

The "Fonds suisse" is, however, available in cases where insurance is impossible, and this now amounts approximately to two million francs. In New Zealand some earthquake insurance is undertaken by private companies, but the liability of these companies for payments under the Workers' Compensation for Accidents Act has been limited by the Government to £50,000 in a single earthquake or a series of earthquakes lasting seven days. In Great

Britain certain companies undertake such insurance on request, but information is unavailable except from the companies concerned, there being apparently no clearing house for such information. In the United States, earthquake insurance is underwritten mostly by the mutual fire insurance companies, which state that the premiums need not be high if due attention is paid to earthquake-proof design in the buildings concerned.

CRYSTALLO-CHEMICAL ANALYSIS

THE BARKER INDEX AT OXFORD

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EVERY chemist is familiar with the well-developed crystals bounded by plane faces which are formed by chemical substances. That the angles between these faces are characteristic of the substance and can be measured accurately by the reflecting goniometer is also common knowledge.

Clearly it would be of advantage to the chemist were he able to make practical use of these characteristic angles for purposes of identification, as an alternative to the ordinary method of analysis. Only a very small amount of material would be required, for a crystal of the size of one cubic millimetre, or even less, can be accurately measured. Moreover, when the measurement is completed, the crystal remains intact. If an index were made which included all measured substances, arranged in the numerical order of their measured angles, any substance could be identified by measuring a crystal of it and seeking in the index the angular values obtained.

Why has the chemist hitherto been unable to make use of this method of identification?

The difficulty arises from the multiplicity of angles which can be measured on any given crystal and from the lack of guidance in the choice of the angles which are to be used as the basis of the index. It is clear that what is wanted is a set of rules which will ensure that two independent workers who have measured crystals of the same substance will choose, as characteristic of that substance, the same set of angles, by which it can be classified.

The number of chemical substances that have been measured considerably exceeds eight thousand, and the measurements of some seven thousand of these have been collected in the five large volumes of Groth's "Chemische Krystallographie", where they are arranged according to *chemical composition*. During the past thirty years, crystallographers have attempted to put this valuable material into such a form that it might be rapidly and successfully used in the identification of chemical substances. First among those to make such an attempt was Fedorov, the great Russian crystallographer. He devised a method of classification based on his theory of crystal structure and, with the help of his pupils, he produced his great index, "Das Krystallreich", which was published in 1920. It contained a list of all the crystals then measured, and by means of this index any of the substances could be identified by the measurement of its angles. The method employed in this remarkable work was, however, complicated, and the calculations required were lengthy and laborious.

The late Dr. T. V. Barker, of Oxford, who was Fedorov's pupil and enthusiastic collaborator, had hoped to make this method of practical use, but he gradually came to the conclusion that it was impossible to do so. After many years he devised a simpler method based, not as Fedorov's was, upon theories of crystal structure, but purely on geometrical form. His book "Systematic Crystallography" (Thomas Murby, London, 1930) describes a set of simple rules based on what he termed the "principle of simplest indices" (*op. cit.*, p. 2), which he proposed to make the foundation for a practical index of crystals. In this index, under each crystal system, a certain angle, chosen by these rules for each substance as the main classification angle, was to be incorporated in order of increasing magnitude. The rules ensured that no ambiguity could arise in the choice of the classification angles. Owing to pressure of other work, Dr. Barker published this short treatise "Systematic Crystallography" instead of a much larger and more ambitious work, the uncompleted manuscript of which is in the University Museum at Oxford. He hoped to begin work on the index in May 1931, but in April of the same year he was taken ill and died.

The possibility of compiling the Barker Index after the untimely death of its originator, and without his direction, was immediately discussed at Oxford by a number of crystallographers who were interested, and they decided to try out the method independently. At the end of a year, they unanimously concluded that the method was simple and workable. It was decided to proceed with the preparation of the Index and, with the kind permission of Prof. H. L. Bowman, to make its headquarters in the Mineralogical Department of the University Museum at Oxford.

In the initial stages of the work, certain unforeseen difficulties arose the solution of which involved time and labour. The first of these was that, in order to cover certain cases, it was found necessary to make minor modifications and additions in the rules drafted by Dr. Barker. The second difficulty was that considerable delay has been, and will continue to be, caused by the misprints and errors of computation found in the original descriptions. These have in all cases to be cleared up before the classification angles can be found. In order to guard against similar errors in the Barker Index itself, every calculation is being made independently by two workers and checked by a third before the results are typed on a card and filed in a card index.

When some years had been spent in the compilation of the Index, it was felt that it was sufficiently far advanced to offer material for a searching test of its usefulness in the actual identification of compounds. Such tests had been carried out successfully by Dr. Barker and were described in "Systematic Crystallography" (pp. 24-27), but his great familiarity with the work and the fact that the material available at that time was limited led us to believe that another trial of the method would be of practical value.

It was decided to carry this out in two of the less simple crystal systems, the orthorhombic and monoclinic, and a list of some 1,230 substances which were ready for the Index was sent to Prof. G. M. Bennett, professor of chemistry, King's College, London, who had kindly offered to collaborate in such a test. From this list Prof. Bennett selected sixteen substances which he sent, numbered, but unnamed, to us at Oxford. Fifteen of the sixteen were successfully identified. The measurement of the remaining one was not possible as the faces were not sufficiently good to give even fair reflections on the goniometer. The list of substances is given below, and it will be seen that many of them have a complicated chemical composition, and would be difficult to identify by other methods, especially if, as was the case, only one or two small crystals were available for examination. The time taken to identify each compound varied from thirty minutes for the easier crystals to four hours for the most difficult.

LIST OF COMPOUNDS IDENTIFIED BY MEANS OF THE BARKER INDEX.

1. Ethyl-2:4-dinitrophenyl-aniline. (Groth, 5, 53.)
2. Methylanilide of benzene sulphonic acid. (Groth, 5, 78.)
3. Benzene-azo- β -naphthyl benzoate. (Groth, 5, 390.)
4. Tribenzylamine. (Groth, 5, 323.)
5. Phenyl benzoate. (Groth, 5, 134.)
6. 1-Phenyl-3-methyl-4-benzylidene-pyrazolone. (Groth, 5, 587.)
7. Methylanilide of p. toluene sulphonic acid. (Groth, 5, 84.)
8. Sodium nitroprusside (dihydrate). (Groth, 1, 432.)
9. Potassium sulphate. (Groth, 2, 337.)
10. Sulphur. (Groth, 1, 26.)
11. (unmeasurable).
12. Ammonium sulphate. (Groth, 2, 344.)
13. Eugenol benzoate. (Groth, 5, 139.)
14. Potassium nitrate. (Groth, 2, 74.)
15. Potassium dihydrogen orthophosphate. (Groth, 2, 795.)
16. Topaz. (Groth, 2, 262.)

The procedure adopted in these identifications, which can only be outlined here, was as follows: The crystal (or in some cases two or three crystals) was measured on a two-circle reflecting goniometer. A gnomonic or stereographic projection was made from these measurements and the crystal system identified so far as possible from the projection and checked (if necessary) by the optics. The selection of the classification angles was made according to the Barker rules. The Index was then consulted under the appropriate crystal system for the main classification angle. Generally, a number of angles within the limits of the error of measurement offered themselves. The remaining classification angles were then compared and, when a set which agreed as a whole with those measured was found, the identification was established. When the classification angles indicated a member of an isomorphous group, a further test of a simple nature had to be made. It was recommended by Dr. Barker that such a test should be made in all cases as a check on the identification. The test may be a simple chemical one, the determination of the density, the observation of the

colour or cleavage, or the examination of some of the optical properties.

No doubt the question will be asked, what happens if the classification angles are not to be found in the Index? This may happen owing to the fact that the faces of a crystal may vary in different circumstances of crystallization. New faces may appear and old faces may be suppressed. Certain new combinations of faces may give rise to classification angles not to be found in the Index. Actual cases of this sort occurred among the compounds given above and were successfully dealt with as follows: By the graphical insertion into the projection of one or two faces not observed, or the suppression of one or two of the faces present, a new set of classification angles was obtained. These were measured graphically in order to save time and then searched for in the Index, with successful results. Although the difficulty arising from the variability of faces, or of combinations of faces, has been brought forward as a disadvantage of the Barker method (see A. K. Boldyrew and W. W. Doliwo-Dobrowolsky, "Ueber die Bestimmungstabellen für Kristalle", *Z. Kristall.*, (A) 93, 321-367; 1936) in actual practice it has not been found to be serious. Nor do the many hundreds of cases of different combinations of faces already recorded give rise to a great number of additional entries in the Index. In working through some 1,800 monoclinic and orthorhombic substances, we have found that about 2,300 entries are required. Donnay and Mélon (see Tables for Tetragonal Substances, Johns Hopkins University, Studies in Geology, No. 11, p. 328; Oct. 1934) in their tables for the tetragonal system found that 456 substances require 582 entries.

A further example of the value of the Barker method may be mentioned. With the help of it, F. A. Bannister and M. H. Hey were able to identify some crystals found in oceanic bottom samples from the Weddell Sea and brought back by the Scotia Expedition (Discovery Reports, 13, 60-69, Cambridge, 1936). The crystals varied in size from 0.2 mm. \times 0.1 mm. to 0.3 mm. \times 0.15 mm., and several of these were successfully measured and the Barker classification angle determined. The tetragonal symmetry of the crystals was confirmed by their optics and by a Laue photograph. The authors identified the salt as hydrated calcium oxalate from a table of tetragonal substances compiled (independently of the tables by Donnay and Mélon) by Dr. Hey on Dr. Barker's method. Identification in the ordinary way, by means of chemical analysis, was in this case out of the question.

The above identifications give practical evidence of the usefulness of the Barker method, and encourage the belief that when once the Index is complete it will be of great service to chemist and crystallographer alike. Its compilation has now made considerable progress, but new collaborators would be welcomed as the work is necessarily slow. Practical help in the compilation of the Index has been given by Mrs. Barker, P. Terpstra, J. H. Haan, P. Stienstra, J. Mélon, J. D. H. Donnay, M. H. Hey, C. Judson and T. W. J. Taylor.

In conclusion, it may be pointed out that, in the descriptions of new substances to be made in the future, a minimum of calculation will be required if the Barker rules are applied, and the lengthy tables of angles frequently met with in crystallographic descriptions will be unnecessary.