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Center-of-gravity method of precision lattice parameter determination.

By J. Ladell, W. Parrish and J. Taylor, *Philips Laboratories, Irvington-on-Hudson, New York, U.S.A.*

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In precision lattice parameter determination with the counter tube diffractometer it has been the practice to use the angles corresponding to peak positions and to extrapolate against some function of θ to $\theta = 90°$ (see for example, Smakula & Kalnajs, 1955). There are at least two difficulties with this method: 1) There is no agreement as to how to measure or define the peak position, 2) the effect of instrumental aberrations on the peaks is known for only a few limited cases. In recent years the effects of the aberrations on the center-of-gravity (c.g.) of a line profile have been analyzed (Wilson, 1950; Pike, 1957; Parrish & Wilson, 1958) and a new approach to the problem is now possible (Ladell, Parrish & Taylor, 1957; Parrish & Taylor, 1957).

The observed diffractometer line profile $f(\theta)$ is a convolution of the incident spectral distribution $h(\lambda)$ and the various instrumental and geometrical aberration distributions such as flat specimen, specimen transparency, axial divergence, and dispersion. These aberrations asymmetrically broaden and shift the lines and cause systematic errors in the angular measurements from which the lattice parameter is determined. Since the c.g.'s of the individual aberrations are known as a function of 2θ and the shifts due to these on the c.g. of the line profile are additive, it is easy to correct for the amount Δ_g by which they displace the observed c.g. and thus obtain the c.g. of the angular representation of the spectral distribution $h(\theta)$, i.e., the c.g. that would be obtained in an ideal diffractometer free of aberrations. For cases where dispersion is not significant, the c.g. of $h(\theta)$ corresponds to the c.g. of $h(\lambda)$ and the d-spacing is obtained from the Bragg equation

$$d = n\tilde{\lambda}/2\sin(\tilde{\theta}-\Delta_g)\,, \tag{1}$$

where $\tilde{\lambda}$ is the c.g. of $h(\lambda)$ and $\tilde{\theta}-\Delta_g$ is the c.g. of $h(\theta)$. $\tilde{\lambda}$ is defined* as

$$\tilde{\lambda} = \int_{\lambda_1}^{\lambda_2} \lambda h(\lambda)\,d\lambda \bigg/ \int_{\lambda_1}^{\lambda_2} h(\lambda)\,d\lambda\,. \tag{2}$$

The integration limits in equation (2) should be $-\infty$ to ∞, but this range is impractical because the tails of the spectral distributions decay too slowly. This difficulty is overcome by a truncation procedure which provides finite limits λ_1, λ_2, preserves the basic features of the distribution and gives a unique c.g. To maintain the correspondence of $h(\lambda)$ and $f(\theta)$ both distributions are truncated in the same manner. The c.g. of the observed distribution $\tilde{\theta}$ is then

$$\tilde{\theta} = \int_{\theta_1}^{\theta_2} \theta f(\theta)\,d\theta \bigg/ \int_{\theta_1}^{\theta_2} f(\theta)\,d\theta\,. \tag{3}$$

The integrated intensity is measured and a line drawn above and parallel to the background level so that the area under the profile between the lines is about 10% of the integrated intensity. The integration limits are taken as the abscissae θ_1, θ_2 where the line intersects the profile and the c.g. is calculated between these limits. Thus less than 5% of the area under the entire distribution is neglected and that portion is in the tails far removed from the central region. Computer calculations using synthetic functions showed that this approximation causes an error in $\tilde{\theta}$ of $< 0{\cdot}001°(2\theta)$. (A truncation method based on symmetrical limits has been derived by Pike & Wilson, 1958.)

The profiles of reflections which occur at large Bragg angles are asymmetrically stretched by dispersion, Lorentz and polarization factors, which are large and changing rapidly and shift the c.g. toward higher angles. In these cases $(\tilde{\theta}-\Delta_g)$ in equation (1) should be replaced by θ_B where

$$\theta_B = \sin^{-1}\left(\int_{\theta_1}^{\theta_2} h(\theta)\sin\theta\,d\theta \bigg/ \int_{\theta_1}^{\theta_2} h(\theta)\,d\theta\right) \tag{4}$$

and the dispersion correction Δ_D is:

$$\Delta_D = \theta_B - \left(\int_{\theta_1}^{\theta_2} \theta h(\theta)\,d\theta \bigg/ \int_{\theta_1}^{\theta_2} h(\theta)\,d\theta\right)\,. \tag{5}$$

To make the correction for the Lorentz and polarization factors, $f(\theta)$ should be modified by multiplying each ordinate of $f(\theta)$ by $J(\theta)$ where

$$J(\theta) = \sin^2\theta\cos\theta/(1+\cos^2 2\theta)\,, \tag{6}$$

and $\tilde{\theta}$ would be defined as the c.g. of the new distribution $J(\theta)f(\theta)$. This is extremely tedious, but at the high angles where the correction Δ_{LP} is significant, the observed profile is virtually the same as the spectral profile and a good estimate of the displacement is

$$\Delta_{LP} = \frac{\int_{\theta_1}^{\theta_2} \theta J(\theta)h(\theta)\,d\theta}{\int_{\theta_1}^{\theta_2} J(\theta)h(\theta)\,d\theta} - \frac{\int_{\theta_1}^{\theta_2} \theta h(\theta)\,d\theta}{\int_{\theta_1}^{\theta_2} h(\theta)\,d\theta}\,. \tag{7}$$

In practice θ_B is obtained from

$$\theta_B = \tilde{\theta}+\Delta_D+\Delta_{LP}-\Delta_g \tag{8}$$

and the d-spacing is calculated from

$$d = n\tilde{\lambda}/2\sin\theta_B\,. \tag{9}$$

To apply the center-of-gravity method it is necessary to know the spectral distributions. Since these have not been published, a satisfactory analytic representation of $h(\lambda)$ has been derived on the basis of the peak wavelengths, widths at one-half peak height, indices of asymmetry, doublet separation (Bearden & Shaw, 1935), and rate of decay (Parratt, 1936; Hoyt, 1932) reported from experimental two-crystal spectrometer data. These synthetic distributions have been used to calculate $\tilde{\lambda}$, Δ_D and Δ_{LP} for Cu $K\alpha$ and Fe $K\alpha$ and the data will be published soon (Ladell, Parrish & Taylor, 1958).

Although the procedure eliminates the necessity for extrapolation, it is still desirable to plot the lattice para-

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* The tilde (~) notation refers to the c.g. of a distribution truncated in the manner described in this note.

meters derived from each of the corrected reflection angles θ_B against 2θ. If the line of regression is horizontal, a correct account has been made for the aberrations and the scatter of points is indicative of the random error. The method has been applied successfully to silicon, but much more experimental work is required to establish its full potential. It is hoped that it may be used to establish a basis for the empirical use of peak measurements which would then be applied to low symmetry substances where overlapping reflections may render the c.g. method impractical.

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The crystal data for the chloro and bromo derivatives of picrotoxinin.

By B. M. Craven, *Auckland University, New Zealand**

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The chemistry of picrotoxinin ($C_{15}H_{16}O_6$) has been thoroughly investigated for many years. These efforts have culminated in the structure proposed by Conroy (1957).

Crystals of α- and β-chloro and bromopicrotoxinin ($C_{15}H_{15}O_6Cl$ and $C_{15}H_{15}O_6Br$) have been examined. It was not possible to prepare iodopicrotoxinin, see Slater *et al.* (1956). The α isomers were all prismatic in crystal habit, while the β isomers were acicular. It was found that α-bromopicrotoxinin crystallized in two forms, here called α_1 and α_2. The nature of the difference between these forms has not been determined. More than one form for α-chloropicrotoxinin has not been discovered.

The cell parameters for these compounds (see Table 1) were determined from oscillation and Weissenberg photographs and the crystal densities were determined by the method of flotation in a mixture of chloroform and bromoform.

The [*a*] Patterson projection for β-bromo and β-chloropicrotoxinin were almost identical and there was no difficulty in finding the heavy atom positions (see Table 2). Although the β isomers are thus isomorphous, the presence of the halogen atoms in a special position ($z = 0$) makes a structure determination by the heavy atom or isomorphous replacement method very difficult.

There was no similarity between the corresponding Patterson projections of any of the α isomers, from which it is inferred that their structures are all different.

Table 2. *Halogen atom positions*

	$x_{\text{hal.}}$	$y_{\text{hal.}}$	$z_{\text{hal.}}$
β-Bromopicrotoxinin	0·312	0·796	0
β-Chloropicrotoxinin	0·31	0·80	0
α_1-Bromopicrotoxinin	0·295	0·027	0·335
α_2-Bromopicrotoxinin	0·316	0·062	0·435

The positions of the bromine atoms in α_1- and α_2-bromopicrotoxinin were uniquely determined from the Pattersons, but there was no unique interpretation of the α-chloropicrotoxinin Pattersons. The chlorine atom is probably at (0·340, 0·063, 0·410).

It has not been found possible to solve the structure of either α_1 or α_2-bromopicrotoxinin in projection because of the difficulty in recognizing any structural features in the approximate electron density maps. Three-dimensional structure determinations of both α_1- and α_2-bromopicrotoxinin are now in progress.

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Table 1. *Crystal data*

Compound	System	*a* (Å)	*b* (Å)	*c* (Å)	Å^3	D_m g.cm.$^{-3}$	D_x g.cm.$^{-3}$	*Z*	Space group
β-Bromopicrotoxinin	Tetragonal	7·08	—	28·30	1420	1·72	1·74	4	$P4_1$ or $P4_3$
β-Chloropicrotoxinin	Tetragonal	7·07	—	28·48	1425	—	—	4	$P4_1$ or $P4_3$
α_1-Bromopicrotoxinin	Orthorhombic	13·40	11·60	8·86	1378	1·78	1·80	4	$P2_12_12_1$
α_2-Bromopicrotoxinin	Orthorhombic	13·65	11·86	8·76	1420	1·76	1·75	4	$P2_12_12_1$
α-Chloropicrotoxinin	Orthorhombic	14·68	11·48	8·46	1425	—	—	4	$P2_12_12_1$

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* Present address, University of Pittsburgh, Pittsburgh 13, Pennsylvania.