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**On the relative scaling of X-ray photographs.\*** By WALTER C. HAMILTON, *Chemistry Department, Brookhaven National Laboratory, Upton, New York, U.S.A.*, JOHN S. ROLLETT, *Oxford University Computing Laboratory, Oxford, England*, and ROBERT A. SPARKS, *Statistical and Computing Center, University of Hawaii, Honolulu, Hawaii, U.S.A.*

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The relative scaling of X-ray intensities from intersecting reciprocal lattice photographs has been discussed by Kraut (1958), Dickerson (1959), and Rollett & Sparks (1960). We present here evidence that each of these methods has limitations. We also present a new formulation which has none of the inherent difficulties of the other methods.

The method of Kraut (1958) has been criticized by Dickerson (1959) because it demands that each possible pair of photographs have at least one reflection in common; this is conveniently arranged when the photographs are all zero-level precession photographs, but is more generally not the case.

The method of Dickerson (1959) is applicable to general reciprocal lattice nets. This method requires holding one scale factor constant and solving a system of linear equations for the others. The weighting of observations in this method is somewhat awkward because of the fact that the coefficients entering into the linear equations to be solved are obtained from sums of intensities in the individual layers. More serious is the fact, which will be illustrated below, that different results are obtained depending on which scale factor is held constant.

The least-squares method of Rollett & Sparks (1960) uses one observational equation for each measurement and hence the weighting is easily handled; more than two intersecting sets of photographs can be treated; and there is no ambiguity involved concerning which scale factor should be held constant. This ambiguity was resolved by imposing the condition that the sum of the squares of the scale factors be held constant. This condition leads to a simple eigenvector problem. Unfortunately, this condition is no more justified than fixing an arbitrary scale factor and, as will be shown below, it can lead to some very peculiar results. Another difficulty is that the weights are dependent on the scale factors. If the least-squares equations are modified to incorporate this dependence, the problem is no longer a simple eigenvector one.

The following is a description of a method which has none of the difficulties mentioned above. Assume that the observational equations are:

$$\varphi_{hi} = \sqrt{W_{hi}(F_{hi}^2 - G_{l(i)}F_h^2)} \quad (1)$$

where  $F_{hi}^2$  is the  $i$ th observation of the independent reflection  $h$ ,  $l(i)$  is the film number for the  $i$ th sequential observation of reflection  $h$ ,  $G_{l(i)}$  is a scale factor for the

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† Instead of (1) one could use observational equations of the form

$$\varphi_{hi} = \sqrt{V_{hi}(K_{l(i)}F_{hi}^2 - F_h^2)}$$

where  $\sqrt{V_{hi}}$  is the weight for  $K_{l(i)}F_{hi}^2$  (*i.e.*  $\sqrt{V_{hi}} = \sqrt{W_{hi}/K_{l(i)}}$ ) and changes in  $K_{l(i)}$  are calculated at each iteration. It can be shown that the final solution will be identical with the solution obtained from the procedure described here.

$l$ th film, and  $\sqrt{W_{hi}}$  is the weight for the  $i$ th observation and is proportional to the reciprocal of the estimated standard deviation for this observation.† We wish to minimize

$$\psi = \sum_h \left( \sum_{i=1}^{N_h} \varphi_{hi}^2 \right)$$

where  $N_h$  is the number of observations of the independent reflection  $h$ .

$F_h^2$ , the best least-squares value for reflection  $h$ , is found from

$$\frac{\partial \psi}{\partial F_h^2} = 0.$$

Thus,

$$F_h^2 = \sum_{i=1}^{N_h} (W_{hi}G_{l(i)}F_{hi}^2) / \sum_{i=1}^{N_h} (W_{hi}G_{l(i)}^2).$$

Because (1) is not linear in the  $G_{l(i)}$  we adopt the usual iterative non-linear least-squares procedure. For each iteration we approximate  $\varphi_{hi}$  by

$$\varphi_{hi} \simeq \sqrt{W_{hi}(F_{hi}^2 - G_{l(i)}F_h^2)} + \sum_{k=1}^{N_h} (\partial \varphi_{hi} / \partial G_{l(k)}) \Delta G_{l(k)}.$$

We start with approximate values for  $G_{l(i)}$ , evaluate the partial derivatives with these values, and solve the resulting linear equations for the  $\Delta G_{l(i)}$  with the usual least-squares method. Because the  $\Delta G_{l(i)}$  are not independent, one of them is arbitrarily set equal to zero. The  $G_{l(i)}$  are corrected by the  $\Delta G_{l(i)}$  and the process repeated until all the  $\Delta G_{l(i)}$  are less than a given  $\epsilon$ . The solution is invariant (apart from a normalization factor) as to which  $\Delta G_{l(i)}$  is made zero. In order to prevent any of the  $G_{l(i)}$  from becoming negative, it has been found necessary to add the following restriction:

Set

$$\Delta G_{l(i)} = -0.7G_{l(i)}$$

if

$$\Delta G_{l(i)} \leq -0.7G_{l(i)}.$$

This method has been programmed in Autocode for the Mercury computer and in FORTRAN IV for the IBM 7040. For the test problems tried the convergence has been fast (6 iterations for a 14 parameter problem). The Fortran program will accept a complete set of raw data (*i.e.* before Lorentz, polarization, film factor corrections have been applied) and will produce appropriately corrected, scaled, and averaged data together with the estimated standard deviations for these averages.

The following examples illustrate the difficulties of the various existing methods. In each case the weights,

*Example 1.* Consider the following set of data:

	Layer 1	Layer 2	Layer 3
$F_1^2$	100	2	
$F_2^2$		1	2
$F_3^2$	100	3	

$\sqrt{W_{hi}}$ , are set equal to 1.0. The  $K_i$  are reciprocals of the  $G_{i(i)}$  of the method described above.

Obviously, the ratio of scale factors for layer 2 and layer 3 in *Example 1* should be equal to 2.0. The following results were obtained from the various methods.

Kraut's method: not applicable (no reflections connecting layer 1 and layer 3).

Dickerson's method:  $K_1 : K_2 : K_3$   
 $K_1$  held constant 0.050 : 2.0 : 1.0  
 $K_2$  held constant 0.050 : 2.0 : 1.0  
 $K_3$  held constant 0.050 : 2.0 : 1.0

Rollett-Sparks' method: 0.042 : 1.666 : 1.0  
 Present method: 0.050 : 2.0 : 1.0

*Example 2.* Consider the following set of data:

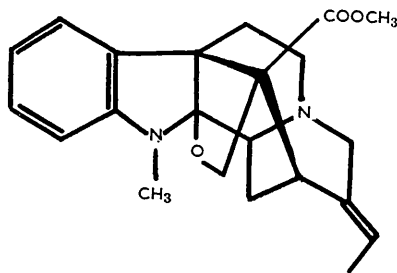
	Layer 1	Layer 2	Layer 3	Layer 4
$F_1^2$	100	2		
$F_2^2$		1	2	
$F_3^2$	100	3		
$F_4^2$			1	4
$F_5^2$	25			1

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### Étude préliminaire de l'iodométhylate de pseudo-akuammigine. Par J. ÉTIENNE, J. LE MEN et J. LÉVY, *Faculté de Pharmacie de l'Université de Paris, France*

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L'étude chimique de la  $\psi$ -akuammigine,  $C_{22}H_{26}O_3N_2$ , un des alcaloïdes extrait des graines de *Picralima nitida* (Apocynacées) a permis de lui attribuer la structure suivante (Lévy, le Men & Janot, 1961; Lévy, 1962; Olivier, Lévy, le Men, Janot, Djerassi, Budzikiewicz, Wilson & Durham, 1963; Taylor, Bartlett, Olivier, Lévy & le Men, 1964).



Afin de confirmer cette structure, une étude cristallographique par la diffraction des rayons X a été entreprise utilisant un dérivé avec un atome lourd: l'iodométhylate de  $\psi$ -akuammigine.

Des cristaux de forme parallélépipédique ont été obtenus par évaporation lente à température ambiante d'une solution de ce dérivé dans un mélange benzène-acétone.

La maille cristalline a été déterminée par les méthodes du cristal tournant et de Weissenberg avec la radiation  $Cu K\alpha$  sur un mono-cristal de dimensions optimales pour limiter l'absorption.

Les données suivantes ont été obtenues:

The following results were obtained.

Kraut's method: not applicable (no reflections connecting layer 1 and layer 3 or layer 2 and layer 4).

Dickerson's method:  $K_1 : K_2 : K_3 : K_4$   
 $K_1$  held constant 0.155 : 6.206 : 3.283 : 1.0  
 $K_2$  held constant 0.154 : 6.222 : 3.289 : 1.0  
 $K_3$  held constant 0.133 : 5.382 : 3.418 : 1.0  
 $K_4$  held constant 0.094 : 3.789 : 2.316 : 1.0

Rollett-Sparks' method: 0.060 : 2.495 : 2.432 : 1.0  
 Present method: 0.060 : 2.560 : 2.542 : 1.0

### References

- DICKERSON, R. E. (1959). *Acta Cryst.* **12**, 610.  
 KRAUT, J. (1958). *Acta Cryst.* **11**, 895.  
 ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273.

Réseau orthorhombique de groupe spatial  $P2_12_12_1 (D_2^4)$ .  
 Paramètres:

$$a=6,82, b=11,88, c=27,57 \text{ \AA}.$$

Densité (mesurée par flottaison)  $d=1,54 \text{ g.cm}^{-3}$ .

En introduisant quatre molécules dans la maille, on est conduit à adopter une densité théorique de  $1,51 \text{ g.cm}^{-3}$  en bon accord avec la densité expérimentale.

Les intensités intégrées lues sur les films de Weissenberg des strates ( $0kl$ ) et ( $h0l$ ), corrigées des facteurs de Lorentz-polarisation ont été introduites dans le calcul de la fonction de Patterson. Les coordonnées des atomes d'iode ont été déduites des deux projections de la fonction de Patterson effectuées parallèlement aux deux axes cristallographiques  $[100]$  et  $[010]$ ; exprimées en fractions de bord de maille, ces coordonnées non raffinées sont:

$$x=0,955, y=0,391, z=0,197,$$

les trois autres s'en déduisant par les opérations de symétrie de la maille.

Les quatre molécules de  $\psi$ -akuammigine ont été ensuite localisées par projection de densité électronique, parallèlement à l'axe cristallographique  $[100]$ . (Méthode de l'atome lourd).

L'étude de la structure se poursuit actuellement.

### Références

- LÉVY, J., LE MEN, J. & JANOT, M. M. (1961). *Bull. Soc. chim. Fr.*, p. 1658.  
 LÉVY, J. (1962). Thèses Doctorat ès Sciences, Paris.  
 OLIVIER, L., LÉVY, J., LE MEN, J., JANOT, M. M., DJERASSI, C., BUDZIKIEWICZ, H., WILSON, J. M. & DURHAM, L. (1963). *Bull. Soc. chim. Fr.*, p. 646.  
 TAYLOR, W. I., BARTLETT, M. F., OLIVIER, L., LÉVY, J. & LE MEN, J. (1964). *Bull. Soc. chim. Fr.*, p. 392.