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QUANTITATIVE X-RAY ANALYSIS OF CRYSTALLINE COMPONENTS IN FERTILIZERS

C.G. VONK, H.G. HECK and A.P. PIJERS

Central Laboratory DSM, PO-box 18, Geleen (Netherlands)

SUMMARY

The analysis comprises the following steps: 1. The relevant part of the X-ray diagram is recorded and punched into tape. 2. These data are computer processed; the output consists of a list of the positions and intensities of all peaks. 3. From this list the components present in the sample are identified either 'by hand', or with the aid of Johnson's search program (Adv. X-ray Anal. 11 (1968), 376). 4. The intensities of the available peaks are subjected to a computerized least squares analysis, in which the observed intensities are compared to those of the pure components.

Analyses of synthetic powder mixtures show average deviations from true concentrations of 1 - 2 % (absolute).

INTRODUCTION

In classical methods of quantitative X-ray powder analysis, which have been reviewed by Klug and Alexander [1], usually one, well isolated diffraction peak is used for determining the concentration of one component. Obviously the accuracy of the analysis might be improved substantially if more peaks were used, including those containing contributions of two or more components. In the present method this is achieved by submitting the intensities of all peaks in the main part of the X-ray diagram to a least squares analysis, in which the concentrations of the components are determined. The use of many peaks requires computer processing of the diffraction pattern; a program was developed for this purpose, which is described below.

DESCRIPTION OF THE METHOD

The analysis comprises the following steps:

1. the relevant part of the X-ray diagram (usually from 10 - 50 degr. 2θ , where 2θ is the angle of diffraction) is recorded with the aid of a powder diffractometer and punched into tape at intervals of $1/32$ degree.

2. These data are computer processed by means of the program XPOWD and the following subroutines:

a. BGR; this serves to find the shape and height of the continuous background on which the peaks in the diagram are superimposed. The method

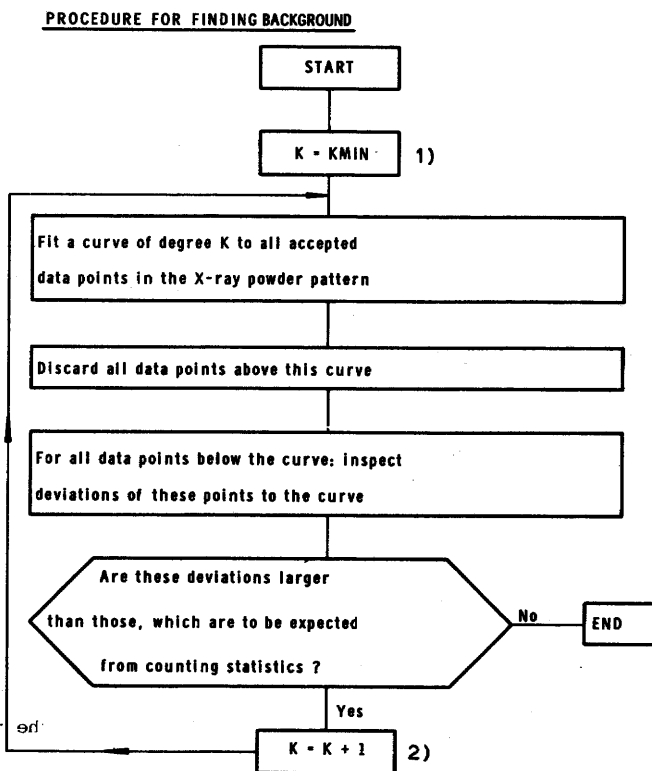


Fig. 1. Flow chart of the subroutine BGR.

1). Usually $K_{MIN} = 1 - 3$

2). The increase of K before starting the next cycle is not essential and may be suppressed. However convergence may be more rapid if K is allowed to increase.

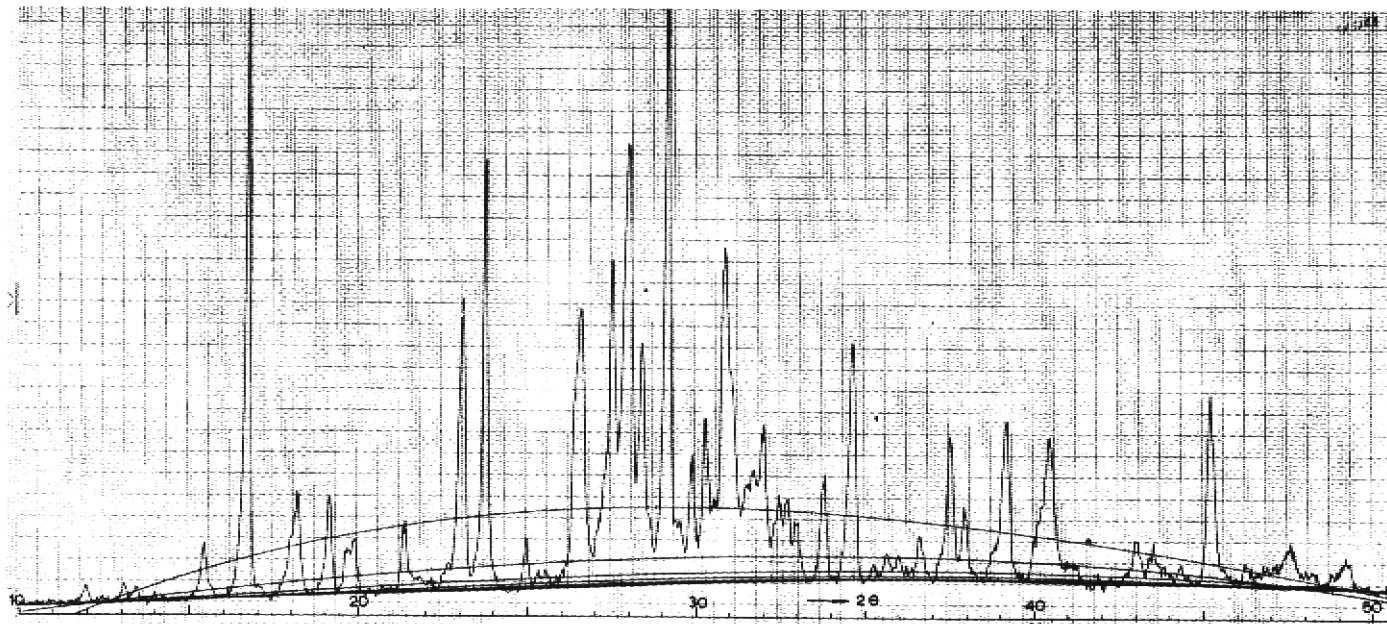


Fig. 2. Application of subroutine BGR to the diffraction curve of a fertilizer sample. The smoothly curved lines are the background curves that have been calculated after different numbers of cycles.

used is indicated in the block diagram presented in fig. 1, whereas an illustration of its operation is given in fig. 2.

b. PKLOC. This subroutine establishes the presence of peaks in the diffraction curve and their approximate positions. It is made to recognize low peaks in a curve showing random noise due to counting statistics. To this end the data point curve is convoluted with a window function as shown in fig. 3. The width of the interval B is equal to the total width of the intervals A; consequently the convolution will be zero if no peaks are present in the region ABA, whereas it will show a maximum or minimum

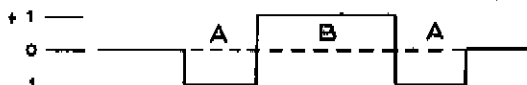


Fig. 3. Window function for locating peaks in diffraction curve.

if the centre of a peak is in the B- or A-interval respectively. (In this case a point in the convoluted curve is found from the sum of the intensities in the region B minus those in the regions A at the corresponding position of the window midpoint). The width of the interval B is fixed in each application, and chosen to be about equal to the width of the peaks. This is however not critical: deviations by a factor 2 will still give satisfactory results. The procedure is illustrated in fig. 4, which clearly shows the improvement in the signal-to-noise ratio obtained by this method. In practice all maxima in the convolution curve above a certain level D (fig. 4) are accepted as corresponding to significant peaks in the original curve.

c. PKSIMP. In this subroutine the accurate positions and integrated intensities of the peaks are determined. Also, the α_1 - and α_2 -components are combined if necessary, and the peak positions are corrected with the aid of a reference peak, of which the position is accurately known. A peak from an internal reference substance, added for the determination of the mass absorption coefficient (see below), may serve for this purpose.

In order to eliminate the effects of changes in instrumental conditions, all intensities are expressed as fractions of the intensity of a

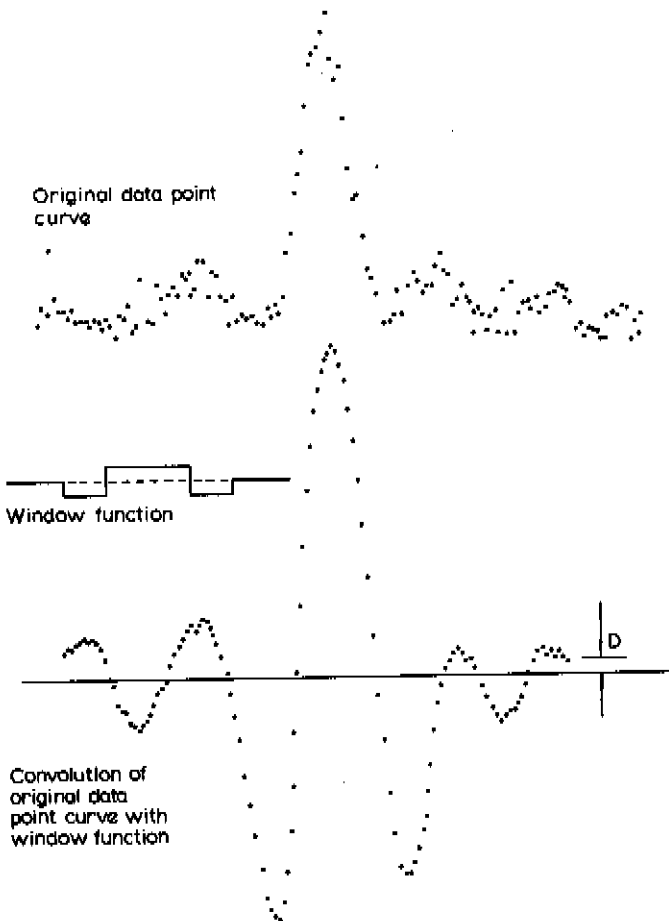


Fig. 4. Application of peak locating method to part of a diffraction curve.

peak from an external reference, which is recorded under the same experimental conditions as the diffraction curve of the sample. At present the strongest peak from a teflon platelet is used as such.

Special attention must be given to the separation of overlapping neighbouring peaks. In the present program this is done simply by drawing a vertical line through the position of minimum intensity that is intermediate between the two maxima (see fig. 5). This may seem an oversimplification of the true situation; however it was found that more sophisticated methods (fitting by Gauss or Hermite functions) usually

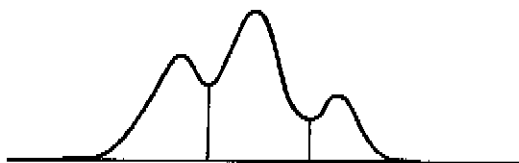


Fig. 5. Division of overlapping peaks in PKSIMP.

failed if small peaks are superimposed on the wings of large peaks. It seems that any algorithm developed for this purpose must be a compromise; the present one, though much simpler than those just mentioned, will preserve the resolution obtained by the instrument but may lead to errors in the positions and intensities of strongly overlapped small peaks.

The entire procedure is again presented in a block diagram, given in fig. 6, whereas an example of the output is given in fig. 7.

3. From the list of peak positions and intensities obtained from the subroutine PKSIMP, the components present in the sample are identified, either 'by hand', or with the aid of a computer program written by Johnson [2]. As far as possible, the observed peaks are ascribed to one or more of the components.

4. From these data the mass fractions c_j of the components j are calculated with the aid of another computer program (QXDA). As explained in [1], the intensity I_n of the n 'th peak in the X-ray diagram is equal to

$$I_n = (\sum_j I_j^0 \mu_j^* c_j) / \mu^* \quad (1)$$

where I_j^0 is the corresponding peak of the pure component j , μ_j^* is the mass absorption coefficient of the pure component j , and μ^* is the mass absorption coefficient of the entire sample. The summation extends over those components which contribute to the n 'th peak. According to the method of the least squares [3] the quantities c_j / μ^* may be found from the matrix equation

$$[f] = [M]^{-1} [v] \quad (2)$$

in which the matrix elements are given by

$$f_j = c_j / \mu^*$$

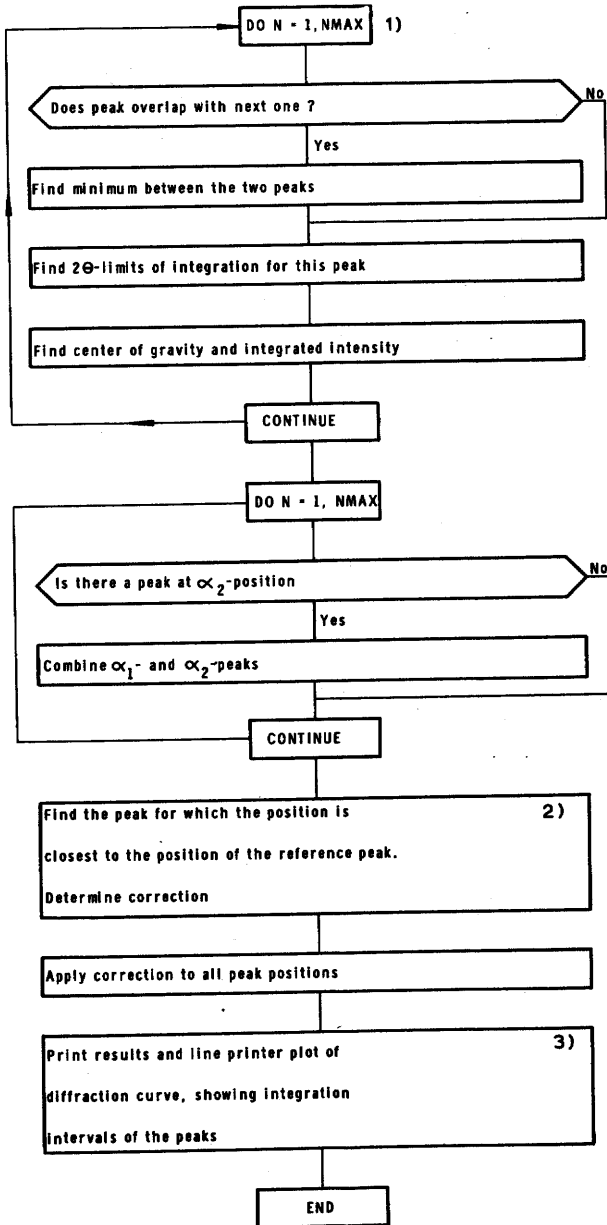


Fig. 6. Flow chart of subroutine PKSIMP

- 1). N = number of the peak found by peak locating procedure.
- 2). This peak is assumed to be reference peak.
- 3). From the peak positions, d -values are calculated.

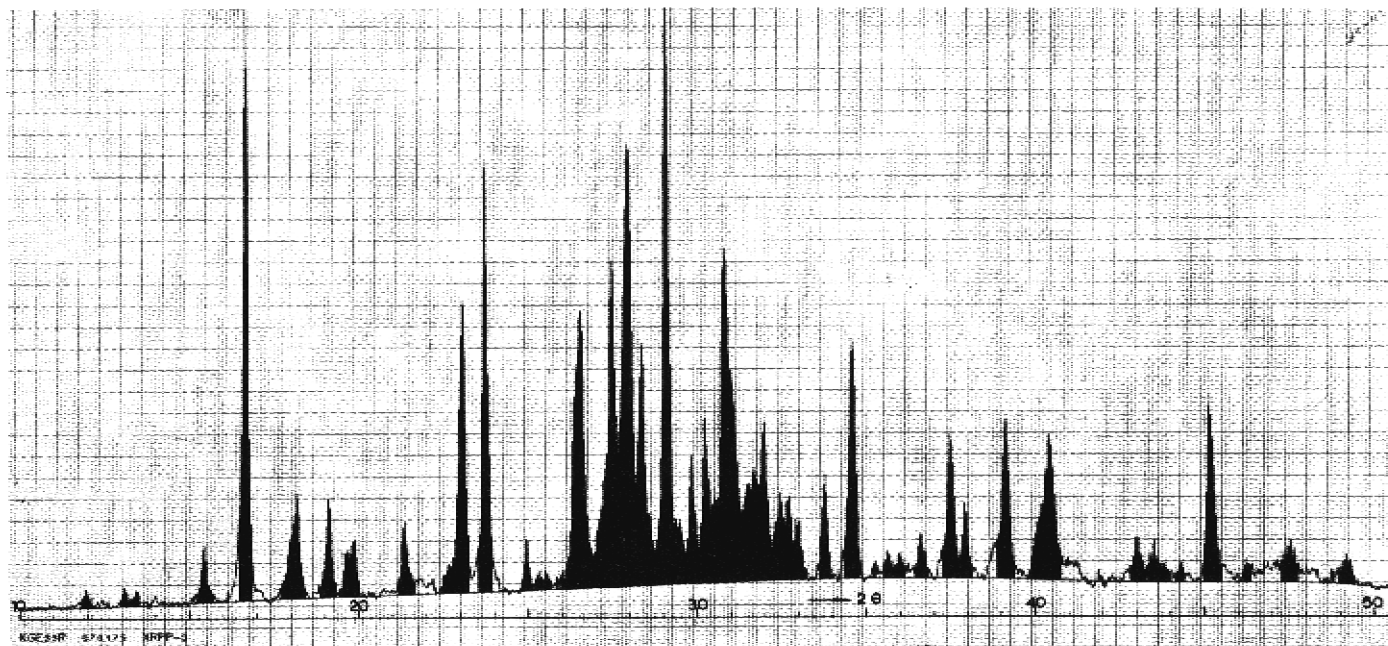


Fig. 7. Application of subroutine PKSIMP to the diffraction curve shown in fig. 2. The hatched parts have been used for the calculation of the peak positions and intensities.

$$M_{jk} = \sum_n w_n A_{j,k}$$

where w_n is the weight assigned to the n 'th peak,

$$A_j = I_j^0 \mu_j^*, \quad A_k = I_k^0 \mu_k^*$$

$$v_j = \sum_n w_n A_j I_{obs,n}$$

where $I_{obs,n}$ is the observed intensity of the n 'th peak.

For calculating the μ_j^* -values, μ^* has to be known. This can be obtained in one of the following ways:

- if the chemical composition is known - by calculation,
- if all components have been identified - by equalizing the sum of the fractions to 1,
- by experiment. To this end, a reference substance (e.g. korundum) is added to the sample in a known concentration. The ratios of the intensities of one or more diffraction peaks from this substance to those of the pure substance are used to find μ^* .

ANALYSIS OF SOLID SOLUTIONS

In most fertilizer samples containing K- and NH_4 -compounds, solid solutions are found in which isomorphous substitution of K^+ and NH_4^+ ions occurs. In the diffraction patterns of such solutions both the positions and the intensities of the peaks vary with the NH_4^+/K^+ ratio. The positions may be assumed to vary linearly with this ratio (Végar's law); the variation of the intensities follows from the relation

$$I \propto F^2 / \mu^*$$

where F is the 'structure factor'. From the theory of X-ray crystal analysis it follows that F of a solid solution can be assumed to vary linearly with the composition. In view of this the following procedure was developed in analyzing these solutions:

- a. A small number of the solid solutions that come into consideration was prepared and their X-ray patterns were recorded.
- b. From these data plots of peak positions as well as of $\sqrt{I \mu^*}$ versus the NH_4/K -ratio were prepared.
- c. In analysing samples containing solid solutions, the NH_4/K -ratio was determined with the aid of the plots of the positions of the principal peaks; next the values of I^0 to be used in eqn. (2) were found from the $\sqrt{I \mu^*}$ -plots of the peaks.

Table I

Compounds that can be analyzed at present.

Compound	Max. nr. of peaks to be used	Compound	Max. nr. of peaks to be used
$(\text{NH}_4)_2\text{H}_2\text{PO}_4$	10	KNO_3 (II)	34
$(\text{NH}_4)_2\text{HPO}_4$	33	NH_4Cl	6
CaHPO_4	52	KCl	4
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	61	$\text{CO}(\text{NH}_2)_2$ (= Ur)	18
$\text{Ca}_3\text{P}(\text{PO}_4)_3$	29	4 Ur . $\text{Ca}(\text{H}_2\text{PO}_4)_2$	67
$(\text{NH}_4)_2\text{SO}_4$	32	4 Ur . CaSO_4	56
K_2SO_4	39	Ur . H_3PO_4	61
$\text{CaK}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$	41	Ur . NH_4Cl	57
CaSO_4	18	$\gamma\text{-Al}_2\text{O}_3$	9
$\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$	25	$\alpha\text{-SiO}_2$	11
$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	34	CaCO_3 (calcite)	18
NH_4NO_3 (IV)	20	CaF_2 (fluorite)	3

Table II

Solid solutions that can be analyzed at present.

Solid Solution	Approximate Range (weight fraction of NH_4 -compound)	Isomorphous with	Max. nr. of peaks to be used
$\text{NH}_4\text{H}_2\text{PO}_4/\text{KH}_2\text{PO}_4$	1.0 - 0.75	$\text{NH}_4\text{H}_2\text{PO}_4$	10
$\text{NH}_4\text{NO}_3/\text{KNO}_3$	0.98 - 0.68	NH_4NO_3 (III)	10
$\text{NH}_4\text{NO}_3/\text{KNO}_3$	0.44 - 0.21	KNO_3 (III)	10
$\text{NH}_4\text{NO}_3/\text{KNO}_3$	0.14 - 0	KNO_3 (II)	13
$\text{NH}_4\text{Cl}/\text{KCl}$	0.18 - 0	KCl	4

Table III

Comparison of compound percentages weighed in and analyzed according to present method.

Compound	Weighed in (%)	Analyzed (%)	Difference (%)
NH_4Cl	17.5	19.5	+ 2.0
$(\text{NH}_4)_2\text{SO}_4$	22.5	21.0	- 1.5
$\text{NH}_4\text{H}_2\text{PO}_4$	44	46.5	+ 2.5

Table IV

a) X-ray component analysis of an NPK 22-11-11 sample.

Component	%
$\text{NH}_4\text{NO}_3/\text{KNO}_3$ 78/22	66
$\text{NH}_4\text{H}_2\text{PO}_4$	15.5
NH_4Cl	10
KCl	7
$\text{NH}_4\text{NO}_3/\text{KNO}_3$ 27/73	1.5

b) Comparison of percentages obtained by chemical analysis and from above component analysis.

	from X-ray component analysis (%)	by chemical analysis (%)	difference (%)
P_2O_5	9.5	10.20	- 0.7
K_2O	12	10.83	+ 1.2
N	25	23.33	+ 1.7

RESULTS

The application of the present method requires the recording and subsequent processing of the diffraction patterns of all pure compounds and solid solutions that may occur in the samples to be investigated. At present such data have been collected for the 24 compounds and 5 solid solutions given in table I and II respectively. With the aid of these data the majority of the common fertilizers can be analyzed satisfactorily; however the list is continuously being extended in order to include also the more rarely occurring species.

In order to obtain an idea of the accuracy of the method, various test samples were analyzed, of which two examples are presented here.

1. A synthetic mixture of compounds occurring in fertilizers was prepared and analyzed. The result, which is shown in table III, shows deviations between true and measured concentrations of 1-2 % (absolute). This is believed to be fairly representative for the accuracy of an average analysis.
2. An NPK 22-11-11 sample of known chemical composition was analyzed in terms of the crystalline components (which contained two solid solutions), from which the chemical composition was calculated back. The result which is given in table IV, shows deviations of the same order of magnitude as those in the previous example.

In daily practice, the method has proved to be a useful tool in following the changes that occur in fertilizers during storing and that may lead to desintegration of the granules, as well as in following the chemical reactions accompanying the take up of water.

Copies of the FORTRAN programs XPOWD and QXDA, with examples of in- and output, are available from the authors on request.

REFERENCES

1. H.P. Klug and L.E. Alexander, 'X-ray diffraction procedures', 2nd ed. John Wiley, New York (1974).
2. G.C. Johnson, Jr. and V. Vand, 'Advances in X-ray Analysis', 11, Plenum Press, New York (1968), p. 376.
3. 'International Tables for X-ray Crystallography' II, p. 92. The Kynoch Press, Birmingham (1959).