

Identification of Crystalline Materials

Classification and Use of X-Ray Diffraction Patterns

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In the course of the past few years, X-ray and spectroscopic methods of analysis have found an increasing usefulness at the Dow Chemical Company. There are a large number of different types of problems on which information can be obtained by the variations of apparatus and technic which are possible in these two fields. It is not the purpose of this paper, however, to discuss these methods or applications in general, but to describe in some detail a scheme of classifying and using X-ray diffraction patterns which has been found very helpful in one particular application of X-rays — namely, that of identifying unknown substances by means of their Hull powder diffraction patterns.

substances, the job of taking the standard patterns, and more especially of finding an adequate system of indexing or classifying thousands of diffraction patterns, is considerable and in general has not been thought feasible⁶. It has been found in this laboratory that the problem of classification of the patterns presents no practical difficulties and that in so far as they can be obtained, they can be effectively used in the identification of unknowns. The real limitations to the field of applicability of the X-ray method are due to more fundamental factors, such as lack of sensitivity to small percentages of the minor constituent and to the small effects sometimes encountered in changes of solid solution concentration and lack of sensitivity because of the poor crystalline structure of some materials. A recent article by Waldo⁵ gives the results of a similar attempt at classification applied

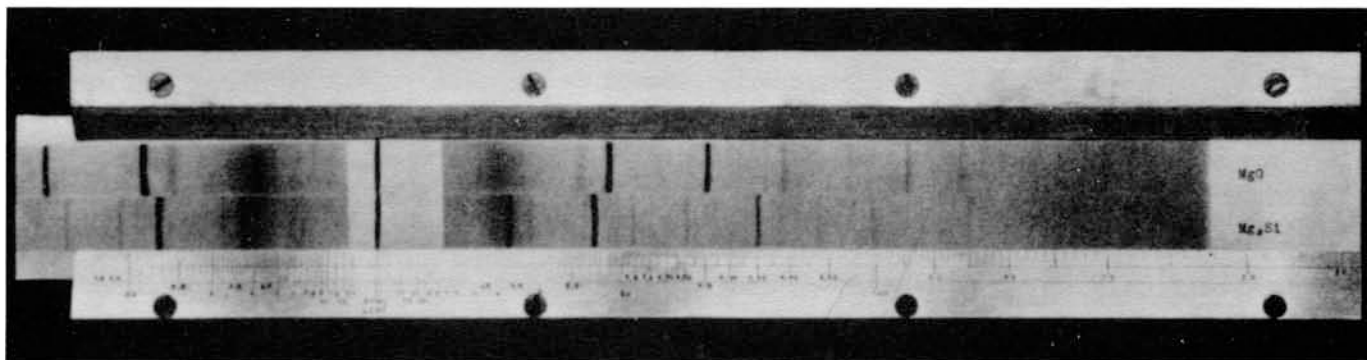


Figure 1. X-ray powder diffraction patterns in calibrated scale. MoK α radiation.

The inherent power of X-ray diffraction as a practical means of chemical analysis was pointed out a good many years ago^{2,4}. Having a different theoretical basis and depending upon an entirely different technic than other methods, it would be expected to supplement the information to be obtained from other methods and, at times, to be applicable where other methods are not suitable. It appears, however, that the use of this method has not increased at a rate commensurate with its unique and valuable features, and that it is used by relatively few academic and industrial laboratories.

Probably one of the main reasons for this is that X-ray diffraction is not a practical, economical method of analysis as long as it involves any time-consuming process such as the determination of crystal structure. For the purpose of analysis, however, there is no advantage in knowing the crystal structure, since any substance is just as uniquely characterized by its diffraction pattern. For practical usage, the X-ray diffraction method must be put upon an empirical basis, as has been done, for example, in spectroscopic analysis. There are available for the spectroscopist portfolios of the arc and spark spectra of the elements, and also convenient tables of wave lengths which serve to assist him in identifying the origin of the unknown lines in the spectra obtained.

Similarly, in the X-ray field, one of the things which will greatly facilitate the use of X-ray powder patterns in identifying unknowns is to have available a reference library of standard patterns of known substances. However, because there are thousands of common chemical

to about 50 copper-ore minerals. A comparison of the classifications will be made in connection with the detailed description of the present method.

Identification of complete unknowns does not form the bulk of the work or the most important part of the application of X-ray diffraction patterns. However, as the stock of patterns obtained in the course of the authors' use of X-ray diffraction continued to enlarge, the advantage of having an index to them became apparent. The system of classification which was finally adopted has been in operation since June, 1934, and, though the number of patterns has greatly increased since that time, has proved to be fully adequate to handle them. The authors now have over 400 patterns, of which 1054 are individual inorganic chemical substances. These constitute a reference file which can be used in this field in much the same way that fingerprints are used to identify persons⁷. This is not a large stock, but it is large enough to permit one to form a judgment of the capacity and practicability of any particular system of classification. This system of classification permits a pattern to be identified in a few minutes, even though it is a composite of individual patterns, provided these individual patterns are present in the reference file.

Method of Classification

Choosing a method of classification is merely a matter of investigating how many measurements of the pattern are necessary to distinguish it from other patterns. Theoretically, no two different substances could have exactly the same pattern. The powder pattern of a substance is made up of

lines in certain positions and of certain intensities. The more of these parameters used, the more certain is the identification. One might choose to measure and record accurately and completely the positions and intensities of all the lines of the pattern, or to measure and record only enough data from the pattern to serve to locate it, and then check all details by comparing directly with the known file pattern (or a print of it). The first method would require a great deal of work in measuring the pattern and even then would be no improvement in accuracy over direct comparison by eye. The second method is practicable because, as investigation has shown, three easy measurements are sufficient to give the approximate location of the pattern in the file, and one can then visually check the entire pattern without ever having to make difficult measurements.

measurement. Actually, the divisions chosen are 5 to 10 times the error of measurement. Using molybdenum radiation and a specimen-film distance of 20 cm. (8 inches), the error of measurement increases in a smooth curve from $\pm 0.001 \text{ \AA.}$ at 1.0 \AA. , through $\pm 0.001 \text{ \AA.}$ at 3.5 \AA. to $\pm 0.06 \text{ \AA.}$ at 8.0 \AA. In order to secure this accuracy, all cassettes used are calibrated against the sodium chloride and copper patterns.

It is not necessary to use a densitometer to measure densities of lines. If two lines appear to be so closely the same density that it is hard to decide by eye which is the more dense, the rule is to list the one of the greater \AA. spacing first. One thus has, as a characteristic of each pattern, three numbers in a certain sequence. The patterns are then listed, at the proper place, in an indexed book which is

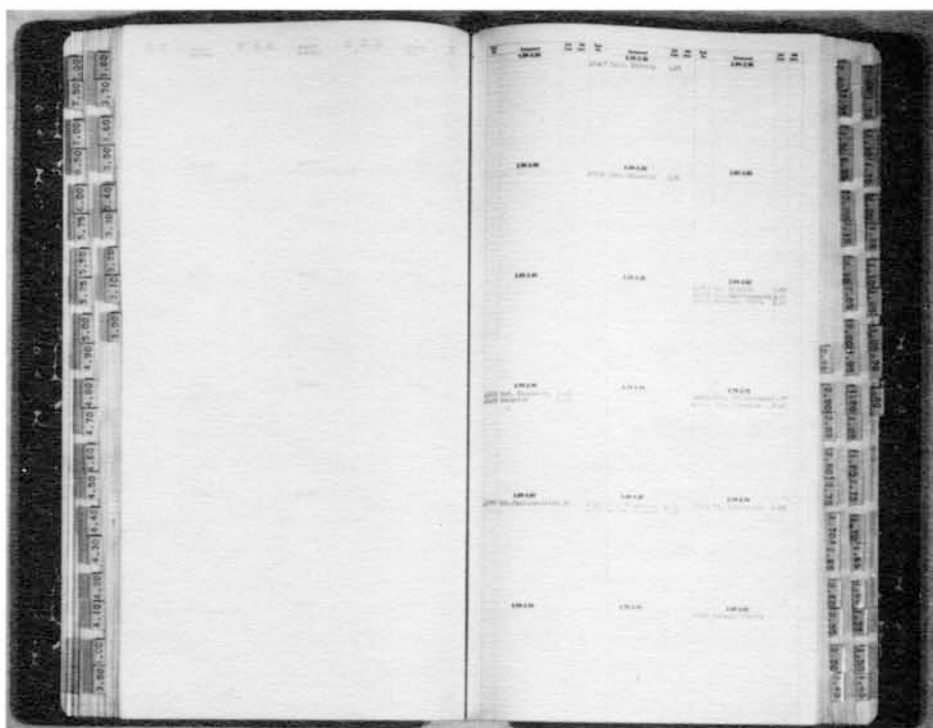


Figure 2. Typical page in classification book.

The powder patterns are produced using molybdenum radiation and the General Electric diffraction unit. Figure 1 shows two such patterns placed in the calibrated scale which gives, in Angstrom units, the interplanar distances of the crystal planes giving rise to the diffracted lines. The \AA. positions of the three strongest lines of the diffracted pattern are read off in the order of decreasing intensity. However, for purposes of classification, the lines are listed only according to the particular divisions of the scale in which they fall. The sizes of the divisions into which the classification book is arbitrarily divided are: 0.1 \AA. divisions below 1.0 \AA. , 0.05 \AA. divisions from 1.0 to 3.0 \AA. , 0.1 \AA. divisions from 3.0 to 5.0 \AA. , 0.25 \AA. divisions from 5.0 to 6.0 \AA. , and 0.5 \AA. divisions from 6.0 to 8.0 \AA. The size of these divisions is determined by the consideration that they can be no smaller than is consistent with the accuracy of measurement of the position of the lines, and that they should be no more numerous than is necessary to handle conveniently all the patterns without conflict, thus minimizing the result of errors of

divided and subdivided into the arbitrarily chosen regions as given above. The first number determines the group, the second number the subgroup, and the third number the location within the subgroup. Figure 2 shows a typical page within the book.

After listing 1054 patterns of common inorganic chemicals in the classification book in this way, it is found that 1 subgroup contains 7 patterns, 5 subgroups contain 5 patterns each, 9 contain 4 patterns each, 38 contain 3 patterns each, 150 contain 2 patterns each, 582 subgroups contain only a single pattern each, and 3836 subgroups are unoccupied. (Because two patterns fall in the same subgroup does not mean that they are identical with respect to their first two lines, since their positions within the divisions may be different, and their relative intensities probably will be different.) Thus among these 1054 patterns it is not necessary to measure more than the two strongest lines in order to limit the possibilities to a few patterns. Looking now at the coincidences of third lines within a subgroup, there

are 11 subgroups in which 2 patterns have the same position (within twice the \pm error of measurement) of the third line, and 4 subgroups in which 3 patterns have the same third line. In seven of these cases, a measurement of the fourth line serves to distinguish the patterns (a column is included in the book for recording the fourth line). However, in practice, after a pattern has been located in the book, it is taken out of the file and compared directly in all its details. It is thus easy to see at a glance differences which otherwise could be established only by careful measurements. When this is done, for the conflicts still remaining, there are only three cases left in which the patterns are not immediately distinguishable from each other, and in these cases, if there were nothing easier to do, a more accurate determination of planar spacings by a different X-ray technic would be sufficient. Probably, however, some other information would be available to assist in separating these very occasional conflicts.

Taking into account the number of subgroups and the distributions of the lines as they occur in the type of pattern with which the authors have worked, they estimate that the classification book in its present form, making use of three lines as described, would easily handle many thousands of patterns. If, for instance, there were 20,000 patterns in the file, there would be a total of only several hundred cases in which one would have to compare his unknown with two patterns from the file, and not more than about twenty cases in which one would have to compare with more than three patterns.

Identification of Mixtures

The problem is complicated somewhat and the process of identification lengthened, if the unknown is a mixture of substances. However, any component of a mixture of substances can be identified with just as much certainty (in so far as enough lines are visible) as if it were an isolated material, provided its pattern is contained in the reference file. The procedure of identifying the unknown is the same whether the unknown pattern is a superposition of separate patterns or not.

To meet the possibility that the unknown is a mixture of patterns, it is necessary to read more than three lines, since the three strongest lines may include certain lines of each constituent. One begins with the strongest line, turns to the subgroup determined by the second strongest line, and sees whether any of the lines of the unknown check lines in this subgroup. (This can be done at a glance, since, of the subgroups which are occupied, the largest contains only seven patterns and most of them contain only one.) If the unknown is a single pattern, the third strongest line will check, and the pattern will have been located. If the second strongest line of the unknown pattern should happen to be the strongest line of a second component, the pattern would not have been found and one proceeds by using the third strongest line of the unknown pattern to determine the subgroup, and so on. When a match is found, the lines of the unknown coinciding with the standard are noted, as are also any intensity variations which would indicate superpositions of lines. The remaining unidentified lines of the unknown are then treated in the standard manner.

If the constituent corresponding to the strongest line of

the unknown pattern is not contained in the file, one must proceed using the second strongest line to determine the main group, etc. One cannot fail to find any or all components of the mixture which exist in the reference file. The authors have numerous examples in which mixtures of three components were resolved and one case in which four components were present in an unknown and all identified. If the pattern cannot be found in the file, even in this case one has obtained considerable negative information about the unknown.

Other Classification Systems

It has been suggested⁶ that, in a limited field, 100 or more patterns might be handled by listing, in the order of planar spacings, all the lines in all the patterns. This is closely analogous to the system commonly used in spectroscopy, in which the wave lengths of all lines are listed in order. This system would be practical for X-ray diffraction if planar spacings were accurately measured to four or five significant figures, but the author's experience indicates that it is not practical when one measures to only 0.01 or 0.1 Å. When technic is developed to permit more precise measurements, it will be possible to multiply further the capacity of the classification book by choosing smaller sized divisions.

Waldo⁵ has described a system of classification listing the exact positions of the lines in the order of their relative intensity, and this does not differ fundamentally from the system here under discussion. It would appear that there are practical advantages in the use of finite divisions and definite subgroups, in that addition of patterns to the file requires no rearranging of the patterns already on record, and, in looking up unknowns, the only possible location is definitely defined except when the line falls on the boundary between divisions, in which case there are two possible locations. Also, as has been emphasized, the present system does not use the book for the final identification of the unknown but simply to locate the pattern in the file. This direct comparison is more accurate than measurements of positions and is particularly important for mixtures of patterns in which occasional superpositions of lines make careful comparisons of intensities desirable.

Weaknesses of X-Ray Diffraction Method

There are some definite limitations to the field of applicability of the X-ray method of analysis, but the important question is the range of usefulness left when these things are taken into account. One should have constantly in mind when using X-ray diffraction that it is valuable for what it does show, not for what it does not show. When a diffraction pattern is obtained, it is decisive evidence of the presence of the particular substance which gives rise to this pattern, but diffraction lines may be so weak that they are not detected and one must therefore be wary of drawing conclusions. There is always the possibility of the presence of amorphous phases. This is a definite weakness of the method and leaves one in the same position as the fingerprint expert who cannot find any fingerprints. The extent of this limitation of the X-ray method applied to inorganic solids is indicated by the fact that of 1000 substances taken at random from the chemical stockroom shelves, only 5 per cent are amorphous while 95 per cent are crystalline and

have a characteristic pattern.

The sensitivity of detection for the lesser constituent of a mixture is relatively low and will vary greatly from one substance to another, but in general will lie somewhere between concentrations of 0.1 and 10 per cent. For the determination of this figure, in any particular case, it is necessary to make up standard mixtures. Standard mixtures for comparison will also enable one to make semi-quantitative analyses throughout the whole range from 0 to 100 per cent. A development of this technic to the quantitative stage has been reported recently¹.

Aids to Experimental Technic

Discussions of the theory and technic of X-ray diffraction can be found in many places (the most recent comprehensive book on the subject is by Davey,³) and are outside the scope of this article. However, a few items of practical experience may be of interest.

To make full use of the X-ray, one should have the necessary equipment to adapt the type of camera and the source of X-rays to the particular requirements of the problem at hand. For general chemical identification, the authors find it most convenient to use molybdenum radi-

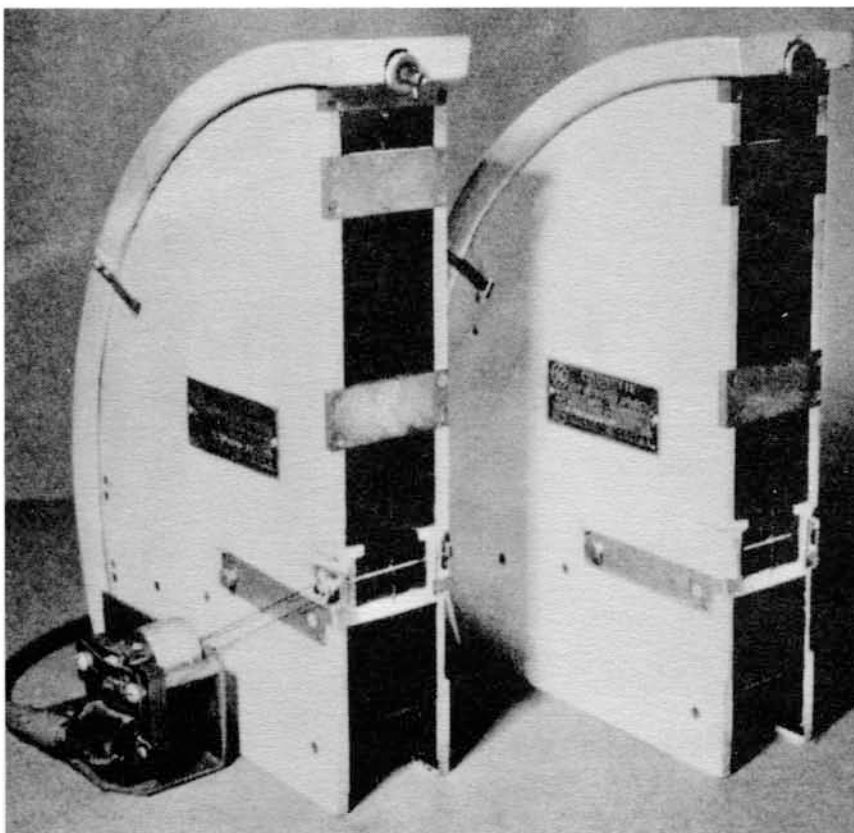


Figure 3. Mechanical aid to ensure uniform patterns.

The type of pattern best adapted for general chemical identification — i.e., one with as many strong lines as possible — is not suited for the study of solid solutions in which it is necessary to measure lattice constants to a high degree of accuracy. Therefore, unless one has other information about the unknown, he may overlook the possibility that the pattern of an unknown really represents a member of a solid solution series. The authors find that the combination of spectroscopy and X-ray diffraction is very fortunate, since they supplement each other's deficiencies by giving very different types of information about the same substance. In the arc or spark, the material is broken up into its elements so that they show regardless of the state in which they were present, while the X-ray without changing the material records the existing chemical and physical state. Thus for a complete unknown, the authors always supplement the X-ray diffraction with spectroscopic analysis or other information to check the possible presence of amorphous components or isomorphous systems.

The greater generation of the molybdenum radiation, as compared with copper or iron or other longer wave lengths, makes specimen mountings easier. The 16-hour exposures necessary with molybdenum radiation are not really a disadvantage, since the diffraction cameras can be loaded with as many as 24 specimens at night and the films are ready to develop in the morning. The batch processes of preparing specimens, developing films, etc., result in economy of time.

Figure 3 shows a simple mechanical attachment, readily installed on commercial cassettes, which ensures uniform patterns. At one end, the usual capillary tube passes through, and is fastened by wax to a metal pulley. The other end passes through a glass tube serving as a bearing. So many substances require rotation because of large crystals that the practical procedure is to rotate every specimen and avoid the necessity of repeating any of them.

Figure 4 shows a drier and loading box which is useful when handling substances which take up water. It is, for

most materials, more convenient than the usual technic of loading under a protective liquid.

Summary and Conclusions

This investigation shows that, with the aid of a classification system as herein described, it is entirely practical to make effective use of a large library of standard X-ray diffraction patterns for the identification of unknowns, even when the unknown is a mixture of materials. This makes possible a more complete utilization of the unique features of the X-ray diffraction method of analysis. The unique features which have been found of practical importance in this laboratory are (1) the substances present show in their true state of chemical combination, especially useful for the study

of reaction mixtures; (2) the analysis is very certain, even though only minute amounts of material are available; (3) substances are studied directly in their "as received" state and are not destroyed; (4) different crystalline phases, states of hydration, and physical state are observable, and (5) the process of preparing the specimen and obtaining the X-ray pattern is very simple. The fundamental limitations of the method lie in lack of sensitivity to small percentages of the minor constituents and in the noncrystalline nature of many substances.

While the present article is based mainly on the results obtained with inorganic substances, it is planned in the near future to investigate in a similar manner other fields, such as organic solids, intermetallic compounds, etc.

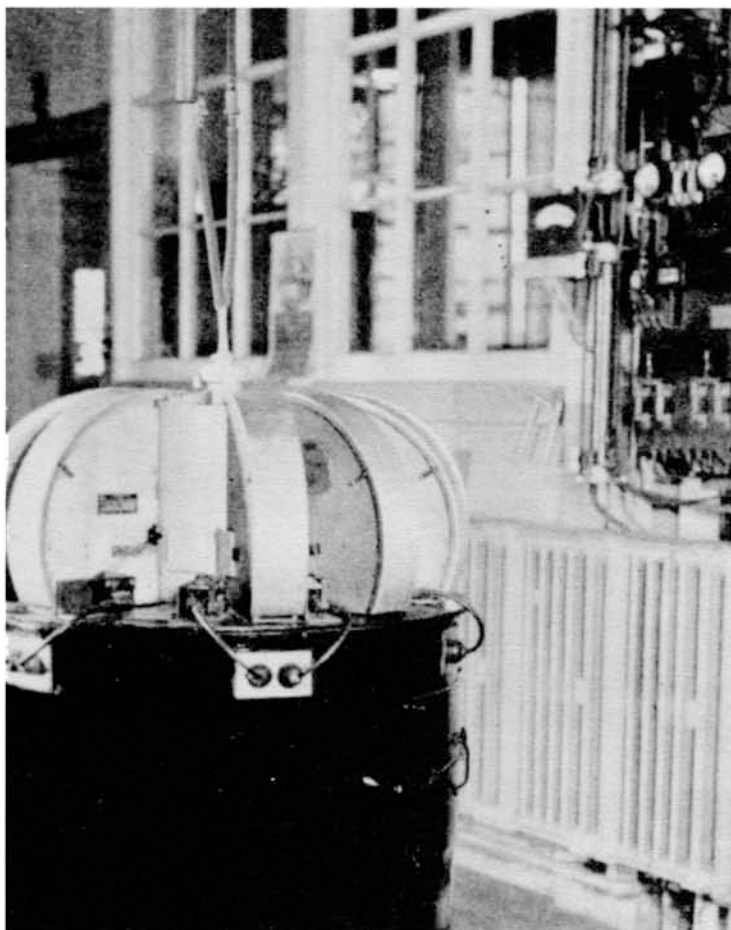


Figure 4. Use of loading box for substances which take up water in air.

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