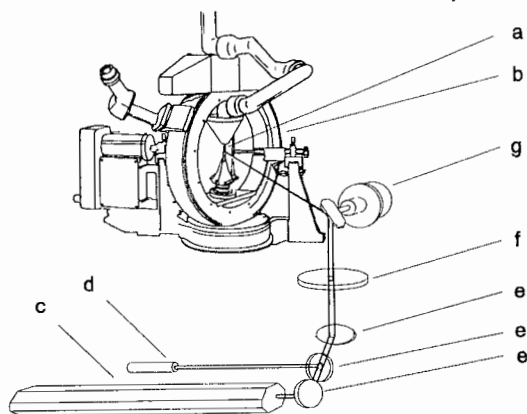# 04-Crystallography of Biological Small Molecules

Fig. 1 *in situ*-crystallization device with IR laser: a) capillary b) Eulean cradle c) IR laser d) pilot (visible) laser e) mirror f) lens g) turnable (controlled) mirror

OCM–04.03.02 SINGLE CRYSTAL DATA WITH SYNCHROTRON RADIATION - WHAT CAN IT OFFER ? Marjorie M. Harding, Department of Chemistry, Liverpool University, PO Box 147, Liverpool L69 3BX, UK

Synchrotron radiation has very high intensity, a continuous range of wavelengths, and very low beam divergence. These can be used with advantage for the study of microcrystals, for time resolved studies, and for a variety of other purposes.

For <u>microcrystals,</u> the practical problems to be faced include the quality of the small crystals (often poor), crystal mounting, radiation damage, and then distinguishing the diffraction peaks from background. The smallest crystal for which we have successfully recorded data with monochromatic synchrotron radiation and determined the structure was $10 \times 10 \times 30$ μm, containing a gold cluster of previously unknown constitution, and shown to be $Au_{10}(PPh_3)_7(S_2C_2(CN)_2)_2$ (Cheetham, Harding, Haggitt and Mingos, 1993, J. Chem. Soc. Chem. Commun. in the press). The structure of an aluminophosphate, $Al_3P_3O_{12}F.C_4H_{10}NO$, was similarly determined from a crystal of dimensions $35 \times 20 \times 15$ μm, and in this case comparison could be made with the results of powder diffraction (Harding, Kariuki, McCusker and Simmen, 1993, in preparation for Zeolites).

<u>White beam methods (Laue)</u> now allow unit cell determination (Dodd, Carr and Harding,1993, J. Appl. Cryst.25, in the press) as well as intensity measurement (Helliwell et al, 1989, J. Appl. Cryst. B22, 483-497). Exposure times can be less than 0.1 s for normal sized crystals, and 1-5 min for very small ones; to record all the unique data, 1-10 film packs or image plates, may be required, according to the crystal symmetry.

The constitution and structure of a new organometallic complex, $AuOs_3(CO)_8PPh_3dppm.PF_6$, were determined from six Laue film packs - one for the unit cell and five for the intensitiy measurements - and structure refinement gave R=0.075 for 7163 unique reflections. In crystalline $P_4N_4Cl_8$ the molecule changes from a boat to a chair conformation at ca 65°C, and the crystal symmetry changes. In a preliminary time-resolved study film packs were exposed at 3 min intervals as single crystals were heated (Carr, Cheetham, Harding and Rule, 1992,Phase Transitions, 39, 33-43); from each film pack

200-300 reflections have been measured and used to follow the course of the change.

OCM–04.03.03   THE BACKGROUND: A NON-EVENT IN SINGLE CRYSTAL DIFFRACTOMETRY by A.T.H.Lenstra*, S.maes & C.Van Hulle, Dept. of Chemistry, Antwerp University (UIA), Universiteitsplein 1, 2610 Wilrijk, Belgium

A net intensity I is routinely obtained by subtracting the local background B(hkl) from the raw intensity R(hkl):
$$I = R - B \qquad (1)$$
Since the observations B and R are taken as independent, the corresponding variance is:
$$\sigma^2(I) = \sigma^2(R) + \sigma^2(B) \qquad (2)$$
This classical interpretation is correct when one deals with a single observation. However, it is a very poor way to deal with the data in a single crystal analysis. Here one deal with a large set of observations, which in a hidden way includes valuable experience, notably on the background.

Let us only summarize the essential features of the observed background intensities. Within a not too large $\sin\theta/\lambda$ –interval all observed B(hkl) values can be contracted into a normal distribution $N(<B>,s^2(B))$,where $<B>$ is the averaged background and $s^2(B)$ is the observed spread. In a standard data set one finds $<B>s^2(B)$, which connects B(hkl)'s to a counting statistical distribution.

The calculated background averages in different $\sin\theta/\lambda$ – intervals appear to be interrelated by:
$$b = B(ref) \times C \qquad (3)$$
where C is theta dependent correction factor and B(ref) is a reference value characteristic for the whole data set. The correction C includes three component parts, viz:

i) $C1=f^2(O)+(Z-f^2(O)/Z)$ where f(O) is the scattering factor for oxygen at the diffractometer angle $\theta_0.F^2(O)$ and $(Z-f^2/Z)$ are the elastic Raileigh and the inelastic Compton scattering produced by the crystal and its emorphous support.

ii) $C2=\cos^2 2\theta m + \cos^2 2\theta o$, which is the polarisation of C1.

iii) $C3=(p+qxtg\theta)(r+sxtg\theta)$, which connects b to the scan angle and the aperture applied during the data collection.

With $C=C1 \times C2 \times C3$ it is evident that B(ref) is easily calculated using all available background counts in the data set. This suffices to show that the value of B(ref) is virtually error free. At the reciprocal lattice point (hkl) we observed a raw intensity R. Its variance is equal to R. Using (3) the local background b is given by $C \times B(ref)$. Now b is an nearly error free estimate of the Bragg intensity of the crystal. An actual observation would reveal a counting statistical variance b.

When we now combine R and b as observation related to (hkl), we get
$$I = R - b \quad \text{and} \quad \sigma^2(I) = R - b \quad (4)$$
So the background model reduces the variance of I from I+2B to I. This lowers the detection limit of your diffractometer by a factor 10 without any increase in the applied measuring time. One could even save time by skipping almost all background observations without loosing accuracyl.

OCM–04.03.04 WHEN AUTOMATIC STRUCTURE SOLUTION FAILS. By E.N. Maslen*, Crystallography Centre, University of Western Australia, Nedlands, Western Australia 6009