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STUDY OF OPTIMUM SIZE FOR HEXAMETHYLBENZENE USING X-RAY POWDER DIFFRACTION

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ABSTRACT. *Crystallite sizes and resulting pattern of hexamethylbenzene, $C_{12}H_{18}$ are studied using x-ray powder diffraction method. It is found that optimum size suitable for x-ray powder diffraction studies are at 63-75 μm.*

KEYWORDS. X-ray diffraction, powder indexing, structural studies, high resolution, crystallite sizes.

INTRODUCTION

X-ray diffraction (XRD) has become the most powerful tool commonly available for the study of crystalline solids in terms of phase identification and measurement of such physical properties as crystallinity, stress and texture (Chi-Tang & Albe, 1993). XRD is one of the best analytical techniques for determining the nature and the quantity of all mineral phases in a polycrystalline or powder material (Alexander and Klug, 1948; Cullity, 1978).

The most important step in powder diffraction analysis is the preparation of the sample. The sample of the material under study must meet all criteria to produce its representative diffraction pattern. If not then the output experimental data may be insufficient to produce the answers needed (Smith, 1993). Considerably more time may be spent trying to interpret the bad data than would have been necessary to prepare the proper sample in the first place. Discussion on sample preparation usually receives minimal attention in modern diffraction papers.

In recent years now, we rely on the computer to assist in all steps from data collection to data analysis. Unfortunately, the computer cannot compensate for bad data. For accuracy work, high-quality data depend on specimen preparation and on the measurement techniques (Aziz, 1989).

In X-ray powder work, grinding process is an unavoidable step in sample preparation. Preparation of samples to the required crystallite sizes remain a critical step in analytical method. Ideally crystallites size should be fine, randomly oriented particles by the X-ray beam. The resulting diffraction pattern of the crystallites comprises both the positions and intensities of the diffraction effects and is a characteristic physical feature of the substance (Aziz, 1989). Particles with a circular and anisotropic shape are prone to orient so that preferred orientation can affect the results of a measurement, even with an error up to 100 % (Stefano et al, 2000).

Hurst et al (1997) has shown that a granulometry between 5 and 10 μm is needed in order to avoid microabsorption and to minimize preferred orientations. Overgrinding the material can cause irreversible changes to it. As a consequence some or all reflections can be broadened and small amounts of amorphous surface layers can be produced (Bish and Reynolds, 1989).

One way to improve the quality of XRD data is to establish the optimum size of samples. The preparation of samples has a direct link in achieving the optimum size of the samples. It remains a critical step in analytical method.

In this work we present the results of experimental study of optimum sizes of crystallites and time taken to grind sample manually for XRD work of hexamethylbenzene, $C_{12}H_{18}$ abbreviated HMB.

HMB is a molecular crystal whose structural, dynamical and thermodynamic properties are of interest. Its structure at room temperature (neglecting H-atoms positions) has been determined by X-ray diffraction technique. It is of a triclinic crystal system with one molecule per unit cell and space group C_i^1 ($P\bar{1}$), thus making HMB one of the simpler molecular crystals available for study (Hamilton et al, 1969).

HMB has been investigated by a number of techniques such as neutron inelastic scattering (Rush and Taylor, 1966), nuclear magnetic resonance (Allen and Cowking, 1967), and Raman, infra-red (Leech et al, 1966), u-v absorption (Schnepp, 1959) and phosphorescence spectroscopy (Sponer and Kanda, 1964). Additional information is much needed particularly concerning the understanding of the position and dynamics of hydrogen atoms on the methyl groups (Hamilton et al, 1969).

FULL-WIDTH AT HALF-MAXIMUM (FWHM)

Resolution of the powder diffraction lines can be expressed as full-width at half-maximum height in 2θ (FWHM) of the peaks in the data profile. The average FWHM can be an indication for improved values of sample powder. It will indicate that line profiles of the patterns from better specimens were generally sharper and measurable. The readings recorded can be better due to the improved location of the centroid of the line profile.

Line positions in powder diffraction are usually defined in terms of the peak (mode) or centroid (center of gravity). Hence ideally, in a perfect fully-resolved, symmetrical line profile, the position of the peak corresponds to that of its centroid.

EXPERIMENTS

The milling system consists of a mortar and pestle as the grinding set. The sieving set used was of model Firstsch Analysette. This apparatus consists of a continuously rotating mortar of an electronic device. Four types of sievers of sizes 63, 75, 90 and 106 μm were being used using the American Society for Testing and Materials (ASTM).

Five set of powder sizes were used, that is, < 63 μm, 63 - 75 μm, 75 - 90 μm, 90 - 106 μm and > 106 μm. The sievers were cleaned using alcohol and then washed with distilled water. It was then dried using an oven at temperature of about 100° C.

Scraper was used to remove the material from the walls of the mortar. X-ray diffraction analysis was performed with an x-ray powder diffractometer, Philips PW 1710, goniometer PW 1800 and using Cu K_α radiation at 40 kV and 45 mA. The parameter setting were at step scan of 0.020 °, scan rate of 0.02 °/sec and 2θ ° range of 10° - 85°.

In the quantitative determinations, several measurements of the sample were taken consists of 2θ and with respect to time of grinding of the samples. Readings of FWHM were obtained. Measurements were being repeated for several ranges of sizes. 2θ is define as the Bragg angle for the samples measured in degrees. |2θ| is the absolute difference of the observed 2θ and the calculated 2θ.

RESULTS

The optimum powder size for HMB sample was at range 63 – 75 μm with mean | 2 θ °| value of 0.02121° as shown in Figure 2 and 4, while HMB sample size of less than 63 μm has its mean | 2 θ °| higher than the observed range 63 – 75 μm , that is, 0.04034° as shown in Figure 3.

As shown in Figure 1 and 6, the mean | 2 θ °| value is 0.02665° for the best grinding time of 0.75 hour. As the grinding time decreases as 0.25 hour, the mean | 2 θ °| value is 0.03299° as given in Figure 5. Meantime, for grinding time of 1.5 hour, the mean | 2 θ °| value is 0.03649° as given in Figure 7. It is observed that grinding HMB sample of more than 0.75 hour will tend to make the sample glomerate with each other. Hence the best grinding time found was at 0.75 hour at optimum powder size.

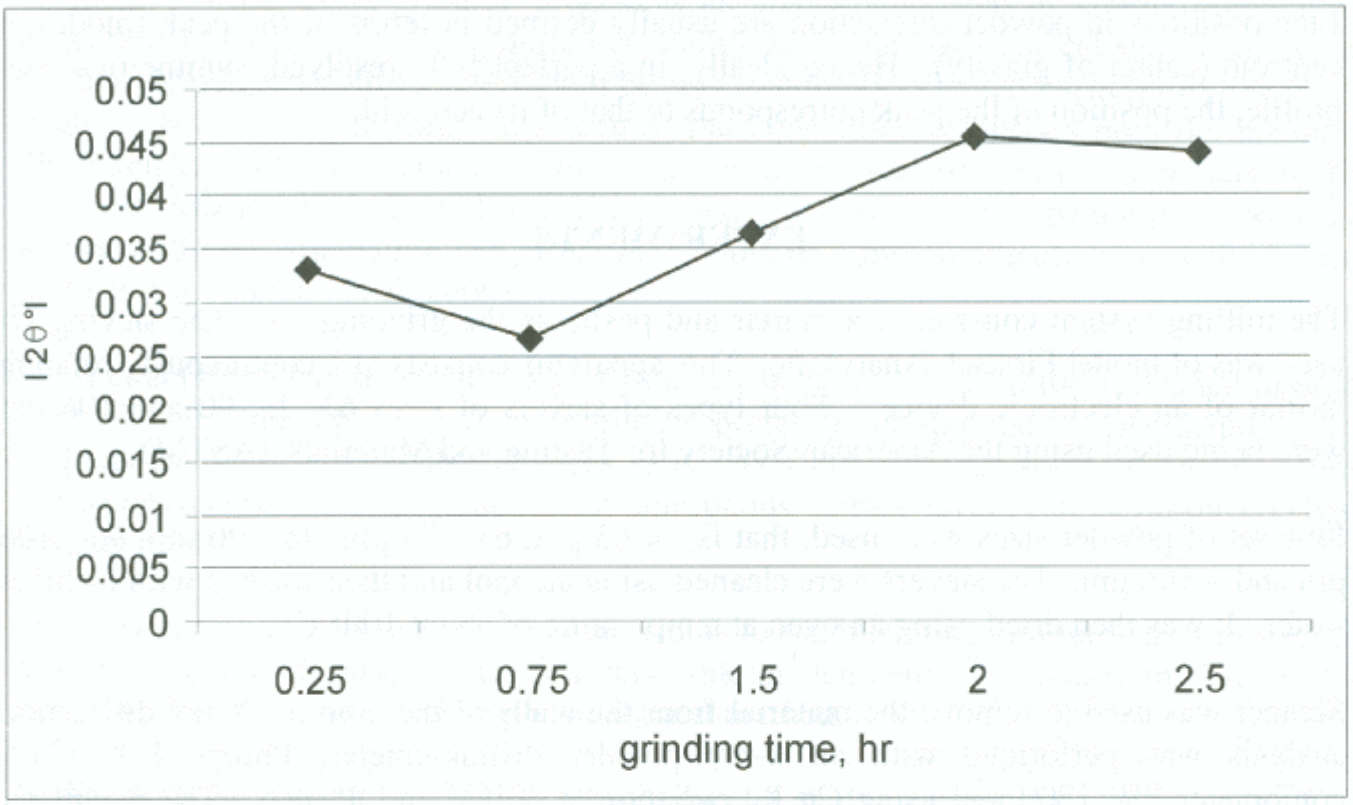

Figure 1. Plotting I 2θ°I versus grinding time.

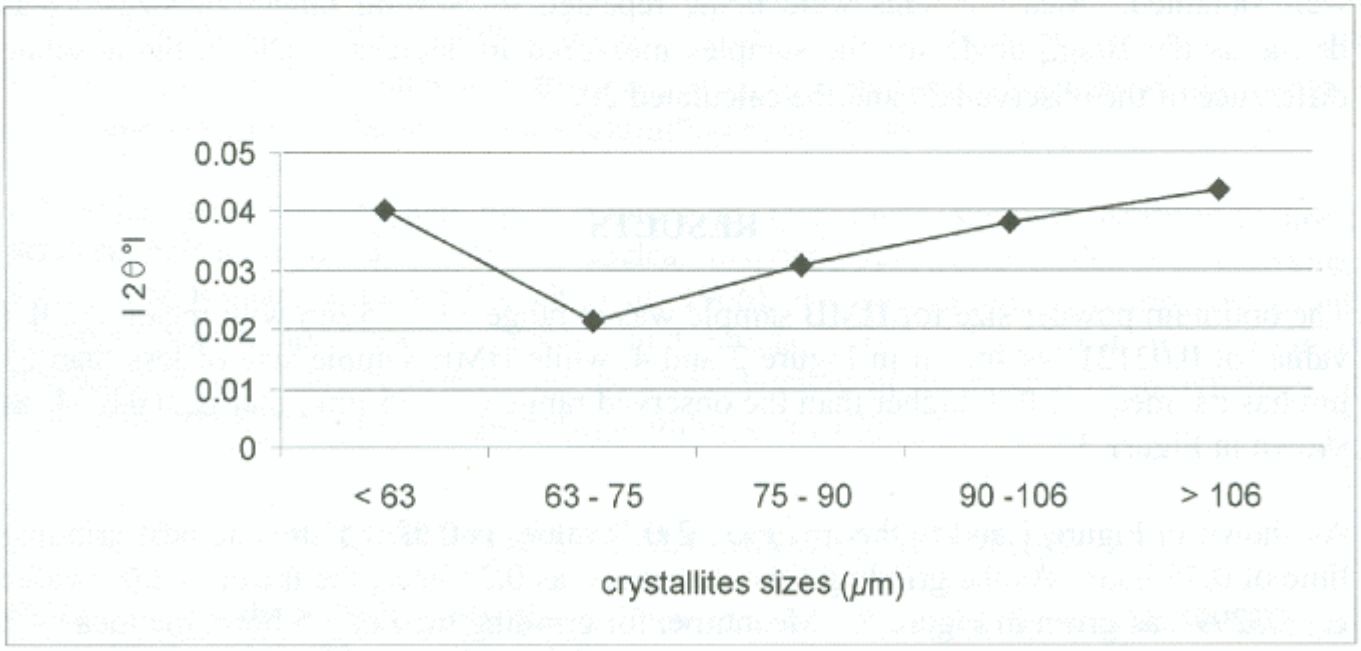

Figure 2. Variation of crystallite sizes with respect to the average I 2θ°I

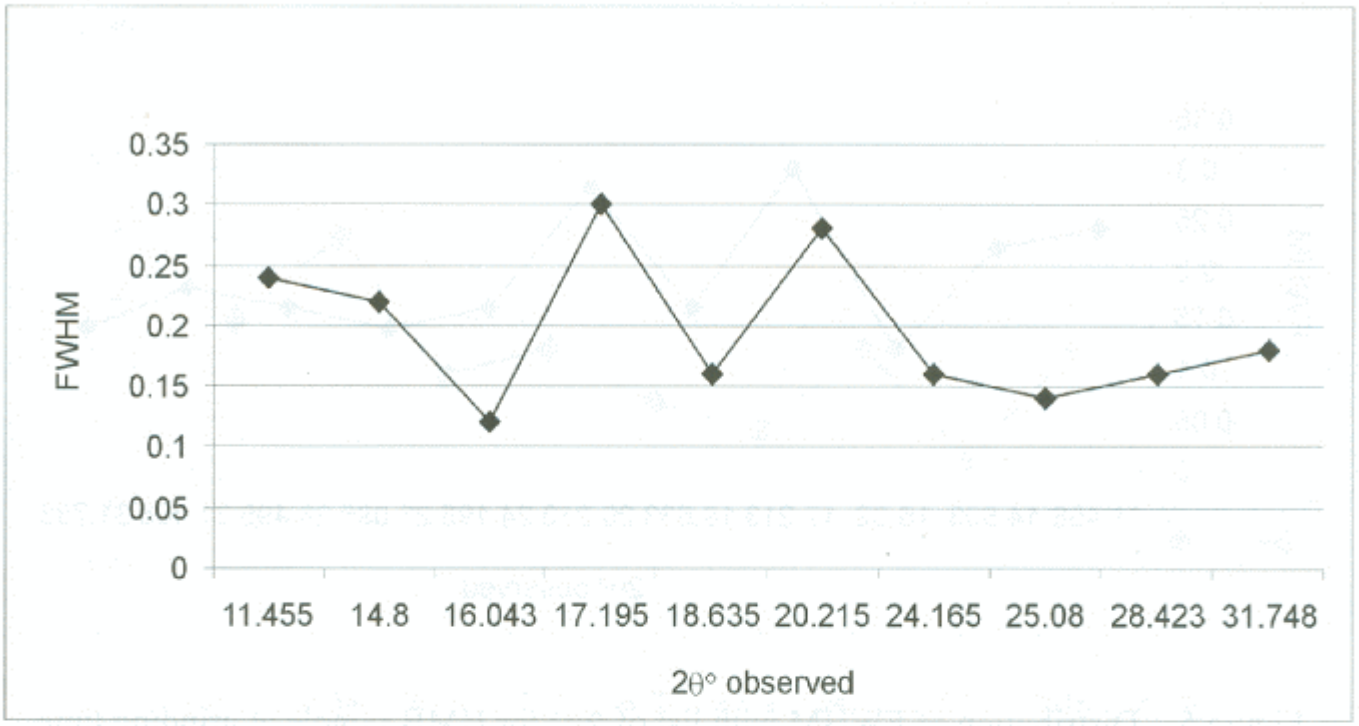

Figure 3. Distribution of FWHM with list of 2θ° for HMB sample of size < 63μm and mean | 2θ°| value is 0.04034°

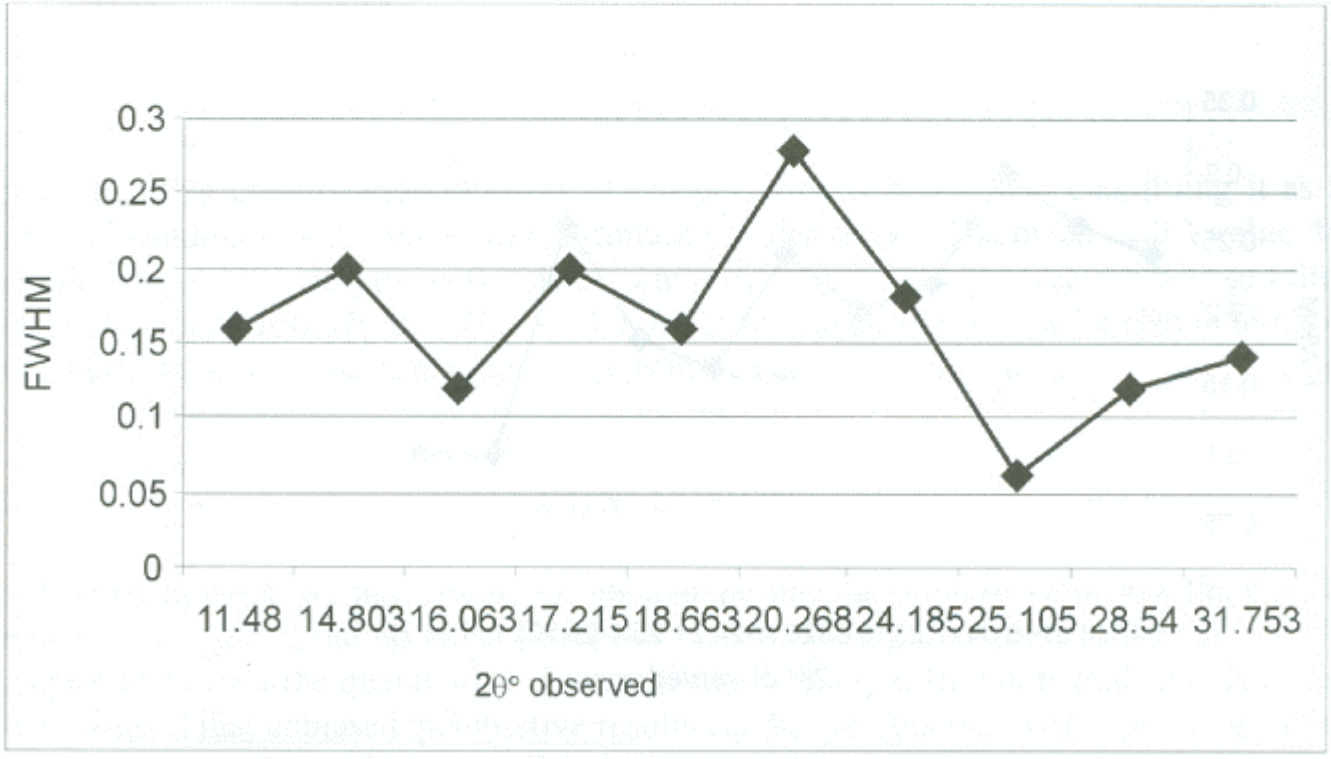

Figure 4. Distribution of FWHM with list of 2θ° for HMB sample of size < 63-75μm The mean| 2θ°| value is 0.02121°

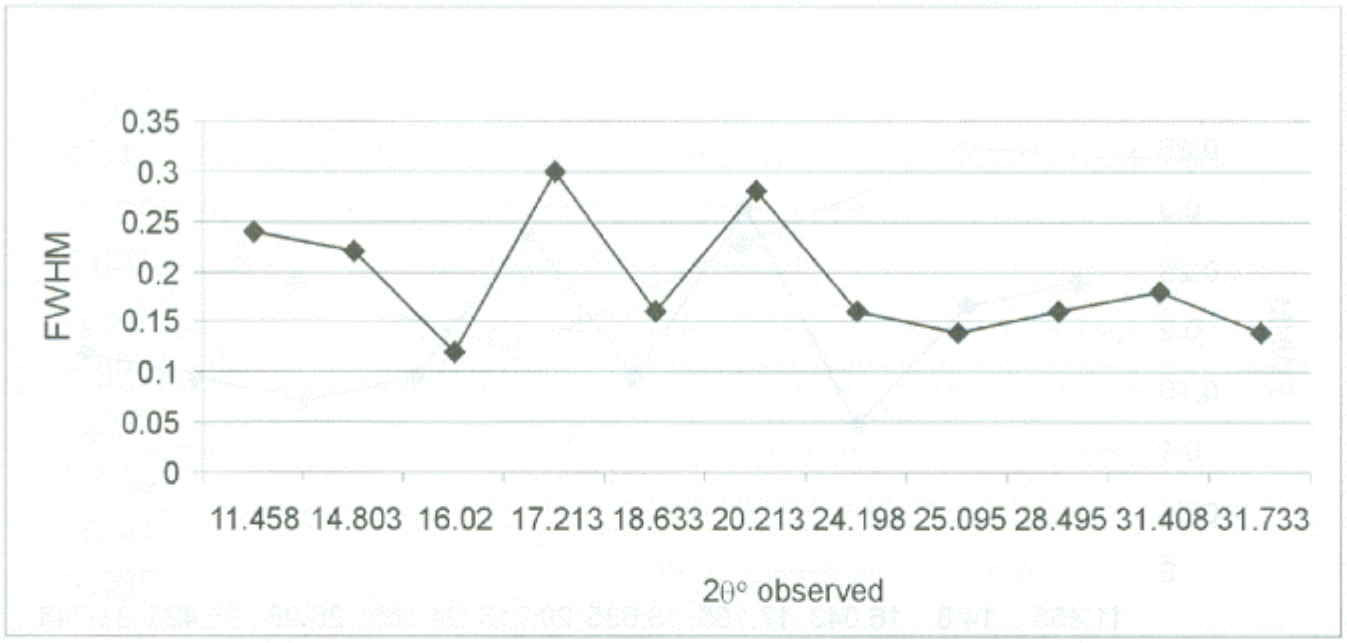

Figure 5. Distribution of FWHM with list of 2θ° for HMB sample at grinding time at 0.25 hr. The mean | 2θ°| value is 0.03299°

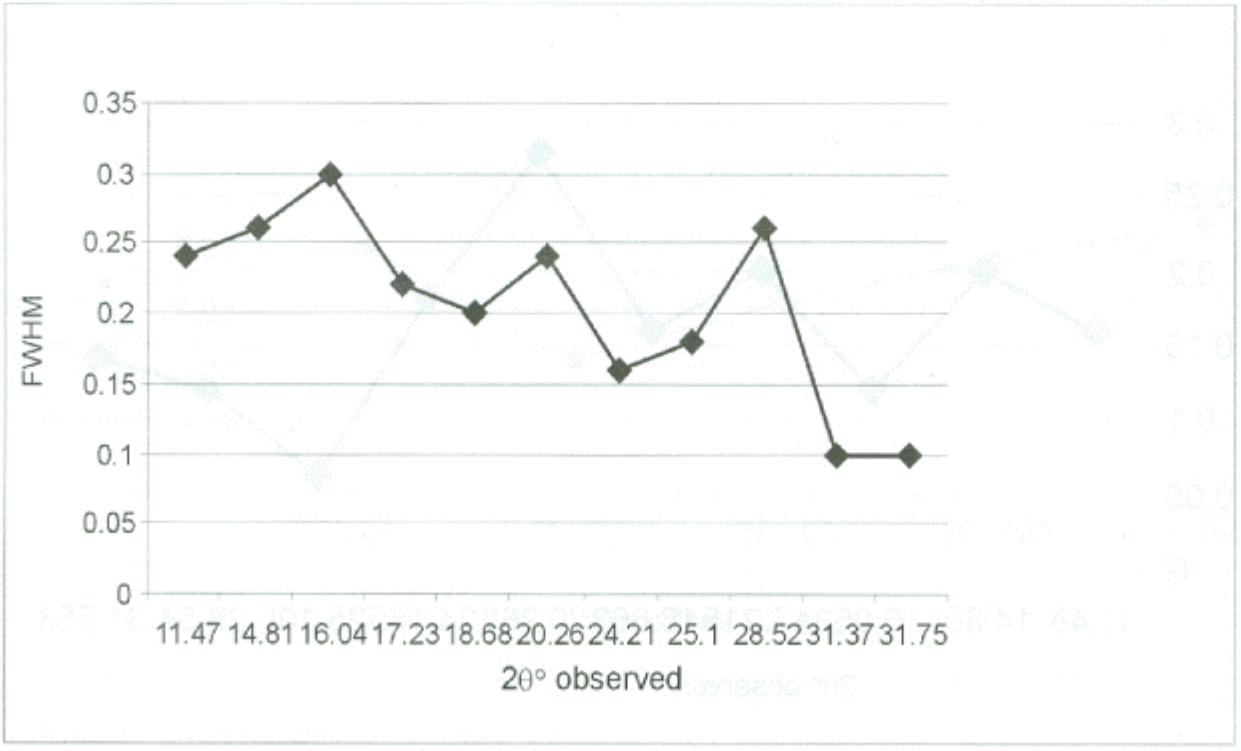

Figure 6. Distribution of FWHM with list of 2θ° for HMB sample at grinding time at 0.75 hr. The mean | 2θ°| value is 0.02665°

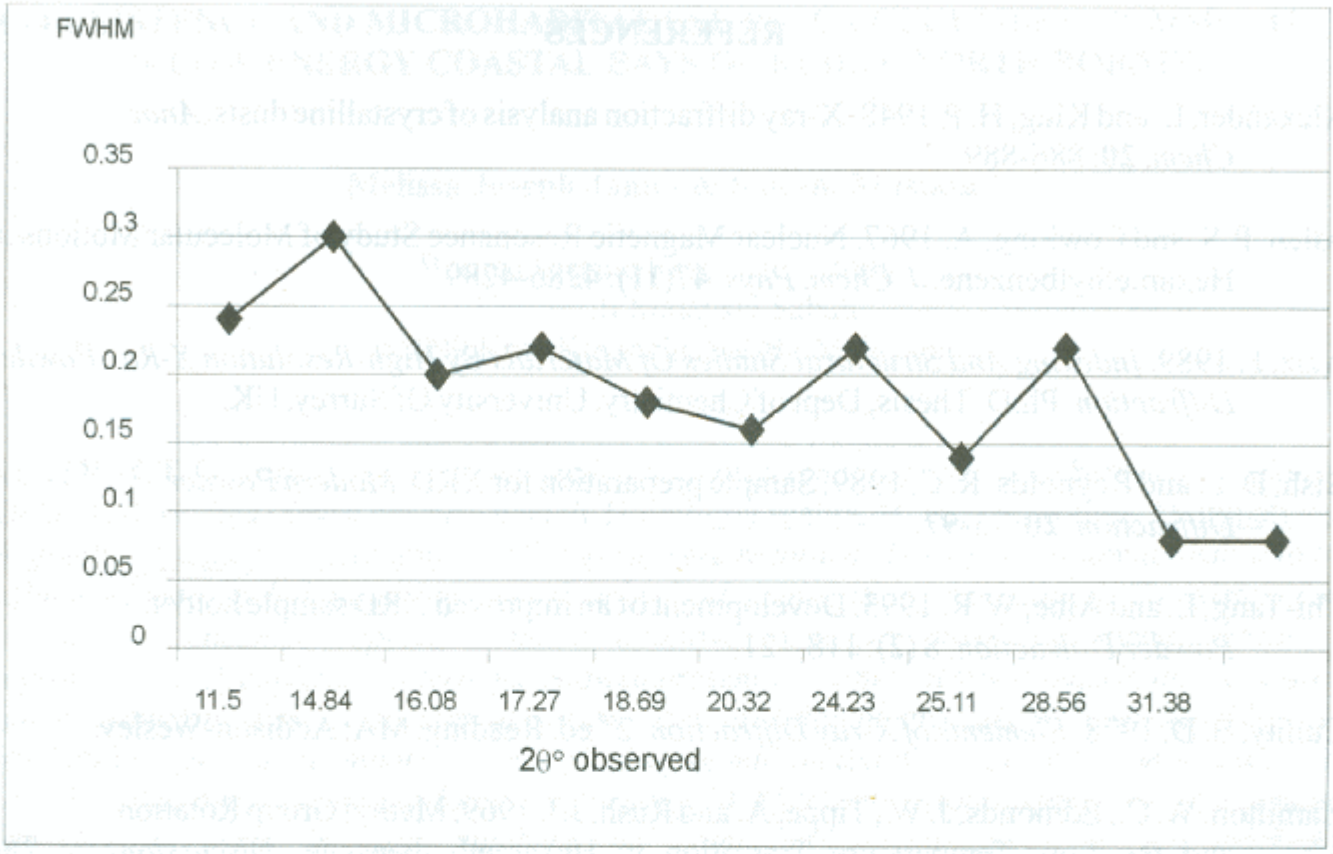

Figure 7. Distribution of FWHM with list of 2θ° for HMB sample at grinding time at 1.5 hr. The mean | 2θ°| value is 0.03649°

It is found that classification in terms of powder sizes is better than classifying it as in terms of grinding time for measuring optimum powder sizes. The mean | 2 θ °| value for sample size of 63 – 75 μm is 0.02121°, while the mean | 2 θ °| value for best grinding time of 0.75 hour is 0.02665°. This shows that to define optimum powder size in terms of actual powder size measurement probably is more accurate and concise.

CONCLUSION

In the present work, we have studied from an experimental point of view how the powder sample sizes and grinding time processes occurs during the preparation of powder samples that affect the quantitative determination in X-ray diffraction analysis. It is also demonstrated that unbiased quantitative results can be are obtained with a proper grinding time and measured at optimum powder size.

REFERENCES

Alexander, L. and Klug, H. P. 1948. X-ray diffraction analysis of crystalline dusts. *Anal. Chem.* **20**: 886-889.

Allen, P. S. and Cowking, A. 1967. Nuclear Magnetic Resonance Study of Molecular Motions in Hexamethylbenzene. *J. Chem. Phys.* **47(11)**: 4286-4289.

Aziz, F. 1989. *Indexing And Structural Studies Of Materials By High-Resolution X-Ray Powder Diffraction*. Ph.D. Thesis, Dept of Chemistry. University Of Surrey, UK.

Bish, D. L. and Reynolds, R. C. 1989. Sample preparation for XRD. *Modern Powder Diffraction*. **20**: 73-97.

Chi-Tang, L. and Albe, W. R. 1993. Development of an improved XRD sample holder. *Powder Diffraction*. **8 (2)**: 118-121.

Cullity, B. D. 1978. *Elements of X-ray Diffraction*. 2nd ed. Reading, MA: Addison-Wesley.

Hamilton, W. C., Edmonds, J. W., Tippe, A. and Rush, J.J. 1969. Methyl Group Rotation and the Low Temperature Transition in Hexamethylbenzene. *Discussions of The Faraday Society*. **48:** 192-204.

Hurst, V. J., Schroeder, P. A. and Styron, R. W. 1997. Accurate quantification of quartz and other phases by powder X-ray diffractometry. *Anal. Chim. Acta*. **337**: 233-252.

Klug, H.P. and Alexander, L. E. 1973. *X-ray Diffraction Procedures*. New York: John Wiley & Sons.

Leech, R. C., Powell, D. B. and Sheppard, N. 1966. Infra-red Evidence for Internal Rotation of CH_3 Groups in Solid Hexamethylbenzene. *Spectrochim. Acta*. **22**: 1-4.

Rush, J. J. and Taylor, T. I. 1966. Neutron-Scattering Study of Hindered Rotational Motions and Phase Transitions in Hexamethylbenzene. *J. Chem. Phys*. **44**: 2749-2754.

Schnepp, O. 1959. Low Temperature Phase Transition of Crystalline Hexamethylbenzene II. *J. Chem. Phys*. **30**: 48-52.

Smith, D. K. 1993. Sample Preparation for Powder Diffraction. *Powder Diffraction*. **8 (4)**: 201.

Sponer, H. and Kanda, Y. 1964. *J. Chem. Phys*. **40**: 778.

Stefano, L. D., Luca, F. D., Buccolieri, G. and Plescia, P. 2000. Milling effects upon quantitative determinations of chrysotile asbestos by the reference intensity ratio method. *Powder Diffraction*. **15 (1)**: 26-29.