Methods, and Fully Automated Methods. Even where purely manual search/match methods are used, the computer based diffractometer systems still give the potential benefit of high quality d/I data, especially where automated angular and intensity calibration is employed. In the case of computer-aided and fully automated techniques, the additional use of newer data processing techniques including profile fitting, α_2 stripping, etc., have all conspired to provide the diffractonist with accurate, artifact-free data, with which to start the search/ matching process. Finally, the ability to search index files containing physical and experimental data, beyond the traditional d/I list, and the availability of comprehensive sub-file selections, has resulted in robust boolean search algorithms, which give the user great flexibility in setting up search strategies.

As to the implementation of the search/match approach, the use of fast, modern PC's, with integrated CD-ROM storage and powerful windows-based operating systems, has allowed the software developer a degree of flexibility, undreamed of a decade ago.

This paper will discuss recent progress in the use of some of these personal-computer based, data collection, processing and analysis programs, with special emphasis on their use in the analysis of multi-phase materials.

**DS-20.02.02 Search / Match Using Full Trace Scans:
A Strong Improvement over Using d/I Files**

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A table of d/I values in many cases represents, quite adequately, the ideal powder diffraction pattern of a single phase reference material. However, reducing the diffraction pattern of a complex mixture to such a list is more difficult and more questionable for several reasons:

- Determining "real" peaks through any "peak search" algorithm or "profile fitting" technique becomes practically impossible for weak lines of the measured diffractogram. This in turn, can preclude the identification of minor phases.

- Clusters of lines are most likely to be impossible to decompose due to (an inevitable) lack of information on the number, positions, and widths of non-resolved lines.

- The information on line-widths is lost - whereas in fact this is also an attribute of the respective phase.

The DIFFRAC AT search/match uses the full trace scan with subtracted background. Therefore it takes full advantage of all available information - particularly very weak lines, line clusters and the line widths.

Examples will be considered to demonstrate how important these features are for successful and reliable phase identifications.

Compared to traditional d/I tables, the DIFFRAC AT search/match uses much more input data which could be expected to have a severe penalty in speed of the search/match. In fact, due to very highly optimized code, a search employing the current whole ICDD data base (sets 1 - 42: 61,993 reference patterns) takes less than 15 seconds when performed on a i486/50-based PC.

DS-20.02.03 QUANTITATIVE POWDER DIFFRACTION PHASE ANALYSIS - RECENT DEVELOPMENT AND CURRENT STATUS. By J. Fiala¹⁾ and H. Toraya²⁾, ¹⁾Central Research Institute SKODA, Czech Republic, ²⁾Ceramics Research Laboratory, Nagoya Institute of Technology, Japan.

Methods for quantitative phase analysis (QPA) by using X-ray powder diffraction technique are reviewed, and their precision and accuracy are discussed in this paper. A development of experimental design shifted the analysis strategy from few-line measurement to many-lines and even to whole-pattern measurements. Preparation techniques, which can suppress detrimental effects of texture, particle size, inhomogeneity and amorphization, have been developed for powder samples while a serious problem remains for bulk samples. Standard reference materials of known phase composition have been produced. Chemical constraints are used to help with phase abundance analysis. Large scale systematic measurements were undertaken (inter-laboratory tests, reference intensity ratios determinations), and they form a necessary base for a quantitative assessment of the reliability of QPA. The main problem of QPA, which consists in the fact that diffraction intensities are influenced not only by phase composition of the mixture under analysis but also by real structure (and variable crystal structure) of its individual components and of polycrystalline aggregate as a whole, is addressed by simultaneous determination of phase composition, real structure and crystal structure of all constituents. However, correlations existing between the individual parameters enhance uncertainty of their estimates obtained by such a multivariate refinement. Factorial analysis of diffraction patterns of different fractions from the mixture analyzed provides intensity factors which are automatically corrected for the influence of real structure. Some forty years ago, accuracy of the QPA was estimated to (1 - 10)% absolute. The present day rather optimistic estimate, 2% absolute, seems to be limited to favorable cases of powder mixtures of phases, in which the real structure does not affect their diffraction appreciably.

DS-20.02.04 QUANTITATIVE ANALYSIS OF MULTIPHASE MATERIALS USING THE RIETVELD METHOD. By Julius Schneider, Institut für Kristallographie, Universität München, Theresienstraße 41, D-8000 München 2, Germany.

Use of the Rietveld method in quantitative analysis of multiphase mixtures has recently found increasing attention. As compared to conventional discrete-peak methods the consideration of the entire

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powder pattern and comparison with a "pure" powder pattern calculated from structural models offers several advantages:

1) It requires no standards or calibration procedures and can be performed with both X-ray and neutron powder diffraction.

2) Analysis can be extended to more complex powder patterns. As the extractable information does not increase linearly with the addition of more and more phases due to line overlap, the limit of multiphase analysis depends on the overall density of the Bragg reflections in the pattern, i.e. on cell dimension and crystal symmetry of the phases, on the purity and wavelength(s) of the radiation and on the resolution of the diffractometer.

3) Systematic errors such as preferred orientation, extinction, line broadening or surface roughness may be detected more easily. Recent progress in modelling these phenomena e.g. use of symmetrized harmonics to describe preferred orientation or of anisotropic line broadening to model crystal imperfections have aided with numerical corrections.

4) Unidentified phases may better be detected through careful refinement and analysis of the difference between the sum of all calculated phases and the observed intensity.

5) Better analytical or graphical modelling of the background considerably enhances the precision of the method. Addition of an amorphous reference material or analytical modelling of an amorphous component permits its quantitative determination.

6) More precise assessment of the quality of the analysis can be achieved by use of phase specific reliability factors (Rw-Bragg and GOF-Bragg) in addition to the conventional overall profile reliability factors Rwp and GOFwp.

7) The accuracy of the method can more easily be assessed by internal or external consistency checks: a) Extinction or surface roughness may be detected by a comparison of high and low angle data. b) Preferred orientation can be varied by use of different sample geometries, i.e. reflection, transmission or capillary. c) Extinction or micro-absorption may be varied through choice of different wavelengths (Cu, Mo...). d) Neutron data are barely affected by preferred orientation, extinction or micro-absorption.

Ease of use of the method has been greatly enhanced by set up of dedicated compilations of structure data and by interfacing to large crystal structure data banks. The method will become even more popular through increasing ease of software handling such as multiphase Rietveld programs on PC's, automatic parameter turn on sequencing and automatic multisample refinements.

More complex X-ray powder patterns may be analysed in the future by use of strictly monochromatic radiation, more flexible profile functions and increased instrument resolution offered by Guinier or Synchrotron diffractometers.

Technical applications such as the determination of mineral contents in rock specimens and analysis of clay minerals in ceramics will be discussed.

The Two-Stage Method is a very promising strategy especially in cases where preferred orientation may cause difficulties and may lead to wrong results. In the two-stage method, the diffraction diagram is decomposed into its individual peaks and thus its contribution to the different phases. The intensity data are normally used for crystal structure refinement, for example by the program POWLS. This procedure of refinement by POWLS also calculates a scale factor K besides positional and other structural relevant parameters. In case of several phases present each structure refined by itself thus yields its own several scale factors K_i . The scale factors K_i are directly related to the amount of material in the sample. By refining two or more crystal structures in the multiphase sample a quantitative analysis can be performed.

Since the whole diffraction pattern enters the analysis and since the crystal structures of the individual components are known, preferred orientation problems are easily recognized and can be taken into account. The biggest advantage of this method is found therefore in samples with considerable preferred orientation, like materials with calcite- or calcite-related-structures or clay and mica minerals.

Besides our own developments efforts and progress has been made in several laboratories, for example by Karimat and co-workers on kaolin samples. A review of recent developments will be presented.

DS-20.02.05 QUANTITATIVE ANALYSIS OF MULTIPHASE MATERIALS USING THE TWO STAGE METHOD. By G. Will, Mineralogical Institute, University Bonn, Poppelsdorfer Schloß, 5300 Bonn 1, Germany.

Besides the conventional methods of phase analysis of multiphase materials using search match methods and the standard procedures for qualitative analysis, like the standard-less method by Zevin, a novel approach is being developed in the last years based on the procedures used in crystal structure refinements. Considerable progress has been made in recent years. In general two different methods are being tested and used today: the Rietveld method or Total Pattern Refinement, and the Two-Stage Method.