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OF MEAN CRYSTALLITE DIMENSIONS IN NUCLEAR MATERIALS
BY X RAY DIFFRACTION LINE BROADENING
AN APPLICATION EXAMPLE USING U_3O_8 MICROSPHERES**

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ABSTRACT

A routine method for mean crystallite size determination by X Ray diffraction line broadening was established. Both step scanning and continuous scanning methods were extensively tested and the precision of the data obtained as a function of the crystallite size is discussed.

Emphasis is given to our contribution in order to eliminate instrumental effects as well as K_{021}/K_{022} doublet effect upon line broadening.

Instrumental correction was performed with a monocrystalline Si sample having mean crystallite size well above 13 000 Å (checked at our Laboratory) improving the accuracy of experimental data.

K_{021}/K_{022} doublet correction was handled with the aid of the modified Rachinger correction. The exact intensity relation between K_{022} and K_{021} peaks was determined instead of taking it for granted as 5.

The mean crystallite dimension of U_3O_8 was calculated and the results show the dependence of this parameter on the quality of the microspheres.

INTRODUCTION

Fission materials used in the form of coated particles have experienced great advances in the Gas Reactor Technology serving as basis for the development and progress of the HTGR concept⁽¹⁾.

One of the main advantages the use of fuels in the form of particles has brought is the possibility of achieving the highest burn ups reached so far by incorporating moderators (as graphite) to the fuel. However emphasis should be given to the fact that high efficiency of these fuels is primarily due to their structural properties.

As part of IEA's program the CEQ (Chemical Engineering Division) has been developing a process for microspheres production and several batches of U_3O_8 and alumina microspheres have been prepared already.

As the microspheres production depends on several physicochemical parameters we focused our attention on one of them namely the mean dimension of the crystallites regions inside the solid where the unit cell repeats itself in an almost perfect fashion a quantity directly related to the feasibility of obtaining microspheres.

The mean crystallite size is an important structural parameter not only where microspheres' production is concerned but is also a meaningful structural parameter of any fuel material and it was the

purpose of our research to establish a fast and efficient method to determine it

FUNDAMENTALS

Scherrer⁽¹⁰⁾ first attempted to determine the influence of the crystallite size on X Ray diffraction peaks broadening and derived a mathematical expression assuming a cubic crystal structure -known today as the Scherrer equation

$$D = \frac{K \lambda}{\beta_{1/2} \cos \theta} \quad (1)$$

Assuming Scherrer's derivation was not general, Stokes and Wilson⁽¹¹⁾ derived an expression valid for any crystal structure. Employing a refined mathematical formalism as well as integrated intensities, these authors have nevertheless obtained an expression similar to Scherrer's, except for the value of K a shape constant. Scherrer equation holds for $K = 0.9$ whereas Stokes proposed $K = 1.00$. In practice K is used as 0.90 because both works were carried on assuming the existence of only one crystallite actually one has an aggregate of them and therefore D is said to be mean crystallite size.

In expression (1) λ is the wavelength of the X Ray radiation θ is the angle where maximum diffraction occurs and $\beta_{1/2}$ is the half-maximum peak breadth due only to the crystallite size of the material under investigation⁽³⁾.

EXPERIMENTAL PROCEDURE

The experimental procedure may be divided into four main parts

- alignment of the diffractometer
- uniform sample preparation
- obtainment of diffraction profiles
- data correction

The alignment of the Rigaku SG B diffractometer is done according to its correspondent Rigaku manual⁽⁸⁾ and deserves here no further comments.

Samples are prepared by pressing (27.5 ton/cm² during 3 minutes) in aluminum sample holders. As for the sake of compactness 5% cellulose may be added. All samples are previously grinded in an agate mortar, thus becoming homogeneous and practically strain free.

Obtainment of a diffraction profile correspondent to a particular crystallographic (hkl) plane can be achieved by two alternative procedures

- conventional scanning where the sample is continually rotated around an appropriate Bragg angle while the intensity is registered by a plotter on a chart. Profiles obtained this way are similar to the one shown in figure 1
- step by step using a step scanning device where the intensity is measured at several angular positions equally spaced by small angle values during a fixed time interval, say 20 seconds. The profiles are similar to the one given in figure 2

In any case the peak obtained has a certain half-maximum breadth $\bar{\beta}_{1/2}$ which is a result of three major contributions

- crystallite mean dimension
- instrumental effect due to apparatus used

– $K_{\alpha 1}/K_{\alpha 2}$ doublet overlap(*)

We are interested only in the effect due to crystallites and therefore we need the other two upon $B_{1/2}$

Effect (c) is easily eliminated using the Rietinger correction (appendix) yielding $B_{1/2}$ the half maximum peak breadth without the influence of $K_{\alpha 2}$

We are left with the problem of eliminating the instrumental effect to be able to calculate $B_{1/2}$. Theoretically this can be accomplished by applying expression (1) to a diffraction peak from any material possessing infinitely large crystallites as a consequence we would have $B \rightarrow 0$. Under these conditions the peak breadth would be due solely to instrumental effect

However an ideal crystal ($D \rightarrow \infty$) is so far impossible to obtain. Many researchers have used as standard-crystals polycrystalline materials having crystallites as large as possible. Anyhow they are seldom larger than 1 000 Å(B)

In the present work we adopted an original solution using a monocrystalline Si sample whose mean crystallite dimension is over 13 000 Å(**) we were able to get diffraction peaks whose half maximum breadth $b_{1/2}$ may well be considered as being due entirely to the particular apparatus used

It is known that the instrumental effect is a function of the Bragg angle i.e. $b_{1/2} = f(2\theta)$. This dependence is determined by obtaining diffraction peaks for several angular positions and plotting it thus constructing characteristic curves for each instrument (fig. 3). When investigating a given material (***) the instrumental effect at the angular positions where the peaks exist may be known by interpolation in the correspondent instrument curve

The correction principle is as follows (12)

Figures 4a, 4b and 4c represent respectively the sample diffraction peak ($K_{\alpha 1}/K_{\alpha 2}$ doublet effect already eliminated), the same diffraction peak if the diffractometer were ideal, only crystallite size effect present, and peak breadth due only to instrumental effect

The origins for $g(z)$ and $h(x)$ are chosen for convenience but at the same value of 2θ . The relation between the three curves is obtained by considering the area $g(z)dz$ on the curve for instrumental broadening, the area $g(z)dz$ is spread out by the function $f(y)$ and at a displacement y the ordinate is the contribution $dh(x)$ at the position $x = z + y$ on the $h(x)$ -curve. Since the ordinates in the two curves are proportional to the peak areas

$$\frac{dh(x)}{f(y)} = \frac{g(z) dz}{A}$$

where A is the area of the $f(y)$ curve

With the replacement $y = x - z$ the ordinate of the $h(x)$ curve is given by

$$h(x) = \frac{1}{A} \int g(z)f(x-z)dz \quad (2)$$

() We are considering the material as strain free although the actual profile is somewhat influenced by the existence of internal stresses. In our case strain is negligible if not absolutely non-existent

() As experimentally verified by using a diffraction apparatus having a highly collimated monochromator designed by and built by I.E.A.'s X-Ray group (see ref. 2)

(***) For each substance diffraction peaks occur at characteristic angular positions

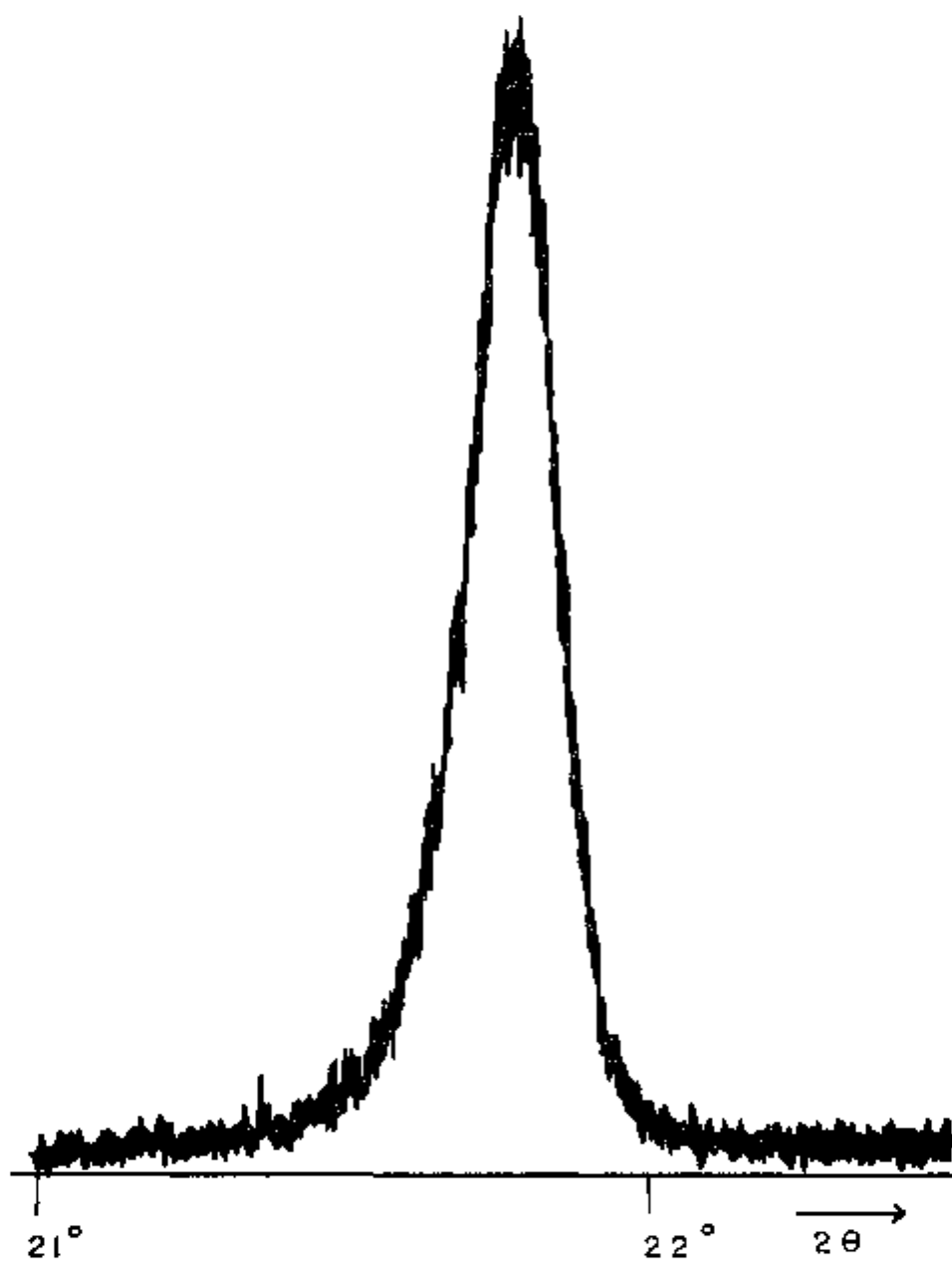


Figure 1 - Strip-chart record of the (001) peak of a U_3O_8 sample (Cu K_α radiation scanning speed $1/16^\circ/\text{min}$)

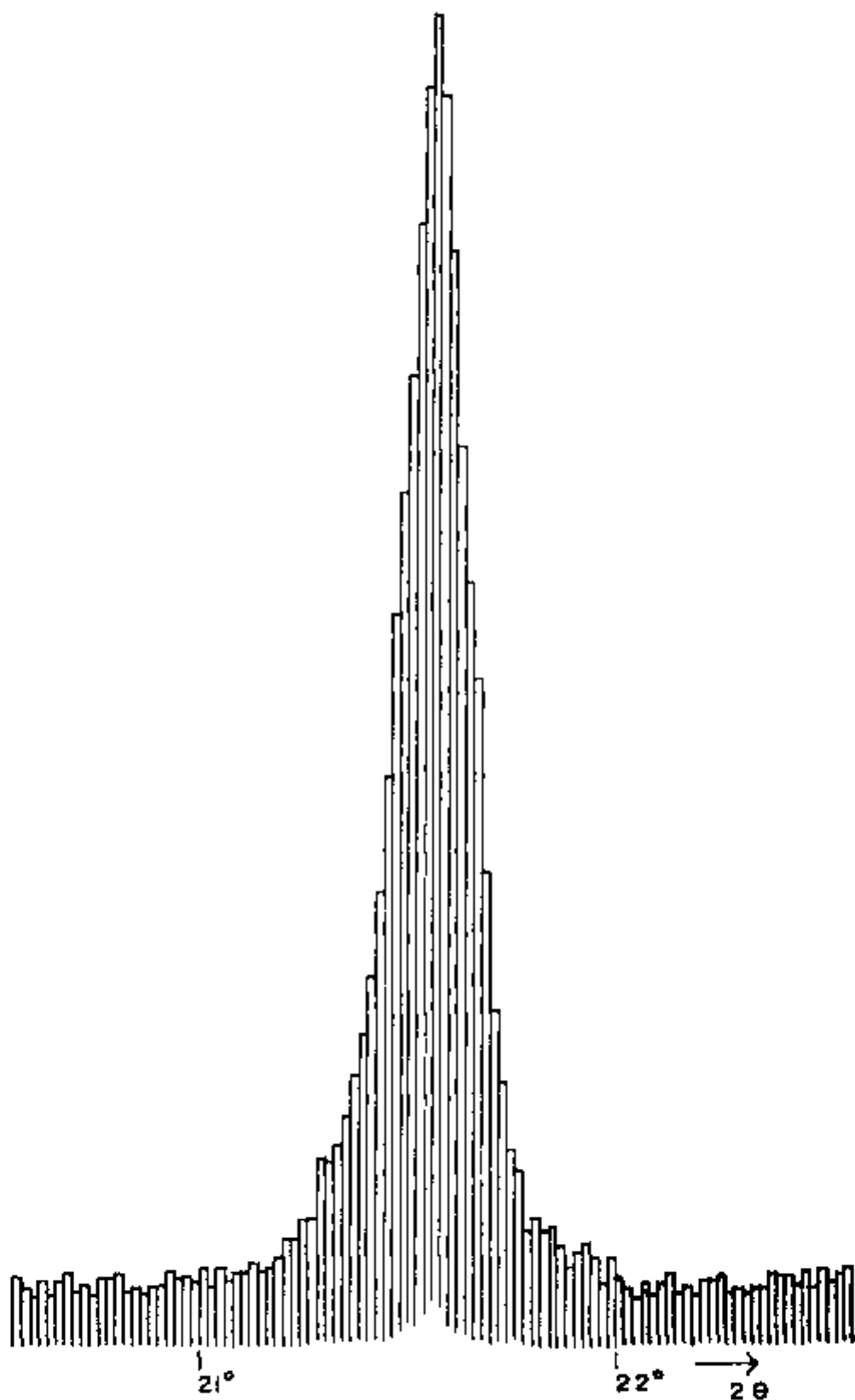


Figure 2 — Strip-chart record of the (001) peak of a U_3O_8 sample (Cu K_α radiation step scanning with step width 0.2° fixed time count 20 seconds)

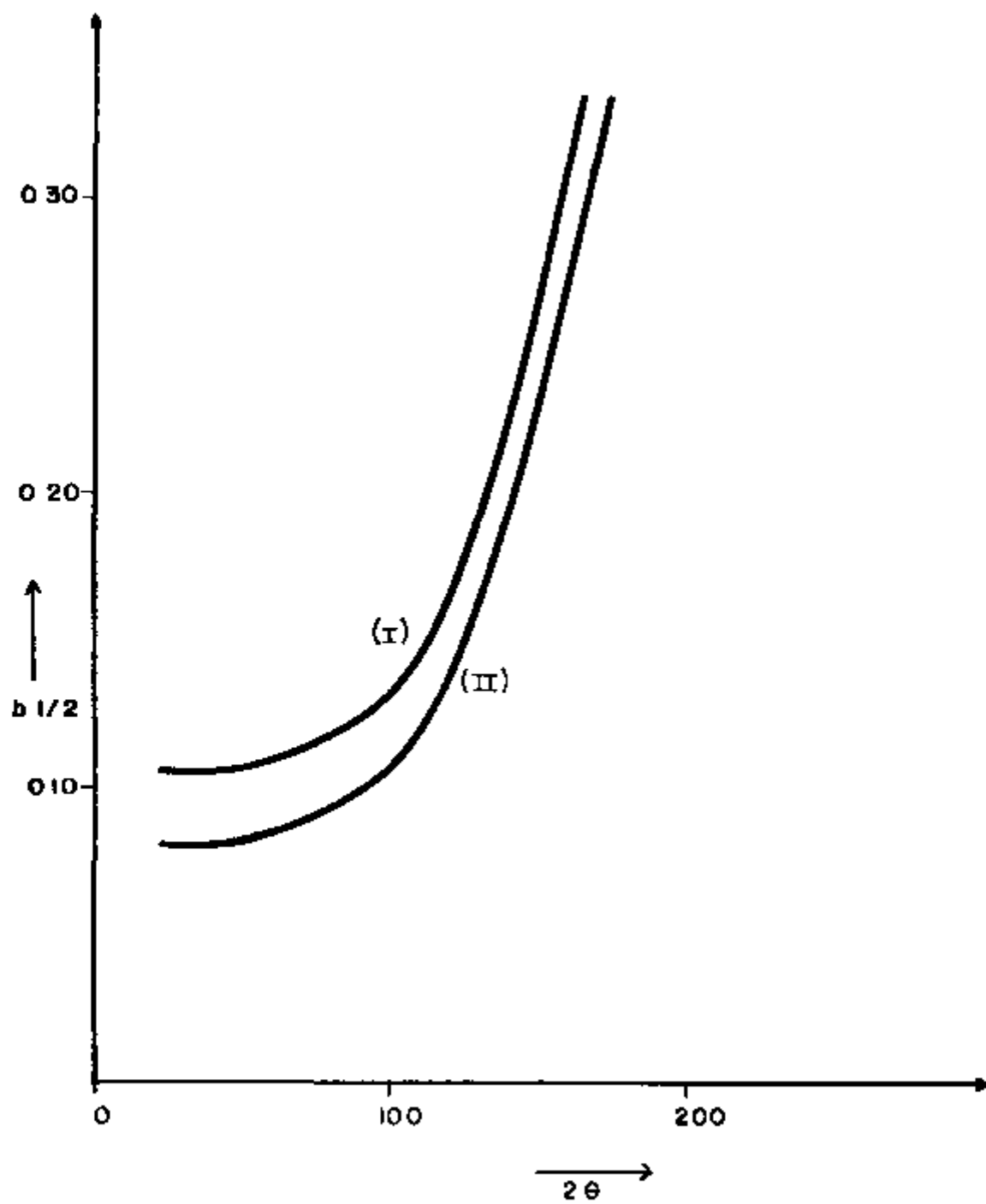


Figure 3 — Instrumental correction curves for diffractometers (I) and (II)

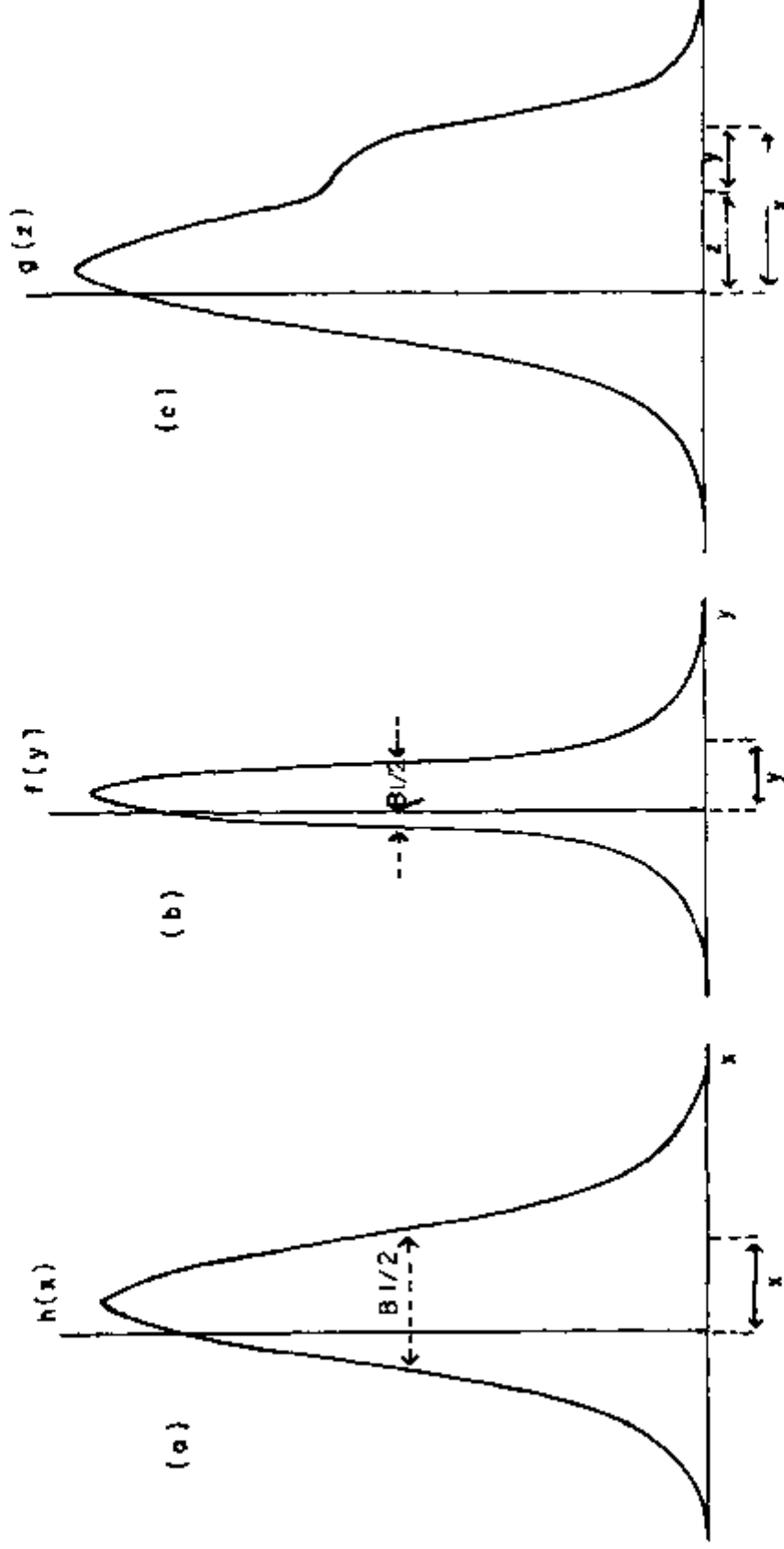


Figure 4 - (a) Sample diffraction peak (K_{02} influence eliminated)
 (b) Diffraction peak Broadening due only to crystallite size
 (c) Diffraction peak Broadening due only to instrument used

Equation (2) indicates that the profile for the sample is a convolution of the functions representing particle size broadening and instrumental broadening. We measure the curves $h(x)$ and $g(z)$ and wish to obtain the particle-size broadening curve $f(y)$. This is not convenient since $f(y)$ is buried inside the convolution integral. By assuming shapes for the three curves, it is possible to use eq. (2) to obtain relations between the half maximum breadths of the curves:

Assuming the three curves are Gaussian, that is $w = W \exp(-k v^2)$, it is possible to show that

$$\beta_{1/2}^2 = B_{1/2}^2 + b_{1/2}^2 \quad (3)$$

4 - APPLICATION OF THE METHOD

The method previously described was applied to finely ground powder from U_3O_8 microspheres. Figure 5 shows the diffraction profile of U_3O_8 for 2θ between 10° and 110° .

Seven samples were prepared and for each diffraction peaks were obtained using both diffractometers available at our Laboratory, denoted by (I) and (II) (*).

The microspheres received for analysis have been previously size selected with 5 different standard sieves, with mesh dimensions varying between 0.420 and 0.053 cm.

Samples numbered 1 to 5 belong to the same lot and samples numbered 6 and 7 to another one obtained under different conditions.

Sample	Diffractometer I (Å)	Diffractometer II (Å)	Average (Å)
1	560 ± 28	575 ± 29	567 ± 29
2	592 ± 31	571 ± 29	581 ± 30
3	590 ± 31	599 ± 31	592 ± 31
4	591 ± 31	580 ± 30	587 ± 31
5	601 ± 31	590 ± 31	595 ± 31
6	377 ± 17	388 ± 17	382 ± 17
7	367 ± 16	375 ± 17	371 ± 17

CONCLUSIONS

We have succeeded in establishing a fast and routinely applicable method for nuclear material control whenever structural parameters play an important role. The determination of the mean crystallite size by measuring Bragg's diffraction peak breadth was computed using Scherrer equation, whose validity has been confirmed by several researchers (references 1, 3, 5, 6, 7) besides Scherrer himself⁽¹⁰⁾.

(*) The angular position for the U_3O_8 (001) diffraction peak is approximately $2\theta = 21.41^\circ$ and under this geometrical condition the instrumental effects for diffractometers (I) and (II) are $b_{1/2}^I = 106^\circ$, $b_{1/2}^{II} = 985^\circ$.

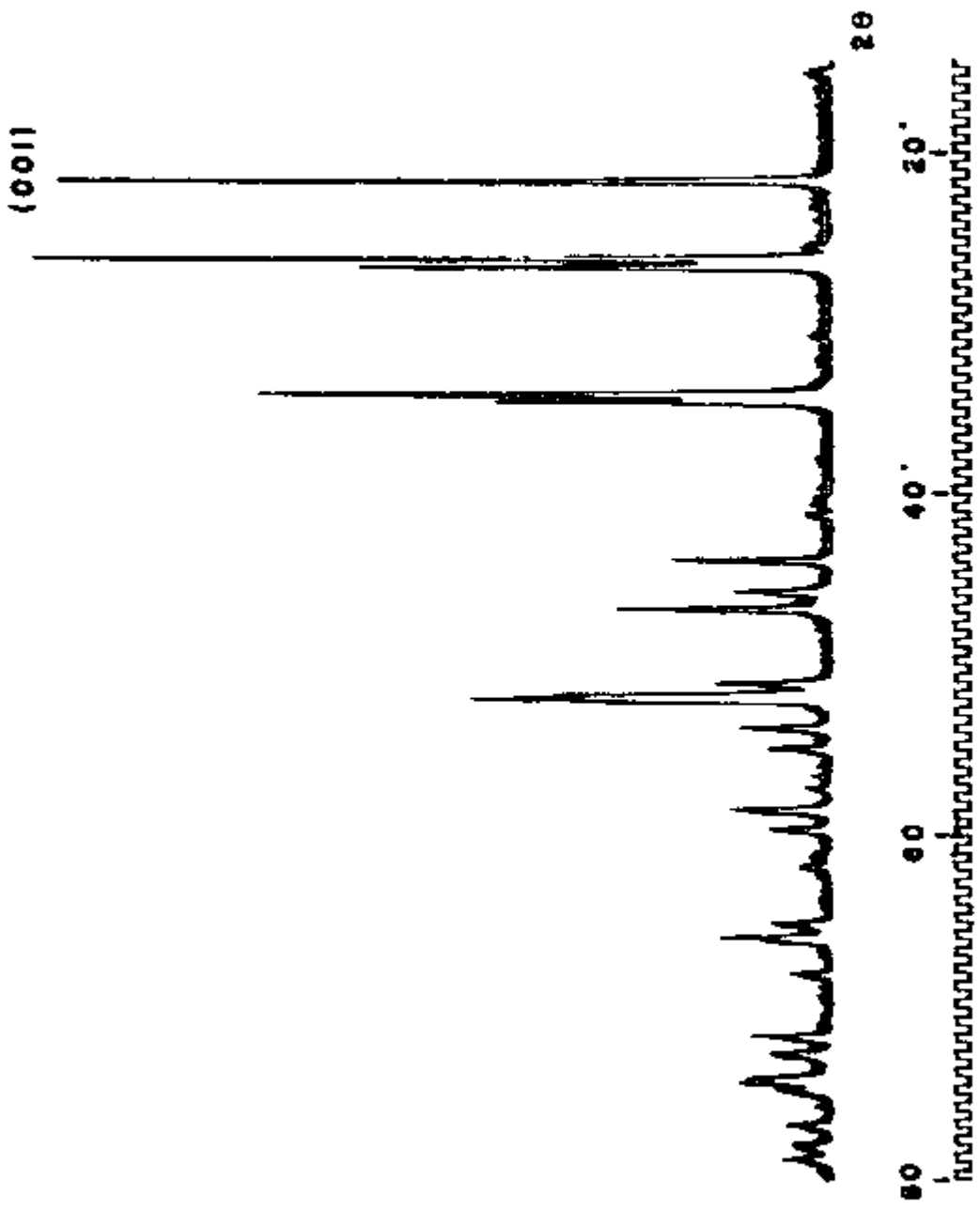


Figure 5 - U_3O_8 diffraction diagram

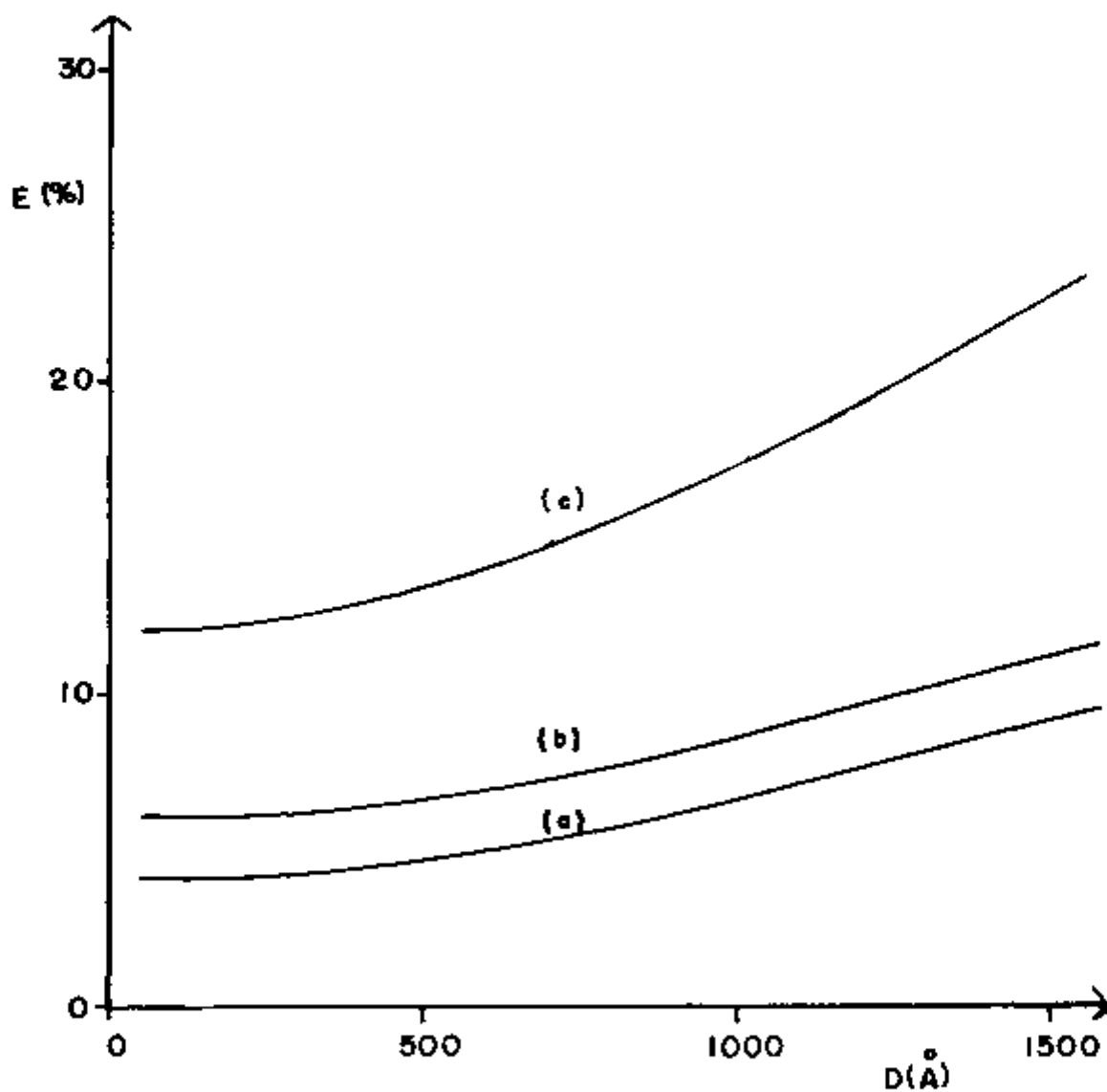


Figure 6 - Per-cent error vs crystallite size

- (a) Step scanning fixed time count
- (b) Conventional scanning scanning speed $1/16^\circ$ min
- (c) Conventional scanning scanning speed $1/8^\circ$ min

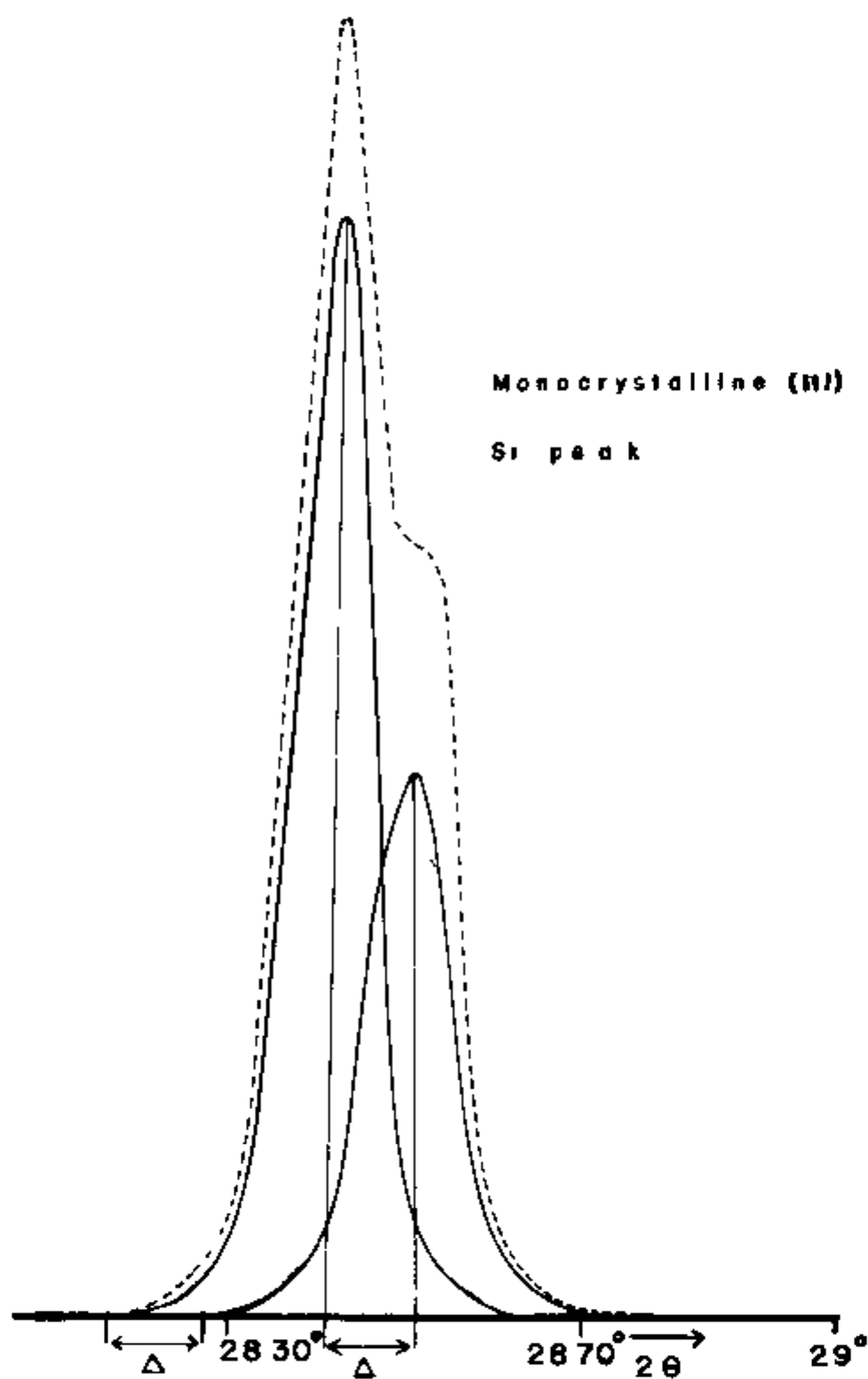


Figure 7 — Curve illustrating the principle of Rietveld correction. Contributions by K_{α_1} and K_{α_2} are shown separately.

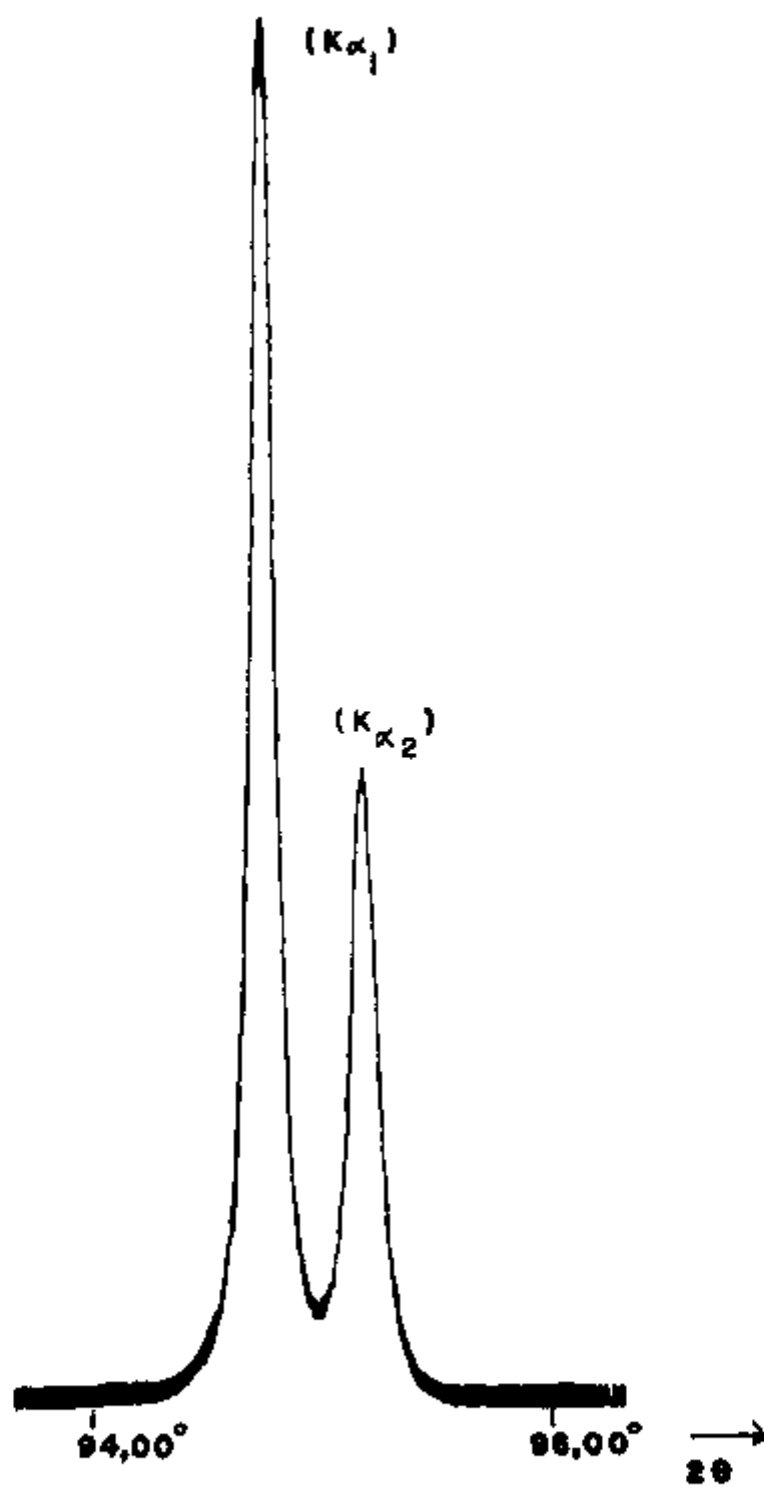


Figure 8 — (333) Si reflexion $Cu K\alpha_1$ and $Cu K\alpha_2$ peaks separated scanning speed $1/8^\circ/\text{min}$

Our results were obtained with a precision not inferior to ones presented on the most outstanding previous works in this field like (1) thanks to the extremely satisfactory performance of the apparatus employed and the pioneer utilization of a standard crystal whose mean crystallite dimension was well over the ones used by other researchers

As our main objective was to apply the method in a rather routine fashion we worked out curves in order to optimise the experimental procedure towards obtaining the highest precision within the time available (which in our Laboratory is invariably very scarce) In fig 6 curves show the percent error as a function of the crystallite size using three ways of obtaining the diffraction profile Curve a corresponds to a step scanning fixed time count curve b to a conventional scanning sample rotation speed $1/16^\circ/\text{min}$ curve c to a conventional scanning sample rotation speed $1/8^\circ/\text{min}$

As the above method was developed using U_3O_8 microspheres fragmented as well as nonfragmented a few conclusions can be drawn concerning structural properties

- once we had samples of non fragmented microspheres the mean crystallite size was found to be 584 Å in average independent of the size of the microspheres analysed
- within the same lot there is no evidence of drastic variations among crystallite sizes for any samples

This suggests that crystallite sizes are strongly dependent upon conditions under which microspheres are produced

In the future we plan to apply this method for microspheres formed under different physicochemical process parameters such as temperature column holding time concentration of the chemicals employed etc This will permit us to determine optimum production conditions in order to obtain UO_2 and U_3O_8 microspheres with the highest degree of structural perfection

APPENDIX - The Rachinger Correction

Rachinger's correction is aimed at the separation of the $K_{\alpha 1}/K_{\alpha 2}$ doublet on diffraction peaks and is based on two assumptions

- 1 - the peaks due to $K_{\alpha 1}$ and $K_{\alpha 2}$ are geometrically identical
- 2 - the intensity of the peak due to $K_{\alpha 2}$ is one half of that due to $K_{\alpha 1}$

Figure 7 illustrates one application of the method using a Si monocrystalline sample (111) reflexion considered The dashed outer line is the peak obtained experimentally using unresolved $\text{Cu } K_{\alpha}$ radiation The two internal curves were obtained using Rachinger's correction and represent the peaks due to $K_{\alpha 1}$ and $K_{\alpha 2}$ separately Δ is the angular separation between the peaks maxima m is a suitable number of intervals Thus

$$I_1(\alpha_1) = I_1 - 5 I_{1/m}(\alpha_1) \quad (\text{A})$$

In expression (A) the numerical coefficient 5 is a consequence of assumption⁽²⁾ which does not prove being absolutely correct mainly because of the alignment of the diffractometer

In order to obtain a more precise value for the quotient $\frac{I(\alpha_2)}{I(\alpha_1)}$ we obtained the Si (333) reflexion where a complete separation of the peaks due to $K_{\alpha 1}$ and $K_{\alpha 2}$ is possible their maximum heights occurring at $2\theta_{\alpha 1} = 94.96^\circ$ and $2\theta_{\alpha 2} = 95.27^\circ$ (fig 8) Under these conditions we found

$$\frac{I(\alpha_2)}{I(\alpha_1)} = 45$$

When inserted in equation (A) we have

$$I_1(\alpha_1) = I_1 - 45 I_{1m}(\alpha_1) \quad (B)$$

Expression (B) is a result of a careful use of the Roshinger correction taking into account the type of apparatus employed and allowed us to resolve the $K_{\alpha 1}/K_{\alpha 2}$ doublet more precisely

In the case of fig 7 $\Delta = 08^\circ$ and we chose $m = 8$ for convenience Therefore

$$\begin{aligned} I_0(\alpha_1) &= I_0 & I_1(\alpha_1) &= I_1 & I_7(\alpha_1) &= I_7 \\ I_8(\alpha_1) &= I_8 - 45 I_0(\alpha_1) \\ I_9(\alpha_1) &= I_9 - 45 I_1(\alpha_1) \text{ and so on} \end{aligned}$$

The origin is also chosen for convenience at the left hand side and the accuracy is satisfactory from this point to about half way down on the right hand side when fluctuations may occur, the right tail of the curve is graphically completed having in mind the fact it is symmetrical to the left tail

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RÉSUMÉ

Une méthode de routine a été établie pour la détermination de la taille moyenne des cristallites par élargissement de la ligne de diffraction des rayons X. Les méthodes de balayage par étapes aussi bien que celles de balayage continu ont été plusieurs fois testées et la précision des données obtenus en fonction de la taille des cristallites a été traitée

On met en relief notre contribution dans le but d'éliminer l'effet instrumental aussi bien que l'effet du doublet $K_{\alpha 1}/K_{\alpha 2}$ dans l'élargissement de la ligne

La correction instrumentale a été effectuée en employant un monocristal de Si avec une taille moyenne de cristallites au-dessus de 13 000 Å (donnée confirmée à notre Laboratoire) améliorant la précision des données expérimentales

La correction des doublets $K_{\alpha 1}/K_{\alpha 2}$ a été effectuée par correction de Roshinger modifiée. On a tenu compte de la relation exacte entre les intensités $K_{\alpha 1}/K_{\alpha 2}$ au lieu de dire que c'est égal à 5

La dimension moyenne des cristallites a été calculée et les résultats montrent la dépendance de ce paramètre par rapport à la qualité des microsphères

RESUMO

Um método de rotina para a determinação do tamanho médio dos cristallitos por alargamento da linha de difração dos raios X foi estabelecido. Tanto os métodos por varredura passo a passo quanto por varredura contínua foram exaustivamente testados e a precisão dos dados obtidos em função do tamanho dos cristallitos é discutido

Destacam-se nossa contribuição original no sentido de eliminar o efeito instrumental bem como o efeito devido ao duplet $K_{\alpha 1}/K_{\alpha 2}$ no alargamento da linha

A correção instrumental foi efetuada com o uso de um monocristal de Si que tem um tamanho médio dos

crystalitos acima de 13000 Å (dado este confirmado em nosso laboratório melhorando a precisão dos dados experimentais)

A correção dos dubletos $K_{\alpha 1}/K_{\alpha 2}$ foi efetuada por meio da correção de RACHINGER modificada. A relação exata entre as intensidades dos picos devidos a $K_{\alpha 1}/K_{\alpha 2}$ foi levado em conta ao invés de se adotá-la igual a 5.

A dimensão média dos cristálicos foi calculada e os resultados mostram a dependência deste parâmetro com a qualidade das microesferas.

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