The maxima giving the corrected sites appear with doubled strength relative to the non-centric case but the maxima at the sites of the correctly postulated atoms are more sensitive to errors in the structure than in the non-centric case, since the rate of fall off in the peak height with the number of erroneously placed atoms of equal weight is doubled.

An application of the function

A brief description of our experience with the function, $C(r)$ as defined in (6), when applied to the crystal structure analysis of dihydromalvalic acid, $C_{18}H_{34}O_2$, will illustrate some of its properties. The function was applied to the $(0kl)$ projection when a satisfactory trial model had not been obtained.

The data consisted of 40 axial reflections $(00l)$ whose signs were known from the $(h0l)$ projection (Craven & Jeffrey, 1960) and twenty each of the low order $01l$ and $02l$ terms. The agreement factor, R, was 0·61 excluding the axial reflections and there was no indication of convergence to a correct solution.

The initial trial model is shown in Fig. 1(*a*) where concentric circles represent oxygens and circles are the carbon positions. The corresponding electron density and $C(r)$ maps are shown in Figs. 1(*b*) and 1(*c*) respectively. The most obvious discrepancies between the model and $C(r)$ were at the center of the molecule, near the cyclopropyl ring, and at the terminal methyl group. Some minor changes in the chain direction and the terminal configuration improved R to 0·52. The model, $\varrho(r)$, and $C(r)$ maps are shown in Fig. 1(*d*), (*e*) and (*f*). The discrepancies again indicated errors at the ends of the molecule, and suggested a reversal of the model. This corresponded to a shift of z coordinates to $\frac{1}{4}-z$, with the carboxyl groups dimerized by hydrogen bonding across a symmetry center at $(\frac{1}{4}, \frac{1}{4})$ instead of the origin of the space group $A2/a$. The correct model is shown in Fig. 1(*g*). Successive Fourier refinement proceeded normally to give an agreement of about 0·20 and the electron density projection shown in Fig. 1(*h*) which contained 220 terms. The corresponding $C(r)$ map appears in Fig. 1(*i*).

A comparison of map (*h*) with the maps (*b*), (*c*), (*e*) and (*f*) shows quite clearly that the $C(r)$ functions gave a better indication of the true atomic positions which were not included in the model than did the electron density functions.

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Analysis of Three-Dimensional Patterson Maps Using Vector Verification

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A new path from the Patterson map to an electron density map has been investigated. The procedure is called vector verification and involves testing all points in x, y, z space. Harker vectors are generated for each point and their presence is sought in the Patterson map. If all vectors are present, the point may be an atomic position. In most cases, over 95% of the positions in x, y, z space are at once eliminated. It has been demonstrated that by using one known atomic position the remaining atomic positions could be determined. One method which may be used to determine the position of a 'known' atom involves the selection of a vector from the vector set, and the use of this vector in a verification procedure leading to the position of an atom in the fundamental set.

Introduction

Most crystal structures are solved by conversion of vector sets to the corresponding fundamental sets. This step is usually the most difficult and time-consuming in the structure determination of a compound, and is especially difficult when heavy atoms are absent. One of the most powerful techniques available is the superposition technique, but this method has the disadvantage of retaining too many incorrect peaks in the early stages. A detailed discussion of the analysis of the Patterson map may be found in the book on vector space by Buerger (1959).

Another path from the Patterson map to the electron density map is now under study in this laboratory. This method, called vector verification, offers certain advantages over ordinary superposition techniques. The first step usually eliminates over 95% of the possible atomic positions and requires no prior assumption as to an atomic position. The vector verification method works best for space groups having four or more equivalent positions; consequently, many structures may be conveniently studied. Another valuable feature of this method is the speed with which it may be run on a large computer. For example, the major part of the verification method requires less than five minutes on the Control Data Corporation 1604 computer.

Theory of vector verification

Before performing vector verification, a three-dimensional Patterson map having 60 to 80 intervals in each direction is stored in the memory of the computer. Each point of the map is read into the computer from magnetic tape and stored either as a one or a zero. A one is stored if the value of the Patterson function is greater than a threshold value, and a zero otherwise. The threshold value can be changed at will and is thus a parameter, the selection of which depends on the atomic numbers of the atoms in the molecule, the scaling constant used when preparing the Patterson maps, *etc.* For instance, if it is desired to store only peaks due to the interaction between heavy atoms, the limit is set at a relatively high value. The loss of the actual height of the peak above the limit makes little difference in the final results, since in the process of vector verification, it is only necessary to know if a peak occurs at a specific (u, v, w) in the vector set.

For an orthorhombic crystal in which there are four equivalent positions the program proceeds as described below. The vectors between an actual atomic position and each of the other three symmetry equivalent positions are three Harker vectors which must be present in the vector set map. Therefore, given any (x, y, z), it is possible to check the validity of this point by checking for the Harker peaks in the Patterson map. The program generates the three Harker vectors and then goes to the Patterson map in the computer and checks to see if the Harker peaks are present. Only if all the peaks are present is this point considered a possible atomic coordinate. In performing the vector verification, all points in electron density space are systematically tested to see if they can represent possible atomic coordinates. The grid scanned is exactly the same size as the grid of the Patterson map.

Experimental results of vector verification

The above procedure was tested with B_8Cl_8, the molecular structure of which has already been determined (Jacobson & Lipscomb, 1959). After checking each point in x, y, z space, it was found that over 97% of the possible positions were eliminated, the correct positions being present among the remaining 3%. Thus in this case, from a Patterson map $(80 \times 40 \times 80)$ grid points in (u, v, w) space, a map was obtained as shown in Fig. 1 with dimensions $(80 \times 40 \times 80)$. The distance between grid points in this map is 0·12 Å, and the x's represent possible atomic positions. Periods, which in the actual output are printed in the 'null' positions, have been eliminated for clarity.

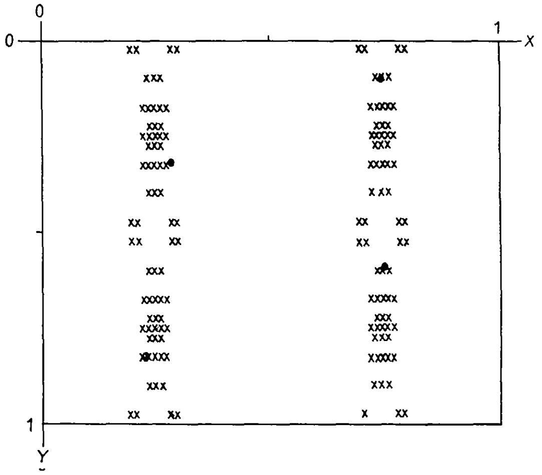

Fig. 1. A typical section which illustrates the results of Harker vector verification on B_8Cl_8. X's represent possible atomic positions in x, y, z space, and darkened circles represent actual atomic positions.

Thus by the above procedure, the Patterson map was converted to a map which more closely resembles an electron density map. It should be noted that so far no assumptions other than those concerning the threshold have been made. Two facts should be noted here. First, some points are accepted which do not represent atomic positions. However, these coincidence points are usually relatively small in number. Secondly, the points which are correct appear in sets related by symmetry elements, such as mirror planes. Usually only one point in a given set can be used in the final structure.

Extension of the original verification method

Maps at this stage are useful in the elimination of most possible atomic positions and in the selection of a suitable point for superpositions. The vector verification method can be extended, however, and can lead directly to the correct set of atomic positions. On the assumption that one correct atomic position can be selected, an extension of the above program was written. For each point in real space, the following series of vectors are checked: Harker vectors, the vector between the test point and the known atom, and the vectors between the test point and the symmetry-related atoms of the known atom. By doing this for B_8Cl_8, a map was obtained which had all the correct atomic positions plus very few coincident peaks. Thus in the unit cell for B_8Cl_8, there should be 32 chlorine peaks, and 40 peaks were found. Fig. 2 shows a typical section resulting from this program. The threshold value was set somewhat lower (140 instead of 165) than in the first vector verification procedure. By using a lower threshold, one obtains broader peaks.

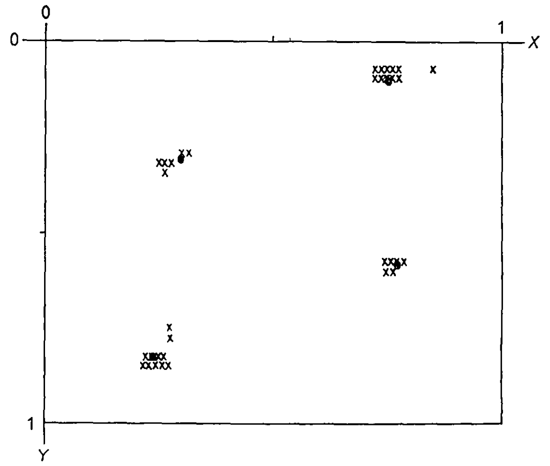

Fig. 2. A typical section (same section and compound as in Fig. 1) which illustrates the results of the vector verification procedure when one atomic position is known. X's represent possible atomic positions in x, y, z space, and darkened circles represent actual atomic positions.

Two methods are being developed to determine the position of the 'known' atom. First, upon inspection of the initial map produced as a result of checking the Harker vectors, one can often directly select one of these points as a correct peak. However, in groups of x's it is sometimes difficult to locate the correct atomic position, since this position may not coincide with the center of the group. A further and even more serious difficulty is that of distinguishing the coincidence points from the true ones. Since, however, the program requires less than five minutes on a large computer, one can try several different x's and thereby make a correct selection.

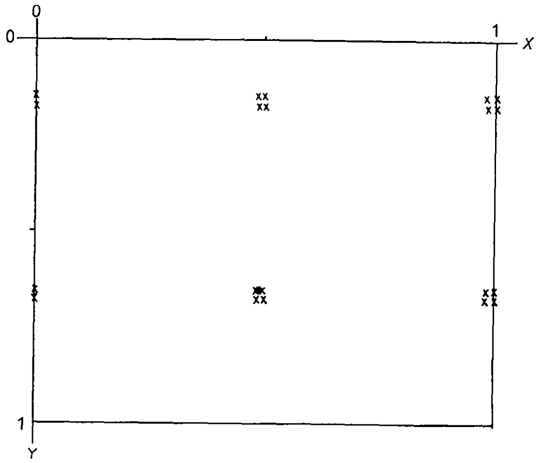

Fig. 3. A typical section showing results obtained when a known vector from the Patterson map is used to locate an atomic coordinate in x, y, z space. X's represent possible atomic coordinates, and the darkened circle represents the actual atomic position.

A second method which should prove more fruitful is also being investigated. Any vector in the Patterson map must connect two atoms. Thus, a necessary condition for an acceptable point (*i.e.*, one for which the Harker peaks check) to represent an atomic position is that some Patterson vector, starting from this point, lead to another acceptable point; and furthermore that the vectors from the initial point to the symmetry-related partners of the new point occur in the Patterson map. If all these conditions are met, then the initial (x, y, z) and the new point (x', y', z') are both in high probability true atomic positions. Fig. 3 shows the results of the procedure when applied to B_8Cl_8. In addition to the correct peak several coincidence peaks resulted.

In conclusion, we feel that vector verification should prove useful in structure determinations both as an independent method and in conjunction with related techniques.

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