

G. BERTI (*), R. CARRARA (**), L. LEONI (*)

CU K_{β} X-RAY POWDER DIFFRACTION PATTERNS RESOLUTION INCREASE

Riassunto — *Aumento della risoluzione di diffrattogrammi di polveri a raggi x con radiazione CuK_{β} .* La risoluzione di un diffrattogramma di polveri a raggi x può essere aumentata eliminando gli effetti strumentali dai profili dei picchi. La funzione strumentale è stata determinata sperimentalmente usando un campione di polvere «standard» privo di difetti reticolari. È stato usato come standard un campione di silicio ed alcuni profili di sostanze cristalline sono stati rappresentati mediante la convoluzione della funzione del picco del silicio con una lorentziana. Il metodo viene usato per risolvere alcuni riflessi sovrapposti.

Abstract — A resolution improvement of the x-ray powder diffractometer pattern may be obtained removing the instrumental effects from the peak profiles. The instrumental function was determined experimentally through a «standard» powder sample free from line broadening causes. A silicon specimen was used as standard and several CuK_{β} crystalline phases peak profiles were fitted by a convolution of the silicon peak function and a lorentzian curve. The first attempts to resolve overlapping reflections give much better results than one could expect from usual procedures.

Key words — X-ray Powder Diffraction Pattern, Resolution Increase, Convolution, Profile Fitting, Standard Sample Method.

INTRODUCTION

In the last few years several attempts have been made to improve the information obtainable from x-ray powder diffraction patterns.

(*) Dipartimento di Scienze della Terra - Università di Pisa - Via S. Maria 53 - 56100 Pisa - Italy.

(**) Dipartimento di Fisica - Università di Pisa - Piazza Torricelli 2 - 56100 Pisa - Italy.

The aim of this research is to implement on a personal computer (Olivetti P 6066) a profile fitting method for an accurate determination of peak positions and integrated intensities. The method (HUANG and PARRISH, 1975; G. WILL *et al.*, 1983) allows to remove the effects of the apparatus geometry and of x-ray line distribution in order to enhance the resolution, as well as, to quantify the physical properties of crystalline powdered samples as the size of crystalline coherent domains, the distribution of crystallite size, the nature and extent of lattice imperfections.

A mathematical approach to determine instrumental aberrations turns out to be very difficult in routine x-ray powder diffraction analysis. To evaluate instrumental function experimentally it should be sufficient to have a well crystallized substance whose peaks are free from broadening causes like the ones deriving from the physical characteristics of the powder sample. In this case the peak profile function represents a good approximation of instrumental effects.

Using a silicon powder as a standard, the peak profiles of some crystalline substances (quartz and fluorite) were represented by the convolution of the silicon peak function with a lorentzian curve.

METHOD

The observed powder diffraction peak profile can be expressed, according to D. TOUPIN (1973), as the convolution:

$$Y(2\vartheta) = A(2\vartheta) * S(2\vartheta) \quad (1)$$

where A represents the instrumental function and S the actual diffraction effect of the powder sample.

The function A, as a whole, is not dependent on the specimen, so we may evaluate it experimentally using as a standard a well crystallized powder sample, free from strains and other broadening causes; KLUG and ALEXANDER (1974). In this case the function S is compatible with the identity in the convolution and the peak profile is determined only by the function:

$$Y(2\vartheta) = A(2\vartheta) \quad (2)$$

To select a standard powder sample we have represented the Cu K_β peak profile of some well crystallized substances as silicon, quartz, and fluorite by semiempirical functions, BERTI CARRARA LEONI

(1984); it turns out that the half width at half maximum (HWHM) of the calculated profiles is related to the Bragg angle by:

$$\sigma(2\vartheta) = k + k_1 \operatorname{tg}\vartheta \quad (3)$$

where k changes with the diffractometer geometry (different slits etc.), while k_1 seems slowly dependent on the sample and decreases from fluorite to silicon (Fig. 1).

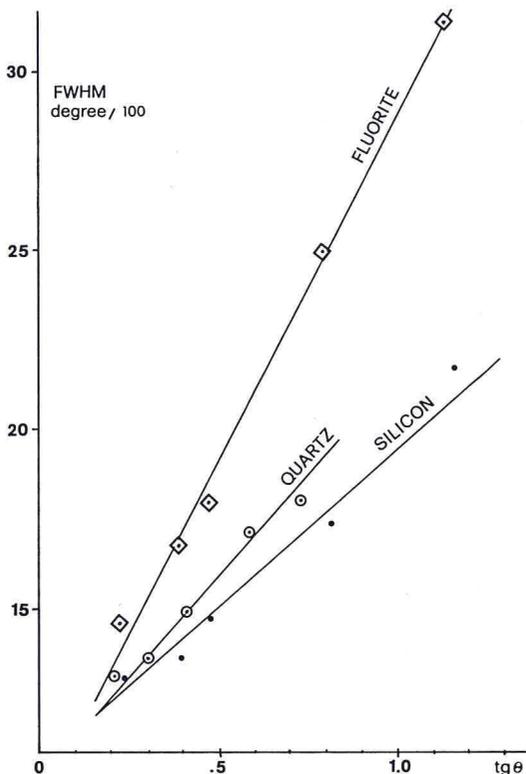


Fig. 1 - Silicon, quartz and fluorite FWHM values plotted against the $\operatorname{tg}\vartheta$, solid lines are computed by the equation: $\text{FWHM} = k + k_1 \operatorname{tg}\vartheta$.

This suggests a method to derive the instrumental and the actual diffraction effects separately using the silicon as a «standard» specimen. In fact for crystalline phases as silicon the experimental peak profiles can be expressed by the simplified representation:

$$Y(2\vartheta) = A(2\vartheta) + B$$

where B is the background.

EXPERIMENT

The intensity of the peak profiles were measured by a PW 1730 Philips automatic X-ray diffractometer on line with a personal computer Olivetti P 6066. The apparatus was equipped by a graphite ANR 2-202 GVW 7038 focusing monochromator. The operating conditions during the measurements were as follows: broad focus Cu X-ray tube supplied by 40 Kv-20 mA (take off angle 6° with a focal spot dimension of $0,2 \times 12$ mm); the divergence slits of 1° and 4° width were used in the 2ϑ regions $18^\circ \div 74^\circ$ and $> 74^\circ$ respectively; the focusing slit 0.2 mm. wide. The counting time was chosen in such a way to have statistical counting errors smaller than 2.5% on the maximum of each peak.

Crystal fragment of quartz, fluorite and synthetic powdered silicon (BHD silicon of the British Drug Houses L.T. chemical division) were used.

All the samples were placed in the agate mortar and ground by hand with an agate pestle until final traces of grittiness had disappeared. Powder sample with a granulometry $< 10 \mu$ were selected for silicon and quartz by decanting the powder in distilled water.

To test the method, two diffraction peaks of fluorite (311, 531) were studied using silicon as standard. In order to simplify the calculation we chose to represent approximatively the silicon peak profiles by a single lorentzian curve. So each fluorite profile was mathematically represented by a convolution of two lorentzian curves:

$$Y(2\theta) = A \cdot S + B = \frac{I_A I_S}{1 + 4 \left[\frac{2\theta - (\theta_A + \theta_S)}{\delta_A + \delta_S} \right]^2} + B \quad (4)$$

where the I_A and I_S are proportional to the integrated intensities; σ_A , σ_S the half widths to half maximum and $2\vartheta_A$, $2\vartheta_S$ the peak positions of the lorentzian curves. The parameters were adjusted by a least-square fitting method using 101 experimental points and minimizing the quantity $\chi^2 = \sum_i W_i (I_i^{\text{obs.}} - I_i^{\text{cal.}})^2$ where $W_i = 1/I_i^{\text{obs.}}$ is the statistical weight. The starting values of the parameters were chosen as follows: the product $I_A \cdot I_S$ and $2\vartheta_A = 2\vartheta_S$ are the maximum and the position of the experimental peak respectively, σ_S is the value $\sigma - \sigma_A$ where σ is the fluorite HWHM manually determin-

ed from experimental peak and σ_A the HWHM of a silicon peak profile in the same angular region collected with the same measure setting. The parameter B may be independently determined from intensity measurements at $\pm 1^\circ$ from the maximum of each peaks and linearly interpolated in this range.

The figures 2, 3, 4a, and 5a show the best fitting of the experimental 311, 531 silicon and fluorite peak profiles; figures 4b and 5b show the contribution of S to the calculated fluorite profiles in (4).

At low angle ($2\vartheta = 25^\circ$) S function vanishes in the fluorite representation by equation (1) and the peak profiles are compatible with instrumental shape; see figures 6a and 6b for 111 silicon and fluorite profiles which appear to be undiscernible.

The results were applied a) to increase the resolution of a powder diffraction pattern using an artificial mixture consisting of silicon and fluorite (43.9% and 56.1% of the total weight, respectively) see figures 7 and 8; and b) to resolve overlapping profiles of quartz in the angular region around 60 degrees see figures 9. In

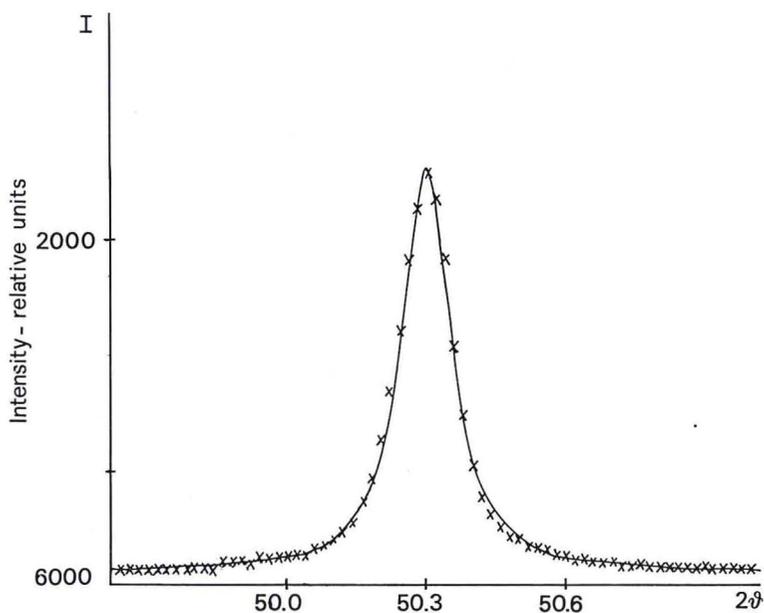


Fig. 2 - Silicon 311 profile used to determine the instrumental function A: experimental points (crosses) and solid curve computed from profile fitting. $\chi^2 = 555$.

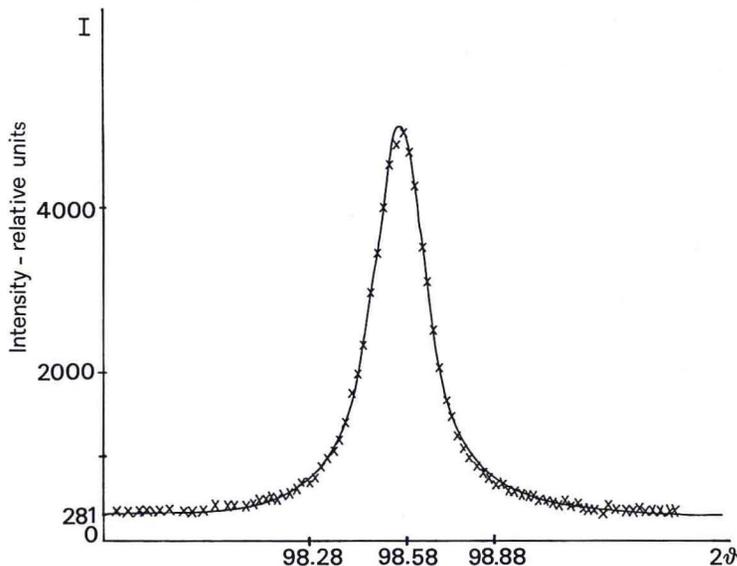


Fig. 3 - Silicon 531 profile used to determine the instrumental function A: experimental points (crosses) and solid curve computed from profile fitting. $\chi^2 = 170$.

the last case an accurate determination of 203, 031 quartz peaks is very difficult by usual procedures. An estimate of the increased resolution may be extracted from the following table:

Peaks	Theoretical Bragg angle and intensity (*)		Bragg angle and intensities determined by this method	
	2ϑ	I/I_{212}	2ϑ	I/I_{212}
212	60.48	1	60.48	1
203	60.83	1.33	60.84	1.23
031	60.98	0.83	60.98	0.92

(*) BORG I.Y., SMITH D.K. (1969) pag. 741 and PARRISH W., MACK M. (1963).

CONCLUSIONS:

The method of profile fitting implemented on a personal computer and using a silicon specimen as a standard produces good results.

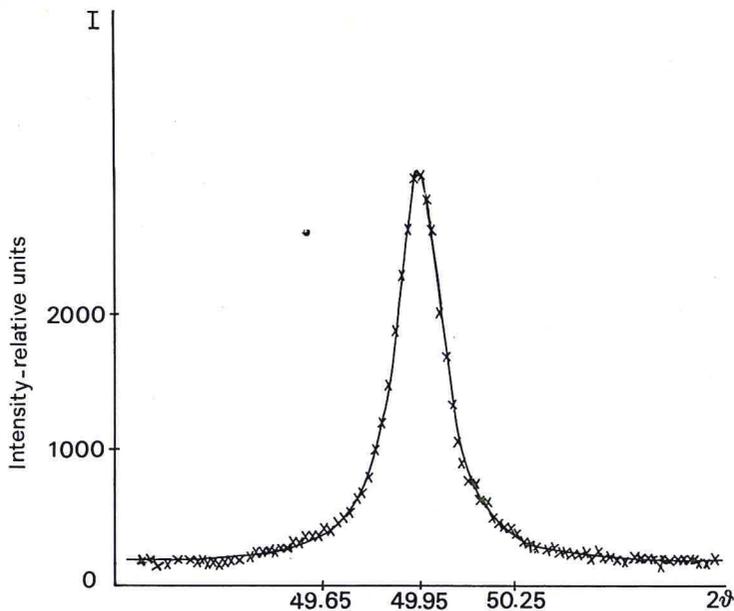


Fig. 4 a - Florite 311 profile: experimental points (crosses) and solid curve computed from profile fitting (A*S convolution). $\chi^2 = 491$.

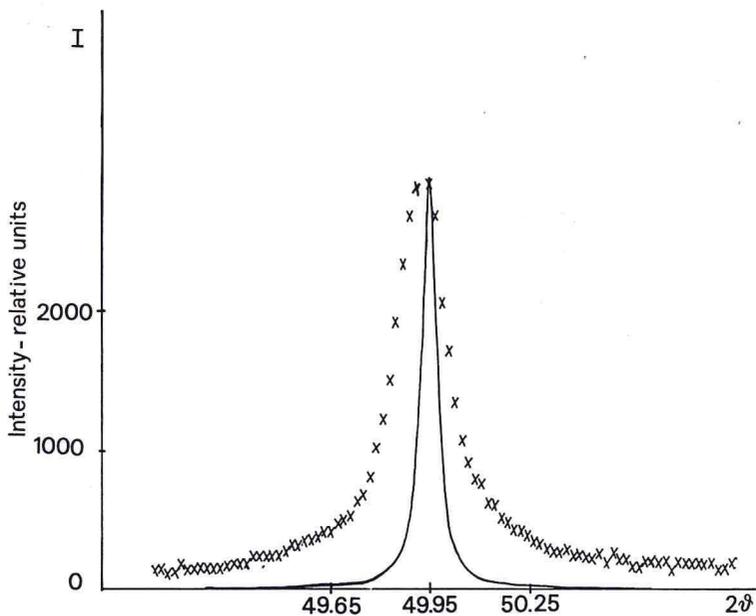


Fig. 4 b - Fluorite 311 deputed profile estimate.

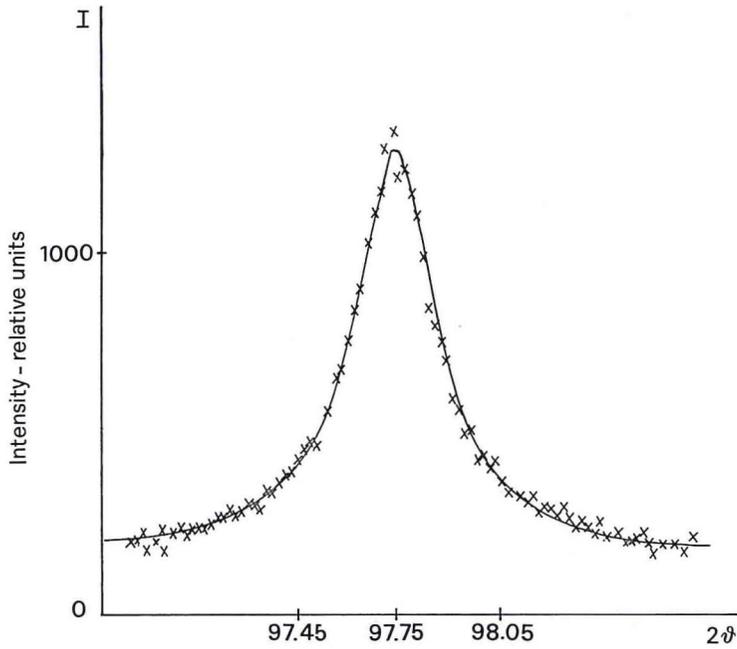


Fig. 5 a - Fluorite 531 profile: experimental points (crosses) and solid curve computed from profile fitting (A*S convolution). $\chi^2 = 125$.

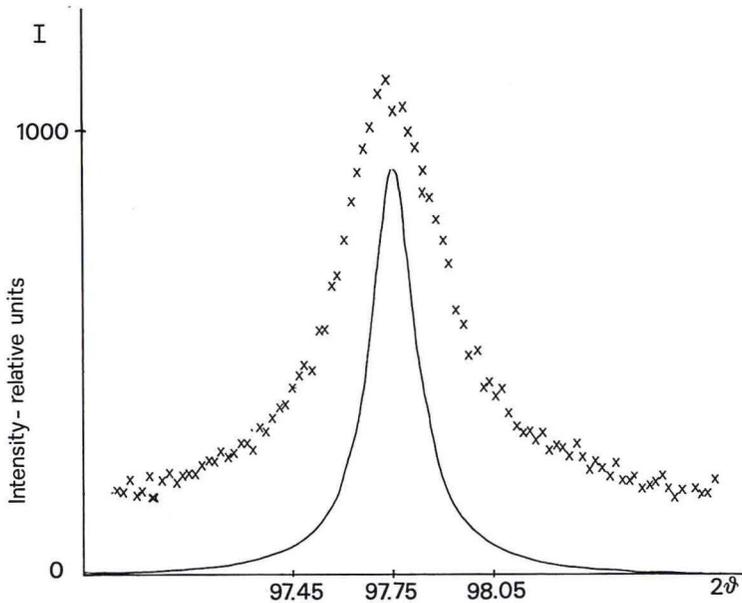


Fig. 5 b - Fluorite 311 deputed profile estimate.

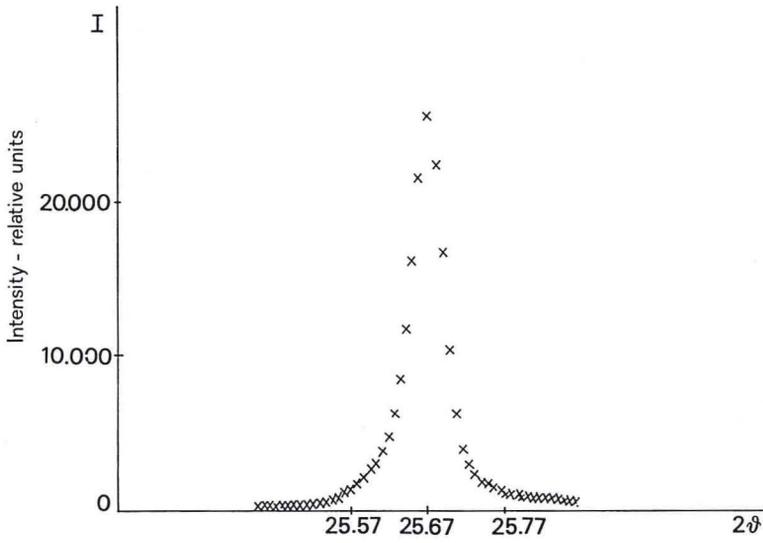


Fig. 6 a - Silicon 111 profile experimental points.

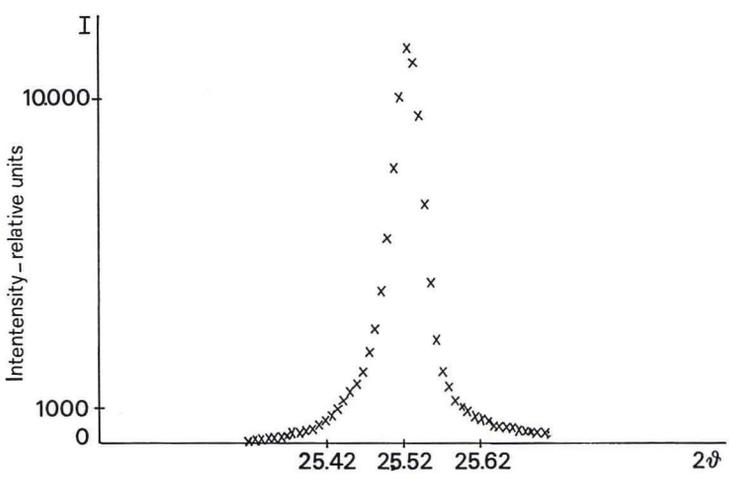


Fig. 6 b - Fluorite 111 profile experimental points.

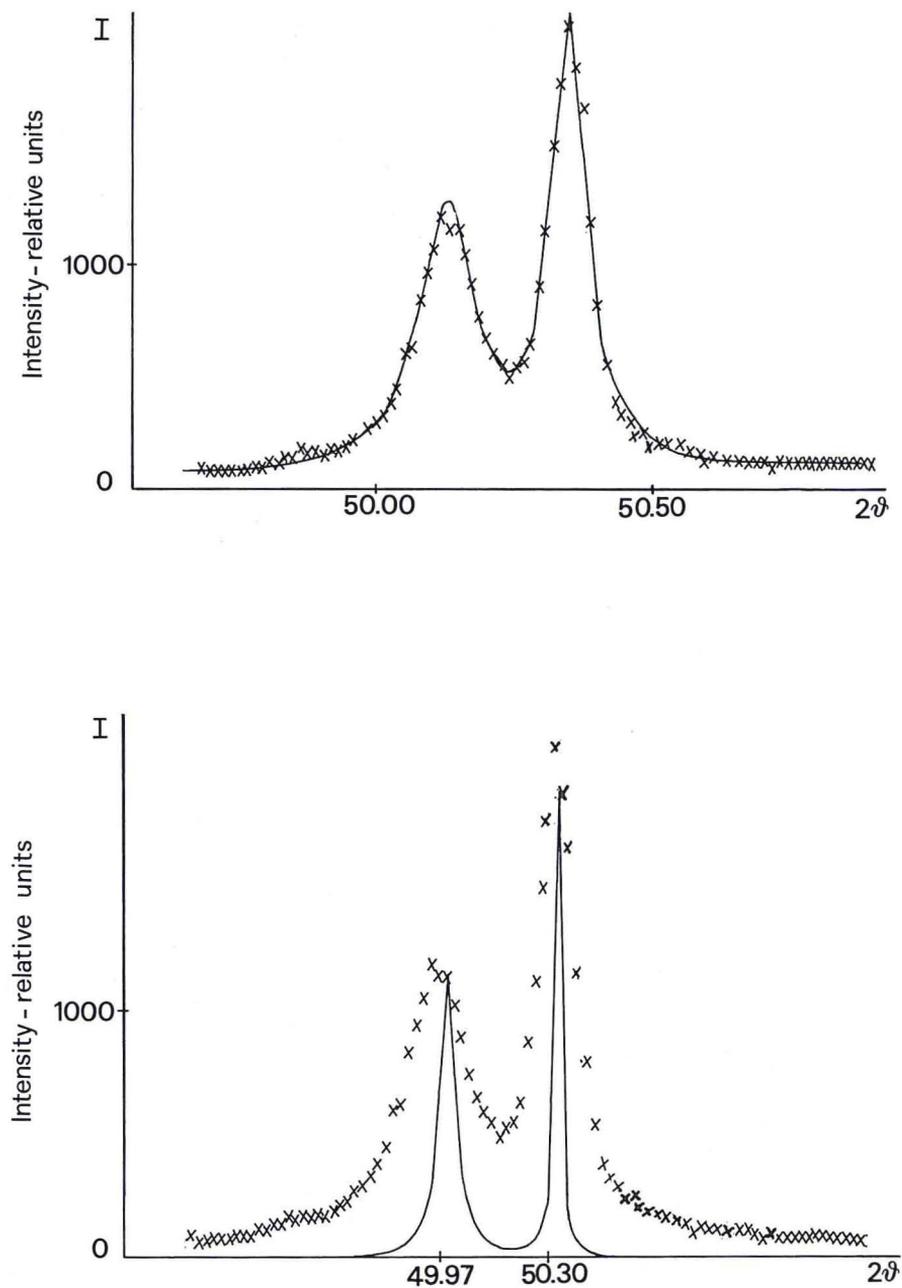


Fig. 7 - Silicon and Fluorite mixture; (a) overlapping profiles in the 2θ region around 50 degree; experimental points (crosses) and solid curve computed from profile fitting. $\chi^2 = 262$; (b) deperated profiles estimate.

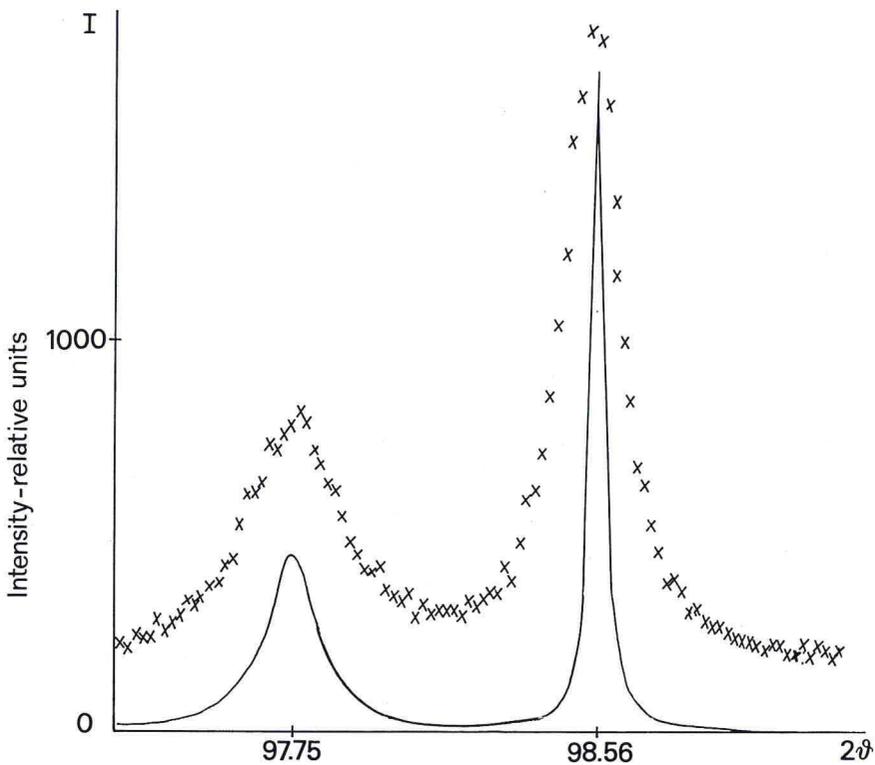
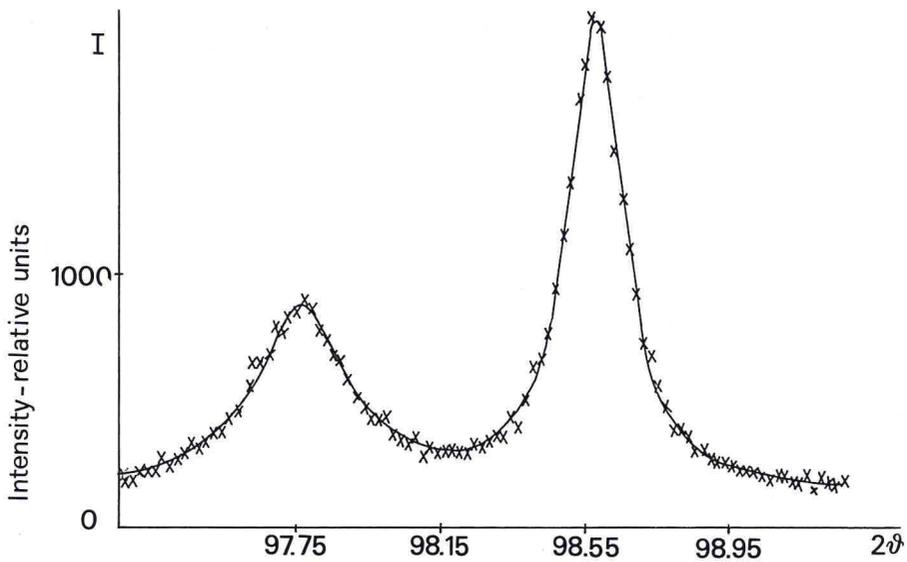


Fig. 8 - Silicon and Fluorite mixture overlapping profiles in the 2θ region around 98 degree: (a) experimental points (crosses) and solid curve computed from profile fitting. $\chi^2 = 111$; (b) deputed profiles estimate.

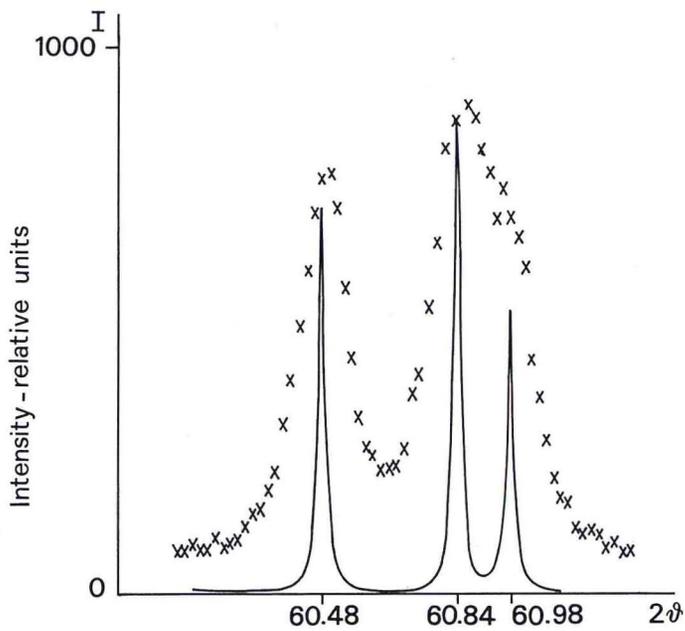
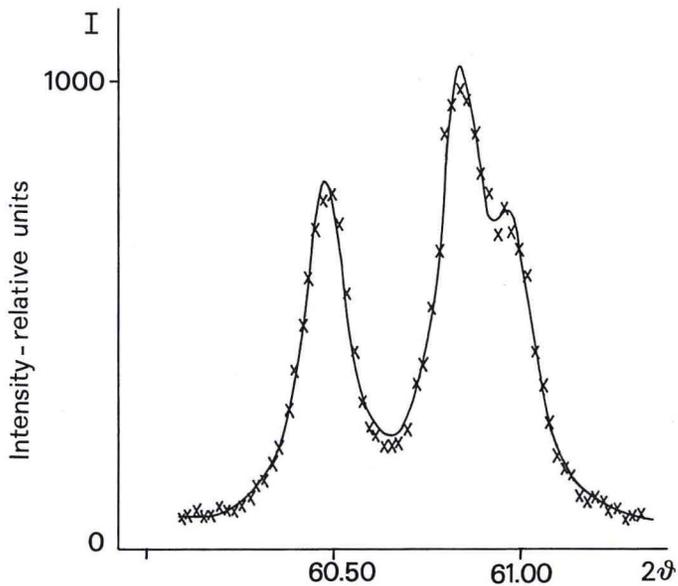


Fig. 9 - Quartz overlapping profiles (212, 203, 031): (a) experimental points (crosses) and solid curves computed from profile fitting. $\chi^2 = 145$; (b) depleted profiles estimate.

The knowledge of instrumental function A is very helpful in resolving overlapping profiles. The resolution is greater than the diffractometer pattern so to exploit the full potentialities of powder diffraction methods better. Further developments of this research require extreme care in the standard specimen selection.

REFERENCES

- BERTI G., CARRARA R., LEONI L. (1984) - A Peaks analysis method in x-ray powder diffractometry. *Rend. Soc. It. Min. Petr.*, **39** (1), 115-122.
- BERTI G., CARRARA R., LEONI L., SAITTA M. (1986) - Peak Shape study in x-ray powder diffractometry. *Atti Soc. Tosc. Sc. Nat., Mem., Ser. A*, **93**.
- BORG I.Y., SMITH D.K. (1969) - Calculated X-Ray Powder Patterns for Silicate Mineral. *Geological Society of American Inc., Mem.*, **122**, Colorado Building, P.O. Box 1719 Boulder, Colorado 80302.
- KLUG H.P., ALEXANDER L.E. (1974) - X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. Wiley & Sons ed.
- HUANG T.C., PARRISH W. (1975) - Accurate and rapid reduction of experimental x-ray data. *Appl. Phys. Lett.*, **27** (3 august 1975).
- PARRISH W., MACK M. (1963) - Data for x-ray Analysis Charts for the solution of Bragg Equation. *Philips Technical Library*.
- WILL G., PARRISH W., HUANG T.C. (1983) - Crystal Structure Refinement by Profile Fitting and Least Square analysis of Powder Diffractometer Data. *J. Appl. Cryst.*, **16**, 611-622.
- TOUPIN D. (1973) - Automatic Peak Determination in X-ray Powder Patterns. *J. Appl. Cryst.*, **6**, p. 266.

(ms. pres. il 15 maggio 1986; ult. bozze il 30 marzo 1987)