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PHASE IDENTIFICATION BY X-RAY POWDER DIFFRACTION

EVALUATION OF VARIOUS TECHNIQUES

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ABSTRACT

Three powder mixtures, each composed of four or more phases, were submitted for phase identification by x-ray diffraction. Laboratory technicians supplied tables of "d" values and of relative intensities as obtained separately and independently by use of the diffractometer, the Debye camera and the Guinier camera. These tables of diffraction data were "solved" by utilization of the Joint Committee search manuals and reference to the Joint Committee Powder Diffraction File (P.D.F.). The same tables of data were then submitted to the 2dTS:Diffraction Data Tele-Search for a computer printout of results. Experimental data are also presented which provide a quantitative comparison of the accuracy of measurement of "d" values and of the resolution of Debye cameras vs Guinier cameras, since this information is necessary for efficient search procedures whether by manual or computer methods.

The "solutions" of the three unknown mixtures confirm the general experience that only those diffraction data of the highest quality with respect to resolution of close lines and with respect to accuracy and intensity of "d" values are adequate for an easy and complete solution of complicated mixtures of phases. The Debye pattern does not entirely meet these requirements though for many simpler problems its great usefulness and especially its sensitivity to minute amounts of sample are well known. The diffractometer is a very versatile instrument which can provide high quality powder data and has as well the considerable advantage that it provides quantitative intensity values directly. Furthermore, units are now commercially available which automatically produce the diffraction data for immediate computer search and printout of results, thus almost completely eliminating manual labor in the determination of unknown phases in a powder mixture. The Guinier camera also provides powder diffraction data of the highest quality though for quantitative intensities the additional step of making a microphotometer trace of the film is necessary. However, for identification purposes relative intensities as can be obtained by the use of a Frevel type visual density gauge are shown to be sufficient.

With respect to the involved question of computer vs manual search methods much more experience is necessary. But the evidence from these three problems is that each method can determine the phases present (insofar as they are included in the P.D.F.) and that while the computer is probably faster the manual method is probably cheaper.

INTRODUCTION

It is almost 60 years since the "discovery" of powder diffraction by Debye and Scherrer and independently by Hull. The type of powder camera designed at that time is still in use today and in most x-ray laboratories is probably still the "work-horse" in the utilization of x-rays for phase identification. The diffractometer is a highly developed instrument likewise in use for the purpose of powder diffraction. So also is the Guinier design of camera which is finding considerably increasing popularity within the last decade.

X-ray diffraction phase identification became more broadly usable and important with the availability of a file of standard patterns and practical search systems. At present the JCPDS powder diffraction file (P.D.F.) contains about 34,000 patterns and is expanding at the rate of about 2000 patterns each year. Computer programs are now available for retrieval of unknown patterns.

Thus, the analyst in an x-ray laboratory has a considerable choice of techniques for obtaining the diffraction data of unknown phases and also a choice of methods of "solving" these data. The objective of the present paper is to make some comparison of the available techniques and methods and to illustrate with some examples how limitations in the "quality" of the data reflect in the degree of completeness and reliability of the identification of the unknowns.

DEBYE AND GUINIER DATA COMPARED

In order to determine the degree of uniformity to be expected in powder diffraction data from various types of x-ray units, x-ray patterns of certain standard materials were solicited from a score of x-ray laboratories in the U.S.A., Canada, and Europe. It would be impractical to reproduce the films in this paper but in Figure 1 is seen the microphotometer traces of two of the best films which were received. The traces in Figure 1 illustrate the greater dispersion, the sharper diffraction lines and the much lower background of the Guinier pattern and are typical of the differences between Guinier and Debye powder patterns.

Accuracy

Experience in measuring the positions of the lines in a Philips vernier scale viewing box indicates that on a Debye pattern this can be done to about ± 0.1 mm, while on a Guinier pattern this figure is about ± 0.05 mm. Since for the same diameter camera the dispersion of the Guinier unit is twice that of the Debye, the accuracy of measurement of "d" values for the Guinier film is four times better. Figure 2

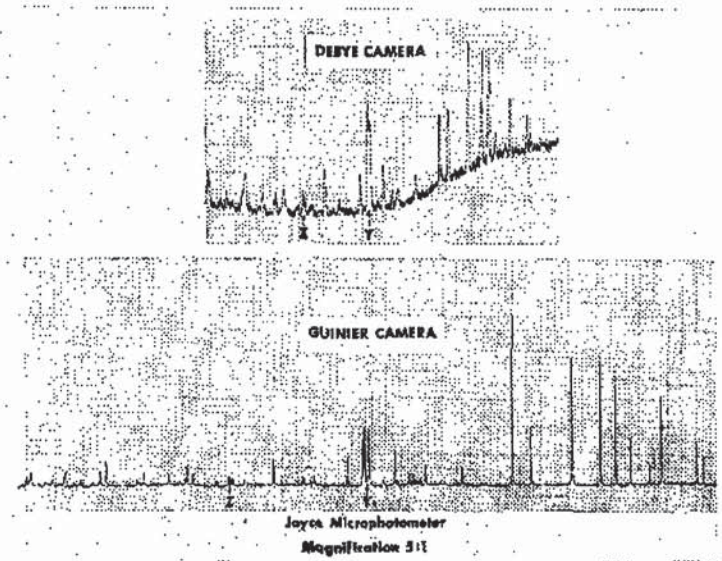

Figure 1. Microphotometer traces of powder patterns of $BaSO_4$. Debye film from Lawrence Radiation Laboratory, courtesy of D.K. Smith. Guinier film from University of Paris, courtesy of A. Guinier.

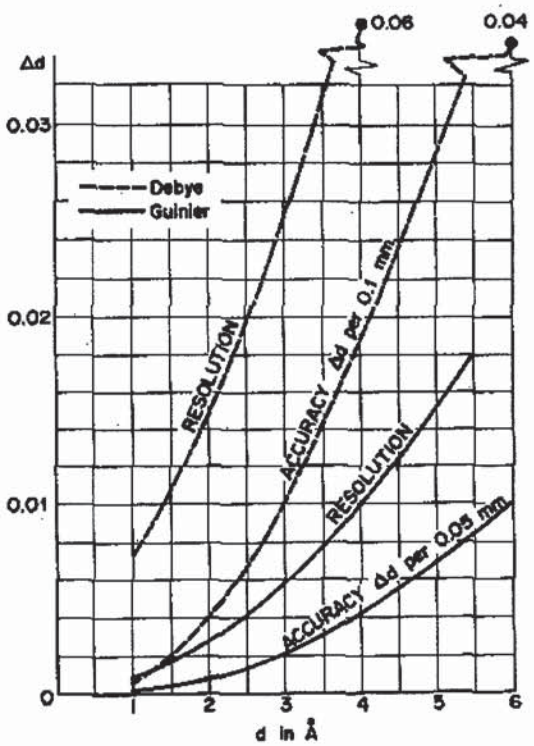

Figure 2. Graph of values of experimentally observed accuracy and resolution for cameras of 114.6 mm diameter.

shows this plot of $\pm\Delta d$ as a function of d for 114.6 mm diameter cameras. Of course to obtain this degree of accuracy of absolute d values, the film must be calibrated by use of an internal standard. For the particular case of the three powder mixtures it can be seen by examining the tables of data that the actual accuracy of measurement for the Guinier films was considerably better than given by the curve of Figure 2. In the range up to about 3.5 Å most all of the d values of the stronger lines agreed with the Bureau of Standards determinations to within $\pm$0.001 Å or less.

Resolution

The question of resolution also involves the sharpness of the lines and the background density and for practical purposes requires an experimentally determined answer. The curves drawn in Figure 2 represent the results of observations of films from a considerable number of different cameras. The Debye cameras were 57.3 mm, 114.6 mm and 140.0 mm in diameter. The Guinier camera diameters were 80.0 mm, 100.0 mm, 114.6 mm and 120.0 mm. Interestingly, while the 140.0 mm Debye did not make a noticeable improvement in the resolution of a 114.6 mm Debye, the 80.0 mm Guinier provided almost as good resolution as the 120.0 mm Guinier. Within the important and most commonly used range of d values for phase identification the resolution of the Guinier type camera is about five times greater than that of the Debye camera. This is illustrated in Figure 3 which compares Guinier and Debye patterns for the KNO_3 two lines at A, 3.78 and 3.73, and the three lines at B, 2.662, 2.647 and 2.632. The separations of 0.05 Å at A and 0.015 Å at B are unresolved in the Debye pattern but clearly resolved in the Guinier pattern.

Another illustration is given in Figure 4 which shows the Y and Z regions of Figure 1 but at a microphotometer magnification of 50 to 1. These close lines can be clearly seen by direct visual inspection of the original film. The four lines at Y, 2.118, 2.1151, 2.1048 and 2.1012 which are separated by Δd 0.0032 Å, 0.014 Å and 0.0036 Å respectively as seen in the Guinier pattern (these measurements are from Professor Andre Guinier's laboratory) are barely resolved into two lines in the Debye pattern. Likewise the three lines at Z, 1.7605, 1.7554, and 1.7509 which are separated by Δd 0.0051 Å and 0.0045 Å respectively are entirely unresolved in the Debye pattern. (None of the Debye patterns received showed better resolution than this pattern from the Lawrence Radiation Laboratory, courtesy of D.K. Smith.)

The curves of Figure 2 showing attainable resolutions of Debye and Guinier cameras have been generated from the above type of experimental observations of many films. It should be mentioned that the resolution of the lines at Y and Z in the $BaSO_4$ diffraction pattern is only possible if the $BaSO_4$ has been heated to above 800°C. However, with this qualification, these lines of $BaSO_4$ provide a quite practical and critical test of the excellence of adjustment of the diffraction camera or instrument. In Figure 5 is shown the resolution by step scanning with a diffractometer by M. Nichols at Sandia Laboratories, Livermore, California. The same resolution can also be observed with the diffractometer with a slow scan of about 1°2θ per minute. In Figure 6 is shown the resolution of these lines of $BaSO_4$ as demonstrated

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