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MacDUST – A POWDER DIFFRACTION PACKAGE DEVELOPED FOR THE "ADONE" HIGH RESOLUTION DIFFRACTION STATION

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ABSTRACT

A High Resolution Powder Diffraction Station (PO.DI.STA.) was installed at the beginning of 1991 on the ADONE-Wiggler magnet beam line. The station and the first powder diffraction spectra, collected with synchrotron radiation, were presented at the EPDIC-1 Conference [1]. More details can also be found in [2].

For this station, a very sophisticated software package "MacDUST" has been developed on an Apple Macintosh computer, using the Microsoft QuickBASIC compiler. It allows very easy and comfortable operations by means of a graphical user interface environment, typical of the Macintosh system. The package consists of five major programs.

The main program, MacDIFF, performs all the graphic operations on the experimental data, including zooming, overlapping, cursor scanning and editing of patterns, control of output operations to printers and HPGL plotters. It also includes several analysis routines for data smoothing, a first derivative peak search algorithm, two background subtraction routines and two profile fitting programs: one based on the simplex method and the other on the Marquardt modification of a least-square algorithm. MacPDF and MacRIC are both dedicated to phase identification. The first program is an archive manager for searching, displaying and printing phase records; MacRIC is a graphic aided search-match program based on the Hanawalt [5] algorithm. Mac3-DIM is a plot program, useful, e.g., for representing kinetics three dimensionally. MacRIET is a Macintosh version of the well known Rietveld [14,15] refinement program. This version, besides conventional structure refinements, also allows the determination of micro structural parameters, i.e. micro strain and crystallite size [9]. The program can also be used to simulate a pattern, once the structure of the compound is known. Taking advantage of the very intuitive Macintosh graphic user interface, through dialog and alert boxes, the program allows straightforward introduction and modification of the structure parameters.

INTRODUCTION

The aim of the software project is to provide a complete powder diffraction analysis tool to the scientist at the PO.DI.STA facility, or at any conventional x-ray source. The package, at the moment, includes routines for profile fitting, Kα2 stripping, peak searching, polynomial and Fourier smoothing, phase identification, three dimensional plotting, Rietveld structure refinement and quantitative phase analysis by the Rietveld method. Due to the high number of utilities and routines included in the package, only the most significant data analysis procedures will be described in this paper.

A SMOOTHING AND PEAK SEARCH

)IFF provides two data smoothing routines: one based on a least square interpolation legree Chebyshev orthogonal polynomials [6,13]. It performs either a five, seven or smoothing on the experimental data.
describes the formulas utilized:

$$= \frac{1}{35}[-3f(x_{i-2}) + 12f(x_{i-1}) + 17f(x_i) + 12f(x_{i+1}) + 2f(x_{i+2})]$$

$$= \frac{1}{21}[-2f(x_{i-3}) + 3f(x_{i-2}) + 6f(x_{i-1}) + 7f(x_i) + 6f(x_{i+1}) + 3f(x_{i+2}) - 2f(x_{i+3})]$$

$$= \frac{1}{256}\{[f(x_{i-4}) + f(x_{i+4})] + 8[f(x_{i-3}) + f(x_{i+3})] + 28[f(x_{i-2}) + f(x_{i+2})] +$$

$$+56[f(x_{i-1}) + f(x_{i+1})] + 70f(x_i)\} \qquad (1)$$

)ther smoothing routine performs a fast Fourier ransformation. The method employed is ng: the spectrum is first Fourier transformed, then filtered by a 60% Hanning filter, pplication range can be chosen by the operator between 10%-90% by a dialog box, and rsely transformed; the resulting spectrum is smoothed because the filter greatly reduces quencies that contain the noise and practically leaves the low frequencies, containing the unmodified.
)eak search routine is based on a first derivative algorithm. The first derivative is ısing eq. 2:

$$Y'(x_0) = \frac{1}{10}\{2[f(x_{-2}) - f(x_2)] + f(x_{-1}) + f(x_1)\} \qquad (2)$$

KGROUND SUBTRACTION

background subtraction routines are available. The first performs a least square fitting of polynomials [17]: due to orthogonality each normal equation reduces to a one equation, i.e., the matrix of the normal equation terms becomes diagonal. Moreover, g higher order coefficients does not modify previously obtained ones. The program l the last obtained coefficients of the polynomial are within a standard deviation from the efficients.
ore general solution to the background problem can be given by the second routine t uses a crossair mouse movable cursor for selecting the background points, where a function will fit. The routine then calculates and displays the spline function and finally e linearization of the background subtracted pattern.

SUBTRACTION

outine subtracts the Kα2 radiation component from a peak profile by the substitution Pompa & Zirilli [12]. Initially, a linear background is calculated and displayed between g points of the selected 2θ range; then the radiation wavelength, the approximated tio (Kα2/Kα1) of the components and the refinement steps, for both the intensity ratio urate positions of the components, are required. The program then starts iterating, by a least square algorithm, two quantities: intensity ratios and relative components

THE PROFILE FITTING ROUTINES.

The MacDIFF program includes two routines for profile fitting. The first is based on the Marquardt [10,16] modification of the least square method. Two profile functions are available, each described by four parameters: pseudo-Voigt (pV) and Pearson VII (PVII). At the beginning, the weighted sum of squares (WSS) is calculated at a certain point Q, with an initial estimate of the parameters. Subsequently, a new set of parameters is calculated at a new point R determining the gradient (dP) of WSS, which can be added to the old estimate: P(R)=P(Q)+dP

The process is repeated iteratively until the convergence is reached or the operator stops iterations. Expanding in Taylor series the gradient of WSS and retaining only the first order terms, it is possible to find an expression for *dP* which contains only the first derivatives of the parameters. This is the Gauss-Newton method, which near the minimum gives a fast convergence. Marquardt, in his algorithm, introduced a further parameter (λ) to modify the direction of the step *dP*.

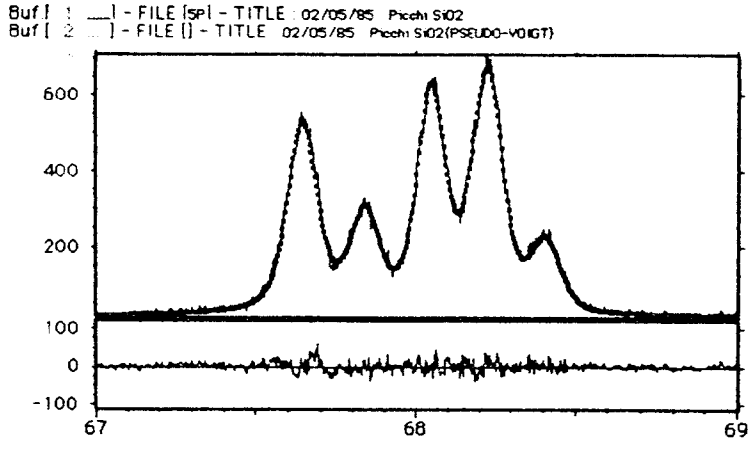

Figure 1: Marquardt pseudo Voigt fit and difference plot on quartz data.

The other fitting routine is based on the Nelder & Mead [11] version of the simplex algorithm and uses a pV as shaping function.

Both programs provide automatic calculation of the Kα2 component, background subtraction, introduction of fitting parameters by mouse pointing or by a data file and a complete set of statistic quantities to check the quality of the fit.

THE MacPDF MANAGER PROGRAM.

MacPDF is a powder diffraction database manager program: it allows all the traditional card searching, retrieving and printing operations on the PDF-2 CD-ROM [20,21] disk. Moreover, it allows graphic display of the cards, overlapping and comparison operations of the cards with an experimental diffraction file. Any card can be accessed within a few seconds and searches can be obtained using chemical names, fragment names, mineral names, chemical formulas and strongest reflection lines as keywords.

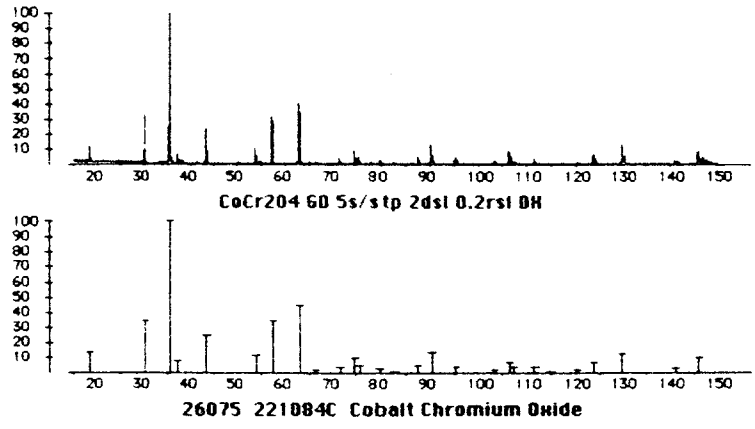

Figure 3: Cobalt Chromium Oxide compared with JCPDS card using MacPDF

HE RIETVELD REFINEMENT PROGRAM.

he Rietveld [14,15] structure refinement program used in the package (MacRIET) is a)sh adaptation of the LS-1 [8].
he main feature of this program is that it adds micro structural parameters to the usual ι, Paoletti & Ricci [3] formula, (eq.3):

$$FHWM = \left(U\tan^2\theta + V\tan\theta + W\right)^{1/2} \qquad (3)$$

angular dependence of the peak width. From the microstructural parameters it possible to he pV parameters by inverting the Warren & Averbach [18,19] method.The anisotropy of stallite size and micro strain is taken into account, as well as the anisotropy of the thermal ters [7].
he instrumental function can be obtained by measurements on a specimen with large lites and free from defect broadening [4]: the profiles can then be fitted with either of the ms described above and the resulting width parameters can be used to fit the Caglioti a.

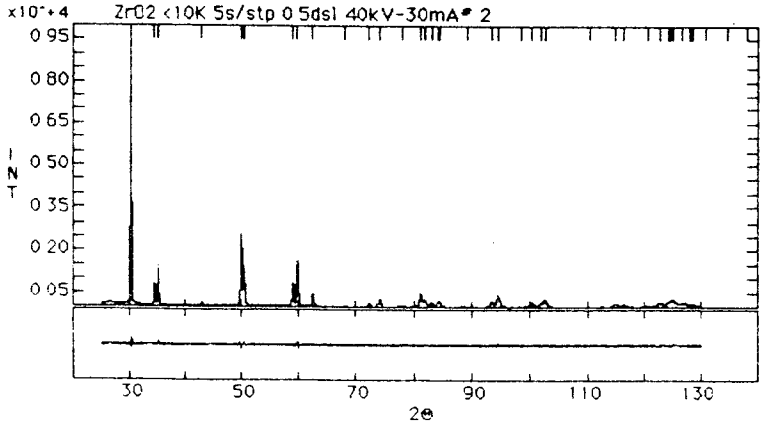

Figure 2: LS1 Rietveld refinement on ZrO2 82%+CeO218% measured at 10°K

The Marquardt [10] algorithm mixes the steepest-descent and the Gauss-Newton methods, guaranteeing fast convergence and direct calculation of estimated standard deviations and parameter correlation. The peak profile is modeled by a pV with asymmetry correction given by the convolution with eq.4:

$$A(2\theta) = \exp\left[-a_s\left|2\theta - 2\theta_0\right|\tan 2\theta_0\right] \qquad (4)$$

The *New parameters* option allows a very easy and fast parameter file creation: it requires some instrumental and sample information, such as goniometer radius, monochromator angle, radiation wavelength, number of phases and estimated phase composition; it then requires the polynomial degree and the number of gaussian curves (whose height, position and width can be refined) describing the background. Moreover, complete structural information for each phase is necessary: the number of atoms in non equivalent sites with their multiplicity, the number of molecules (Z) in the cell, the symbol for each atom or ion, the atomic coordinates and the cell parameters. The program automatically provides defaults to all the remaining parameters.

At any time any parameter can be edited, fixed, freed or bonded to any other, by simply clicking, with the mouse, on the desired parameter listed in a scrolling window. The parameter is then highlighted and a dialog box, with edit fields and radio buttons, is displayed showing all the settings of the selected parameter. This on-line method for changing parameter settings and values, together with all the internal graphic displaying, printing and plotting capabilities, improves functionality and accelerates refinement processes quite a lot.

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