Pak. J. Sci. Ind. Res. 2006 **49**(2) 72-76

A Method for the Determination of Relative Crystallinity of Minerals by X-Ray Diffraction

Abdul Mannan[a]*, K. R. Kazmi[a], Muhammad Shafiq Khan[b] and I. H. Khan[a]
[a] PCSIR Laboratories Complex, Ferozepur Road, Lahore-54600, Pakistan
[b] Pharmacy Department, Islamia University, Bahawalpur, Pakistan

(received January 14, 2004; revised December 28, 2005; accepted December 29, 2005)

Abstract. X-ray diffraction spectra of smithsonite, fluorite, zircon, gibbsite, quartz, aragonite, albite, calcite, dolomite, anatase, barite, wollastonite and siderite have been recorded. The relative percentage crystallinity of these were calculated with the help of two programmes, namely, PowderX and WinPlotr. These two programmes have simplified the calculation of relative percentage crystallinity of various materials. Most of the X-ray spectra were very good and without noise. The noise of the spectra, when present, was removed with the programme PowderX and the spectrum was also levelled before the calculation of percentage crystallinity. The spectra of highly crystalline materials showed sharp high intensity peaks with small base. The degree of crystallinity has been determined by WinPlotr using integration method and by PowderX programme using area of the triangle method. Both of these programmes showed similar results, with the exception of a few spectra where the specimens were paracrystalline and amorphous.

Keywords: relative crystallinity, minerals, x-ray diffraction, software WinPlotr, software PowderX, percentage crystallinity

Introduction

A material can be considered partially crystalline and partially amorphous. The determination of percentage crystallinity is of significance in understanding the material properties and qualities. The degree of crystallinity not only affects the long-term stability of the chemical compounds, but also their bioactivity, which could mean the difference between effective and ineffective doses. Even the clay used for medicinal purposes must have good quantity of the crystalline material to be effective (Osol, 1955). Relative percentage crystallinity determination is also essential for the polymeric materials to evaluate their qualities. Kratos Analytical (1999) determined the percentage crystallinity of polymeric materials to be about 50% by Fourier method. A standard method for the determination of percentage crystallinity for zeolite only has been developed (ASTM, 2003). There are a number of methods for the determination of percentage crystallinity. However, the accuracy, precision, and general validity of each technique is still being investigated (Al-Aloush and Al-Raqibah, 2000). Crystallinity of only one or two organic or inorganic crystalline compounds has been reported by each method.

During the development of clay catalysts, Ehsan *et al.* (1999) observed that crystallinity and amorphous ratio of the clay and associated minerals play an important role in the activity of the catalyst. This led us to investigate further the relative crystallinity of minerals and clay minerals. In this study is reported the relative percentage crystallinity of smithsonite, fluorite, zircon, gibbsite, quartz, aragonite, albite, calcite, dolomite, anatase, barite, wollastonite and siderite. These minerals are commercially exploited as gemstone, ornamental stones, abrasives and building stones. Relative crystallinity is an essential property which must be measured for the evaluation of these materials, since chemical evaluation of these materials will only tell us the chemical composition of the materials.

In this study, we have used WinPlotr (Roisnel *et al.,* 2002) and PowderX (Dong, 1999) programmes for the calculation of relative percentage crystallinity. These programmes were used with the permission of their developers, which have not been previously employed for the determination of relative crystallnity. As such, the relative crystallinity of the studied minerals is being reported for the first time. When this work was in progress, ASTM published a standard test method for the determination of zeolite sodium by X-ray diffraction as the Standard Number D5357-98 (ASTM, 2003).

Materials and Methods

All the specimens used in the present study (Table 1) were ground to 200-300 mesh size (74 to 50 μ). These samples were run on Siemens D5000 X-ray diffractometer. The noise (Fig. 1) present in the spectrum of siderite was removed, and was levelled (Fig. 2 and 3). The X-ray diffraction patterns of these specimens were verified by using the JCP.CAT programme provided with the Siemens D5000 X-ray diffractometer. This programme contains D/I values of about 60,000 Standards. The files of these XRD spectra were copied onto another com-

---

*Author for correspondence; E-mail: scientist3355@yahoo.com puter which contained WinPlotr (Roisnel *et al.,* 2002) and PowderX (Dong, 1999) programmes. The intensities of crystalline and amorphous peaks of these minerals were determined by both the programmes.

The crystalline peaks were selected by visual observation. The area was calculated by second derivative method of the PowderX (Fig. 4). The total area of the crystalline and amorphous phase was obtained by simply adding areas of all the peaks. The total crystalline phase was determined by adding the areas of all the crystalline peaks (Table 1). The relative percentage crystallinity was determined by dividing the area of total crystalline phase by the total area of the crystalline and amorphous phase (Table 2). The total area of the spectrum was calculated with the WinPlotr programme using integration method (Fig. 5). The crystalline peaks were selected by visual observation. Their area was also calculated by applying integration between two points (Table 1). The relative percentage crystallinity was determined by dividing total area of the crystalline peaks with the total area (total intensity) of the spectrum (Table 2).

The relative percentage crystallinity was then given by the ratio between these two intensities (Kratos Analytical, 1999):

$I_c / I_c + I_a$

where:

I_c = total intensity of the crystalline peaks
I_a = total intensity of the amorphous peaks

The relative percentage crystallinity of various clays and minerals determined by the PowderX and WinPlotr programmes, along with their chemical composition are recorded in Table 2.

Results and Discussion

Powdered specimens (200 mesh; 74 μ) are best prepared by placing the powder on a glass or on a plastic plate and compacting under just sufficient pressure to cause cohesion, without the use of a binder, and smoothing of the surface. Too much pressure causes preferred orientation of the powder particles. Culty (1956) recommended 325 mesh or 43 μ (for the method using Debye Scherrer carmera) for metals and alloys. It was further recommended that if relative line intensities are to be accurately reproducible, powder should be ground extremely fine, to a size of 10 μ or less (for diffractometer). Generally, all types of samples are best ground to a fine powder (200-300 mesh; 74 to 50 μ). Plastic samples are also ground to 200-300 mesh (Raymond and Myers, 1953). It has been also suggested that samples should be ground to below the particle size of 0.0002 to 0.0005 mm (2 to 5 μ) (Scintag Inc., 1999). Particle size can be measured by XRD, as the width of XRD peaks broadens as the crystallite size decreases. When crystallites are less than approximately 100 nm, appreciable broadening in the X-ray diffraction lines occurs (H and M Analytical Services, 2001).

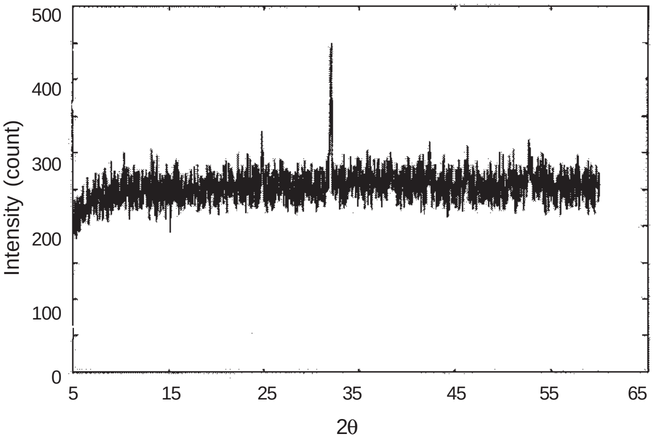

Fig. 1. Siderite (with noise).

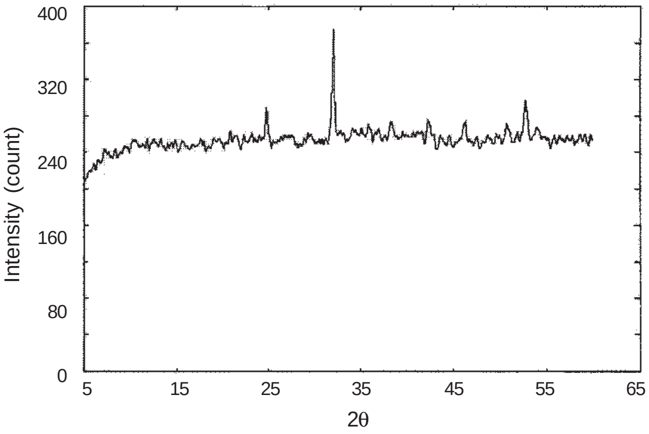

Fig. 2. Siderite (without noise).

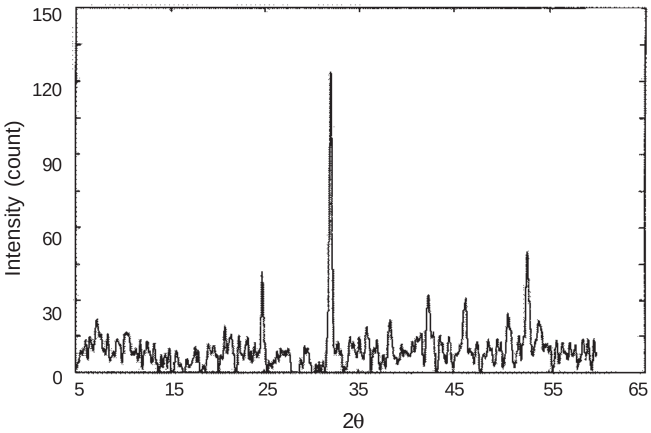

Fig. 3. Siderite (levelled).

It may be pointed out here that most of the work for the specimen preparation was related to the particle size measurement, where the particle size was reduced to the minimum, which is why the particle size of the specimens varied between 2 - 70 μ. For the relative crystallinity determination, the specimen was ground to a level where a high intensity peak of limited base was obtained. In this study, the most suitable size for crystallinity determination was noted to be 200 mesh or 74 μ. The relative crystallinity and chemical composition of the minerals are recorded in Table 2.

The curvature of diffracted intensity versus 2θ for a crystalline solid is almost always zero, except at certain angles where sharp maxima occur (Culty, 1956). These are diffracted beams. For the crystalline material, the periodic repeating electron density would give rise to well defined diffraction peaks whose widths are determined by the crystalline quality. High quality

Table 1. Relative percentage crystallinity of different minerals

Minerals	PowderX programme		WinPlotr programme	
	area of the crystalline peaks (Ic)	total area of the crystalline and amorphous peaks (Ic+ Ia)	area of the crystalline peaks (Ic)	total area of the crystalline and amorphous peaks (Ic + Ia)
Smithsonite	46819	47911.3	943.23	958.86
Fluorite	27668.9	28696.2	570.01	586.80
Zircon	27552.1	28551.4	784.51	841.48
Gibbsite	62174.5	65904.7	1115.56	1188.29
Quartz	35667	36960.62	998.53	1085.36
Aragonite	9143.5	9980.1	232.92	252.60
Talc	34779.9	37706.3	877.43	955.81
Albite	48266.1	55224.3	848.81	1006.54
Calcite	5283.8	6397.6	57.52	65.41
Dolomite	4145.4	5330.3	109.02	124.52
Anatase	21102.9	28238.9	496.97	697.12
Barite	20325.1	28813.58	428.95	610.78
Wollastonite	3396.5	5214.9	74.16	109.68
Siderite	4023.9	19486.5	131.70	475.30

Ic = total intensity of the crystalline peaks; Ia = total area of the amorphous peaks

Table 2. Relative crystallinity of minerals

Minerals	Chemistry	WinPlot programme	PowderX programme
Smithsonite	zinc carbonate ($ZnCO_3$)	98.37	97.72
Fluorite	calcium fluoride (CaF_2)	97.14	96.42
Zircon	ziconium silicate ($ZrSiO_4$)	93.23	96.50
Gibbsite	aluminum hydroxide ($Al(OH)_3$)	93.88	94.34
Quartz	silicon dioxide (SiO_2)	92.0	96.50
Aragonite	calcium carbonate ($CaCO_3$)	92.21	91.61
Talc	magnesium silicate hydroxide ($Mg_3Si_4O_{10}(OH)_2$)	91.80	92.23
Albite	sodium aluminum silicate ($NaAlSi_3O_8$)	84.33	87.40
Calcite	calcium carbonate ($CaCO_3$)	87.94	82.59
Dolomite	calcium magnesium carbonate ($CaMg(CO_3)_2$)	87.56	77.77
Anatase	titanium oxide (TiO_2)	71.29	74.73
Barite	barium sulfate ($BaSO_4$)	70.23	70.54
Wollastonite	calcium silicate ($CaSiO_3$)	67.62	65.13
Siderite	iron carbonate ($FeCO_3$)	27.71	20.65

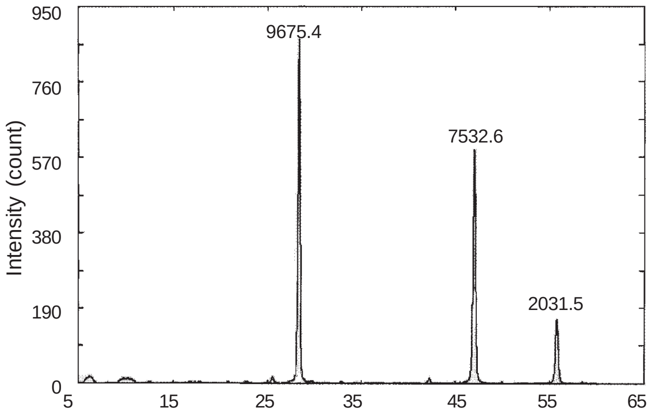

Fig. 4. Calculation of area of the peak (PowderX programme) for fluorite.

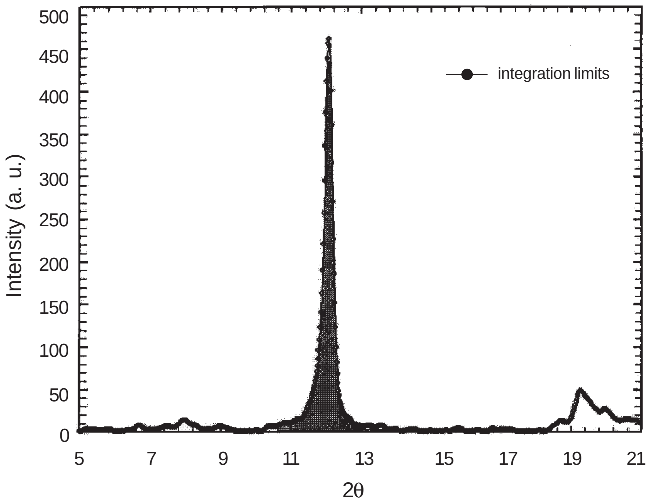

Fig. 5. Calculation of area of the peak by integration (WinPlotr programme).

crystalline materials give rise to sharp peaks of high intensity. Smithsonite, flourite, zircon, gibbsite, quartz, aragonite, talc, albite and calcite spectra are very good examples of the high quality crystalline peaks. These materials yield high frequency, sharp, and well defined peaks, which show that these were very high quality crystalline materials. Dolomite, anatase, barite and wollastonite contained wide width and slightly broad based peaks due to paracrystalline materials. Siderite showed the presence of a reasonable amount of amorphous material.

In most of the cases, the crystallinity determined by the two methods was very close within the experimental error range. The difference in the calculated relative percentage crystallinity increased with the increase of the paracrytalline material. There are a number of methods for the determination of percentage crystallinity. Specifically, density, differential scanning calorimetry, and modulated differential scanning calorimetry are used to study crysallinity of polyethyleneterepthalate (PET) chips, preforms, and bottles (Reading *et al.*, 2001; Mallapragada and Narasimhan, 2000). The accuracy, precision, and general validity of each technique and the interpretation of the observations obtained are still being investigated (Al-Aloush and Al-Raqibah, 2000). Most recently, ASTM (2003) has recommended XRD method for the determination of percentage crystallinity for only zeolite.

The results reported here demonstrate that with the help of WinPlotr and PowderX, relative percentage crystallinity can be determined by XRD for the routine evaluation of crystalline minerals.

Conclusion

Percentage crystallinity is a very important property of minerals and clay minerals, as these are found in nature to vary considerably in physical aspects which significantly influence their end-usage. The present study was conducted on highly crystalline minerals. Percentage crystallinity is of particular interest as it influences the brightness, whiteness, opacity, gloss, film strength, viscosity, catalytic activity, and the medicinal activity of minerals. The degree of purity of these minerals can also be assessed from their percentage crystallinity. The presently described simple method can be used to determine the percentage crystallinity of minerals.

Acknowledgements

We thank Prof. Dr. Cheng Dong (Institute of Physics, Chinese Academy of Sciences, Beijing, Peoples Republic of China) for allowing us to use PowderX; we also thank Theiry Roisnel (Laboratoire de Chimie du Solide et Inorganique Moleculaire, CNRS), Juan Rodriguez-Carvajal (Laboratoire Leon Brillouin, CEA-CNRS) and Javier Gonzalez-Platas (Departamento de Fisica Fundamental II, Universidad La Laguna) for making available the WinPlotr software.

References

Al-Aloush, B.Z., Al-Raqibah, I. 2000. Evaluation of three methods for the measurement of crystallinity of PET resins, preforms, and bottles. *Polymer Engg. Sci.* **40:** 2442-2455.

ASTM. 2003. Standard test method for the determination of relative crystallinity of zeolite sodium by X-ray diffraction. In: *Standard No: D5357-98; Volume: 05. 05, ASTM International*, 100 Barr Harbor Drive, PO Box C700, West Gonshohocken, USA.

Culty, B.D. 1956. *Elements of X-Ray Diffraction*, Addison Wesley Inc., Massachusetts, USA.

Dong, C. 1999. PowderX: Windows-95-based program for powder X-ray diffraction data processing. *J. Appl. Cryst*. **32:** 838.

Ehsan, A., Ahsan, A.H., Mannan, A. 1999. Development of catalyst from natural clays for Friedel-Crafts alkylation and new synthesis of 9, 10-dihydroanthracene. *Pak. J. Sci. Ind. Res.* **42:** 156-160.

H and M Analytical Services. 2001. *Particle Size and Strain Analysis by X-Ray Diffraction*, http://www.h-and-m-analytical.com/pdfs/size_strain.pdf

Kratos Analytical (a Shimadzu group of company). 1999. *XRD 6000 Application Brief: Percentage Crystallinity Determination by X-Ray Diffraction*, http:// www.kratos.com/XRD/Apps/pcent.html.

Mallapragada, S.K., Narasimhan, B. 2000. Infrared spectroscopy in analysis of polymer crystallinity. In: *Encyclopedia of Analytical Chemistry,* R. A. Meyers (ed.), pp. 7644-7658, John Wiley and Sons Ltd., Chichester, UK.

Osol, A.F. 1955. *The Dispensary of the United States of America*, pp. 147-148, 25th edition, J. B. Lippintot Company, Philadelphia, USA.

Raymond, B.L., Myers, W.M. 1953. *Non-Metallic Minerals*, 2nd edition, McGraw Hill Company, New York, USA.

Reading, M., Price, D.M., Orliac, H. 2001. Measurement of crystallinity in polymers using modulated temperature differential scanning calorimetry, materials characterization by dynamic and modulated thermal analytical techniques. In: *ASTM STP 1402*, A.T. Riga, L.H. Judovits (eds.), pp. 17-31, American Society for Testing Materials, West Consholhocken, PA, USA.

Roisnel, T., Rodriguez-Carvajal, J., Gonzalez-Platas, J. 2002. *WinPlotr, A Graphic Tool for Powder Diffraction*, http://www-llb.cea.fr/fullweb/winplotr/winplotr.htm

Scintag Inc. 1999. *Chapter 7: Basics of X-Ray Diffraction*, pp. 7.1-7.25, http: //epswww.unm.edu/xrd/xrdbasics.pdf