$\xi_{1\mathbf{h}_\mu}$ as II(5). Let this distribution be Q. Q may be interpreted as a function of x, y, z giving the most probable coordinates of atom 1, and

$$\log Q = \log K - \sum_{\mu=1}^{m} \frac{(A_{\mathbf{h}_\mu} - f_{1\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu})^2}{2m_2 \sum_{j=2}^{N/n} f^2_{j\mathbf{h}_\mu}} \,. \qquad (9)$$

Put

$$m_2 \sum_{j=2}^{N/n} f^2_{j\mathbf{h}_\mu} = \tau_{\mathbf{h}_\mu} \,,$$

then

$$\log \frac{Q}{K} = -\sum_{\mu=1}^{m} \left[\frac{A^2_{\mathbf{h}_\mu}}{2\tau_{\mathbf{h}_\mu}} - \frac{2f_{1\mathbf{h}_\mu} A_{\mathbf{h}_\mu} \xi_{1\mathbf{h}_\mu}}{2\tau_{\mathbf{h}_\mu}} + \frac{f^2_{1\mathbf{h}_\mu}\xi^2_{1\mathbf{h}_\mu}}{2\tau_{\mathbf{h}_\mu}} \right] . \qquad (10)$$

The first term on the r.h.s. is a constant; in the space group $P\bar{1}$, the third becomes

$$-\sum_{\mu=1}^{m} \frac{f^2_{1\mathbf{h}_\mu}}{2\tau_{\mathbf{h}_\mu}} (2+\xi_{1,2\mathbf{h}_\mu}) \,,$$

which has large negative peaks at 0 or $\frac{1}{2}$; and the second term is a Fourier series sharpened by the factors $f_{1\mathbf{h}_\mu}/\tau_{\mathbf{h}_\mu}$. The distribution obtained by a probability approach when the phases of the structure factors are known is thus very similar to a sharpened Fourier series.

When the signs of the $A_{\mathbf{h}_\mu}$ are not known, Karle & Hauptman suggest the use of II(8),

$$\begin{aligned} \frac{Q}{K} &= \prod_{\mu=1}^{m} \left\{ \exp\left(\frac{-(|A_{\mathbf{h}_\mu}| - f_{1\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu})^2}{2\tau_{\mathbf{h}_\mu}} \right) \right. \\ &\qquad\qquad \left. + \exp\left(\frac{-(|A_{\mathbf{h}_\mu}| + f_{1\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu})^2}{2\tau_{\mathbf{h}_\mu}} \right) \right\} \\ &= \prod_{\mu=1}^{m} 2 \exp\left(\frac{-(|A_{\mathbf{h}_\mu}|^2 + f^2_{1\mathbf{h}_\mu}\xi^2_{1\mathbf{h}_\mu})}{2\tau_{\mathbf{h}_\mu}} \right) \\ &\qquad\qquad \times \cosh\left(\frac{f_{1\mathbf{h}_\mu}|A_{\mathbf{h}_\mu}|\xi_{1\mathbf{h}_\mu}}{\tau_{\mathbf{h}_\mu}} \right) . \qquad (11) \end{aligned}$$

Reference above shows that only terms in $A_{\mathbf{h}_\mu}\xi_{1\mathbf{h}_\mu}$ are important, so that the structure-dependent part of $\log (Q/K)$ is

$$\sum_{\mu=1}^{m} \log \cosh \left(\frac{f_{1\mathbf{h}_\mu}|A_{\mathbf{h}_\mu}|\xi_{1\mathbf{h}_\mu}}{\tau_{\mathbf{h}_\mu}} \right) . \qquad (12)$$

Using the series expansion of $\log \cosh x$ and interchanging the order of summations, this term becomes

$$\sum_{s=1}^{\infty} \frac{2^{2s}}{2s} \frac{(2^{2s}-1)}{(2s)!} B_{2s} \sum_{\mu=1}^{m} \left(\frac{f_{1\mathbf{h}_\mu}|A_{\mathbf{h}_\mu}|\xi_{1\mathbf{h}_\mu}}{\tau_{\mathbf{h}_\mu}} \right)^{2s} , \qquad (13)$$

where the B_{2s} are Bernouilli numbers. Since (13) contains only even powers of $|A_{\mathbf{h}_\mu}|$ it must be of the Patterson type. Indeed the corrections obtained for $s = 2, 3$, etc., to the Patterson obtained by taking $s = 1$, are even less significant than those made by (4) and (7) to (3), since with all like atoms (13) becomes, in $P\bar{1}$,

$$\sum_{s=1}^{\infty} \frac{2^{2s}}{2s} \frac{(2^{2s}-1)}{(2s)!} \frac{B_{2s}}{(N-2)^s} \left. \sum_{\mu=1}^{m} \frac{|A_{\mathbf{h}_\mu}|^2}{\tau_{\mathbf{h}_\mu}} (2+\xi_{1,2\mathbf{h}_\mu}) \right\}^s , \qquad (14)$$

the successive coefficients for the summations over μ being approximately $1/(2N)$, $-1/(12N^2)$, $1/(45N^3)$, etc. for $s = 1, 2, 3$ etc. Thus the probability distribution for coordinates when the structure-factor signs are not known is essentially a sharpened Patterson, which is on half scale in x, y, z, and thus has some peaks coincident with atomic positions.

Similar discussions can be given for the distributions in II for non-centrosymmetric crystals. If the position of one atom is arbitrarily fixed and the phase angles are assumed unknown, the resulting Patterson-like distribution is of normal scale in x, y, z with the fixed atom as origin; thus again some peaks coincide with the atomic positions.

It may be remarked that II(5) can be written down directly by appealing to the central limit theorem (Cramér, 1946) on the assumption of the independence of the $\xi_{i\mathbf{h}_\mu}$, $\mu = 1, \ldots, m$, for each set i. The assumption of independence is clearly equivalent to taking the first term alone in the series referred to in II. It does not seem possible, however, to obtain better than the sharpened Patterson if this assumption is made.

References

Clastre, J. & Gay, R. (1950*a*). *C. R. Acad. Sci., Paris*, **230**, 1976.

Clastre, J. & Gay, R. (1950*b*). *J. Phys. Radium*, **11**, 75.

Cramér, H. (1946). *Mathematical Methods of Statistics*. Princeton: University Press.

Hauptman, H. & Karle, J. (1952). *Acta Cryst.* **5**, 48.

Karle, J. & Hauptman, H. (1954). *Acta Cryst.* **7**, 375.

Acta Cryst. (1954). **7**, 599

Conversion of Norelco fluorescent spectrograph to an X-ray diffractometer.

By R. J. Weiss, J. J. DeMarco and G. Weremchuk, *Ordnance Materials Research Office, Watertown Arsenal, Watertown, Mass., U. S. A.*

(*Received* 21 *December* 1953 *and in revised form* 25 *February* 1954)

The North American Philips Fluorescent Attachment consists of an OEG-50-Machlett tungsten tube, which is run at 50 kV., 50 mA. and sprays X-rays on to a sample. An elemental analysis of the sample is made by analyzing the characteristic K and L fluorescent lines by means of a single crystal and a goniometer.

By utilizing a pure element such as cobalt one obtains the characteristic $K\alpha$ and $K\beta$ lines practically free of continuous background. A filter will essentially eliminate the $K\beta$. To make use of this plane source of monochromatic radiation for powder diffraction one must create a focal spot so as to utilize the geometrical focusing conditions necessary for high resolution. This is done by use of a slit between the plane source of fluorescent radiation and the powder specimen. In addition, the plane source of Co radiation is tilted upward so as to obtain a take-off angle of about 10° empirically determined to be an optimum.

A 110 peak of annealed powdered iron was obtained on the standard diffractometer (Fig. 1(*a*)) and the same sample run on the converted spectrograph (Fig. 1(*b*)). With only a 20% decrease in resolution the intensities differed by less than a factor of 2 while the background was reduced by a factor of about 25.

The intensity of the *Kα* line on the fluorescent unit varied approximately as $(V-V_0)^{1\cdot 2}$, where V is the potential in the primary tungsten tube and V_0 is minimum potential for *Kα* excitation ~ 7·8 kV. for Co *Kα*.

Details of the geometry are given in Fig. 2.

The advantages of this new method for diffraction are:

1. Negligible background (about 50% above cosmic background).
2. Complete freedom in choice of radiation since a fluorescent source offers no heating problem.
3. Ultimate use of high-intensity industrial sources of primary tungsten radiation since absence of any focusing conditions for the primary source eliminates cathode loading problem.
4. Uniform illumination of line focus.

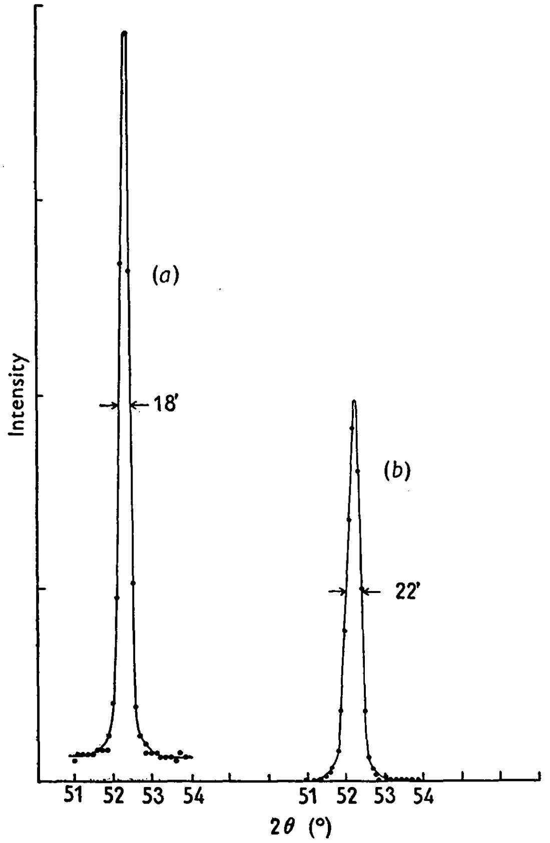

Fig. 1. Comparison curves of (110) reflection of iron powder taken on the North American Philips Diffractometer. (*a*) Standard X-ray diffractometer using a cobalt tube at 10 mA., 30 kV.; divergence slit 1°; receiving slit 0·30 mm. (*b*) Curve of the same sample taken with the converted spectrograph, divergence 1·25°, the primary tungsten tube being run at 50 mA., 50 kV.

A 0·0006″ iron filter was used for both curves and the cosmic ray background has been subtracted.

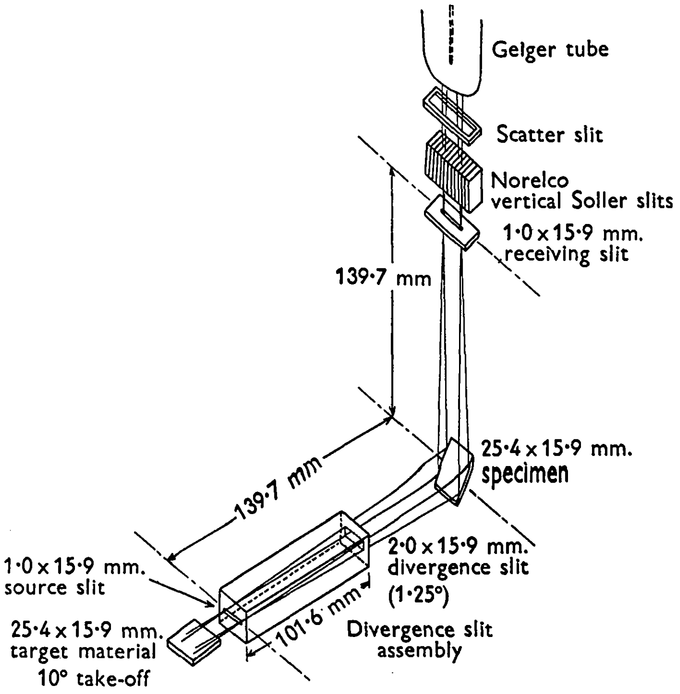

Fig. 2. Focusing arrangement of X-ray spectrograph modified for diffraction. The target material is located ~ 9·5 mm. below high-voltage X-ray tube port.