

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Table 2.3.2.3. Position of Harker sections within a Patterson

Symmetry element	Form of $P(x, y, z)$
(a) Harker planes	
Axes parallel to the b axis:	
(i) 2, 3, $\bar{3}$, 4, $\bar{4}$, 6, $\bar{6}$	$P(x, 0, z)$
(ii) 2 ₁ , 4 ₂ , 6 ₃	$P(x, \frac{1}{2}, z)$
(iii) 3 ₁ , 3 ₂ , 6 ₂ , 6 ₄	$P(x, \frac{1}{3}, z)$
(iv) 4 ₁ , 4 ₃	$P(x, \frac{1}{4}, z)$
(v) 6 ₁ , 6 ₅	$P(x, \frac{1}{6}, z)$
(b) Harker lines	
Planes perpendicular to the b axis:	
(i) Reflection planes	$P(0, y, 0)$
(ii) Glide plane, glide = $\frac{1}{2}a$	$P(\frac{1}{2}, y, 0)$
(iii) Glide plane, glide = $\frac{1}{2}c$	$P(0, y, \frac{1}{2})$
(iv) Glide plane, glide = $\frac{1}{2}(a + c)$	$P(\frac{1}{2}, y, \frac{1}{2})$
(v) Glide plane, glide = $\frac{1}{4}(a + c)$	$P(\frac{1}{4}, y, \frac{1}{4})$
(vi) Glide plane, glide = $\frac{1}{4}(3a + c)$	$P(\frac{3}{4}, y, \frac{1}{4})$
(c) Special Harker planes	
Axes parallel to or containing body diagonal (111), valid for cubic space groups only:	
Equation of plane $lx + my + nz - p = 0$	
(i) 3	$l = m = n = \cos 54.73561^\circ = 0.57735$ $p = 0$
(ii) 3 ₁	$l = m = n = \cos 54.73561^\circ = 0.57735$ $p = \sqrt{3}/3$
Rhombohedral threefold axes produce analogous Harker planes whose description will depend on the interaxial angle.	

quality of the data. A useful rule of thumb is that the ratio

$$r = \frac{\sum_{\text{heavy}} Z^2}{\sum_{\text{light}} Z^2}$$

should be near unity if the heavy atom is to provide useful starting phase information (Z is the atomic number of an atom). The condition that $r > 1$ normally guarantees interpretability of the Patterson function in terms of the heavy-atom positions. This 'rule', arising from the work of Luzzati (1953), Woolfson (1956), Sim (1961) and others, is not inviolable; many ambitious determinations have been accomplished *via* the heavy-atom method for which r was well below 1.0. An outstanding example is vitamin B₁₂ with formula C₆₂H₈₈CoO₁₄P, which gave an $r = 0.14$ for the cobalt atom alone (Hodgkin *et al.*, 1957). One factor contributing to the success of such a determination is that the relative scattering power of Co is enhanced for higher scattering angles. Thus, the ratio, r , provides a conservative estimate. If the value of r is well above 1.0, the initial easier interpretation of the Patterson will come at the expense of poorly defined parameters of the lighter atoms.

A general strategy for determining heavy atoms from the Patterson usually involves the following steps.

- (1) List the number and type of atoms in the cell.
- (2) Construct the interaction matrix for the heaviest atoms to predict the positions and weights of the largest Patterson vectors. Group recurrent vectors and notice vectors with special properties, such as Harker vectors.

(3) Compute the Patterson using any desired modifications. Placing the map on an absolute scale [$P(000) = \sum Z^2$] is convenient but not necessary.

(4) Examine Harker sections and derive trial atom coordinates from vector positions.

(5) Check the trial coordinates using other vectors in the predicted set. Correlate enantiomorphic choice and origin choice for independent sites.

(6) Include the next-heaviest atoms in the interpretation if possible. In particular, use the cross-vectors with the heaviest atoms.

(7) Use the best heavy-atom model to initiate phasing.

Detailed and instructive examples of using Pattersons to find heavy-atom positions are found in almost every textbook on crystal structure analysis [see, for example, Buerger (1959), Lipson & Cochran (1966) and Stout & Jensen (1968)].

The determination of the crystal structure of cholesteryl iodide by Carlisle & Crowfoot (1945) provides an example of using the Patterson function to locate heavy atoms. There were two molecules, each of formula C₂₇H₄₅I, in the $P2_1$ unit cell. The ratio $r = 2.8$ is clearly well over the optimal value of unity. The $P(x, z)$ Patterson projection showed one dominant peak at $\langle 0.434, 0.084 \rangle$ in the asymmetric unit. The equivalent positions for $P2_1$ require that an iodine atom at x_1, y_1, z_1 generates another at $-x_1, \frac{1}{2} + y_1, z_1$ and thus produces a Patterson peak at $\langle 2x_1, \frac{1}{2}, 2z_1 \rangle$. The iodine position was therefore determined as 0.217, 0.042. The y coordinate of the iodine is arbitrary for $P2_1$ yet the value of $y_1 = 0.25$ is convenient, since an inversion centre in the two-atom iodine structure is then exactly at the origin, making all calculated phases 0 or π . Although the presence of this extra symmetry caused some initial difficulties in the interpretation of the steroid backbone, Carlisle and Crowfoot successfully separated the enantiomorphic images. Owing to the presence of the perhaps *too heavy* iodine atom, however, the structure of the carbon skeleton could not be defined very precisely. Nevertheless, all critical stereochemical details were adequately illuminated by this determination. In the cholesteryl iodide example, a number of different yet equivalent origins could have been selected. Alternative origin choices include all combinations of $x \pm \frac{1}{2}$ and $z \pm \frac{1}{2}$.

A further example of using the Patterson to find heavy atoms will be provided in Section 2.3.5.2 on solving for heavy atoms in the presence of noncrystallographic symmetry.

2.3.2.4. Superposition methods. Image detection

As early as 1939, Wrinch (1939) showed that it was possible, in principle, to recover a fundamental set of points from the vector map of that set. Unlike the Harker–Buerger implication theory (Buerger, 1946), the method that Wrinch suggested was capable of using all the vectors in a three-dimensional set, not those restricted to special lines or sections. Wrinch's ideas were developed for vector sets of points, however, and could not be directly applied to real, heavily overlapped Pattersons of a complex structure. These ideas seem to have lain dormant until the early 1950s when a number of independent investigators developed superposition methods (Bevers & Robertson, 1950; Clastre & Gay, 1950; Garrido, 1950a; Buerger, 1950a).

A Patterson can be considered as a sum of images of a molecule as seen, in turn, for each atom placed on the origin (Fig. 2.3.2.3). Thus, the deconvolution of a Patterson could proceed by superimposing each image of the molecule obtained onto the others by translating the Patterson origin to each imaging atom. For instance, let us take a molecule consisting of four atoms $ABCD$ arranged in the form of a quadrilateral (Fig. 2.3.2.3). Then the Patterson consists of the images of four identical quadrilaterals with atoms A, B, C and D placed on the origin in turn. The Pattersons can then be