

THE "NORELCO" X-RAY DIFFRACTOMETER

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The X-ray spectrometer, described in this Review a number of years ago, has been completely re-designed. The new instrument, which has now been commercially available for some years, will be the subject of this and a following article. The present description is not intended for the instruction of potential users (these are served more fully by special publications of the Company): its main purpose is to reveal the technical basis and implications of the new design.

Introduction

The application of X-ray diffraction analysis as a tool for technical and scientific investigations has gained a firm footing in an ever-increasing number of industrial and university laboratories. The last decade has witnessed the successful introduction into this field of a new method, the direct measurement and recording of line intensities in X-ray diffraction patterns by means of a Geiger counter tube. An instrument based on this principle and known as the "Norelco" Geiger counter X-ray spectrometer was designed and marketed by the North American Philips Company in 1945, and described in this Review about six years ago ¹⁾. Fig. 1 offers a schematic picture of this instrument; the caption recapitulates some details concerning

the forming of the X-ray diffraction pattern and the focusing method.

This article describes a completely re-designed version of the spectrometer, whose performance and facilities represent a great advance on those of the first instrument. The new instrument, which from now on will be termed an X-ray *diffractometer* ²⁾, is pictured in fig. 2. It comprises three parts, which may be purchased separately and each of which can be used in conjunction with other equipment if desired: a basic diffraction unit (X-ray tube with high voltage generator and controls), a Geiger counter goniometer, and an electronic circuit panel with automatic recorder. The Geiger counter goniometer is shown separately in fig. 3.

Although this and a subsequent article will give a self-contained description of the diffractometer, it will be based on a comparison with the former instrument, as this should enable the reader more readily to grasp the significance of a number of details of the design.

Features of the diffractometer

The old and the new instrument alike offer the features characteristic of the method, viz., the instantaneous indication and recording of line intensities and a very considerable saving of time in cases where only part of the diffraction pattern need

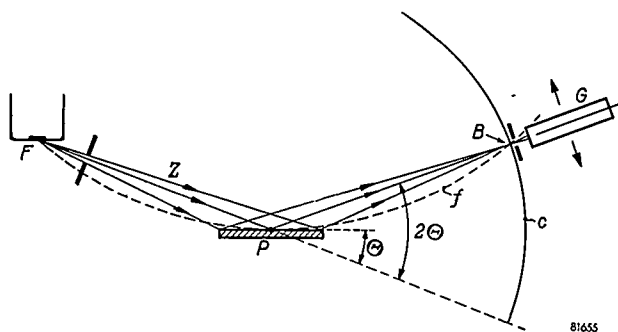


Fig. 1. Focusing arrangement of the Geiger counter X-ray diffraction instrument. A divergent X-ray beam Z coming from the focus F irradiates the surface of a flat specimen positioned at P . All the rays diffracted at Bragg angle Θ by suitably oriented crystallites on the specimen surface converge approximately to a single line, at B . Here the receiving slit of a Geiger counter tube G is placed. The counter tube is moved along the goniometer circle c about the axis P , in order to scan angles 2Θ ; the flat specimen is rotated about the same axis at half the angular speed, thus always remaining tangential to the "focusing circle" f through F , P , B (Bragg focusing). (The "focusing" effected is, of course, not true focusing in the optical sense.)

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¹⁾ J. Bleeksma, G. Kloos and H. J. di Giovanni, X-ray spectrometer with Geiger counter for measuring powder diffraction patterns, Philips tech. Rev. 10, 1-12, 1948.

²⁾ The instrument has been manufactured and marketed for some time by North American Philips Company, Inc., New York, U.S.A., again under the name of X-ray spectrometer. It has now been agreed to reserve the name X-ray spectrograph or spectrometer for the proper classical use in the measurement of X-ray spectra (and for a modified form of the X-ray diffractometer applied to X-ray fluorescence analysis).

Features of the instrument have been previously described by W. Parrish and E. A. Hamacher at A.S.X.R.E.D. meetings 1947-1949, in Science 110, 368-371, 1949 and in Trans. Instr. Meas. Conf. Stockholm 1952, p. 95.

A similar X-ray diffractometer is now in production in the Philips Works at Eindhoven; the electronic circuit of the latter instrument, although built on the same principles, is somewhat different in detail.



Fig. 2. The "Norelco" Geiger counter diffractometer consists of three independent parts: a basic diffraction unit (X-ray tube with high voltage generator and controls, at left), the high angle precision Geiger counter goniometer placed on top of it, and an electronic circuit rack with automatic 10" strip chart recorder (at right).

be analysed. In the new design, however, a number of substantial improvements were obtained, which may be enumerated as follows:

- 1) Higher resolution in the diffraction pattern.
- 2) Better accuracy in the measurement of diffraction angles and line intensities.
- 3) Higher diffraction angle range including the "back reflection" region up to angles of $2\theta = 165^\circ$.
- 4) More universal and more flexible use of the instrument. Two goniometers and (for example) two normal photographic powder diffraction cameras can be used simultaneously in conjunction with one basic diffraction unit.

A more precise and quantitative indication of these improvements will be given below, but this short list may serve us as a guide in the description that now follows.

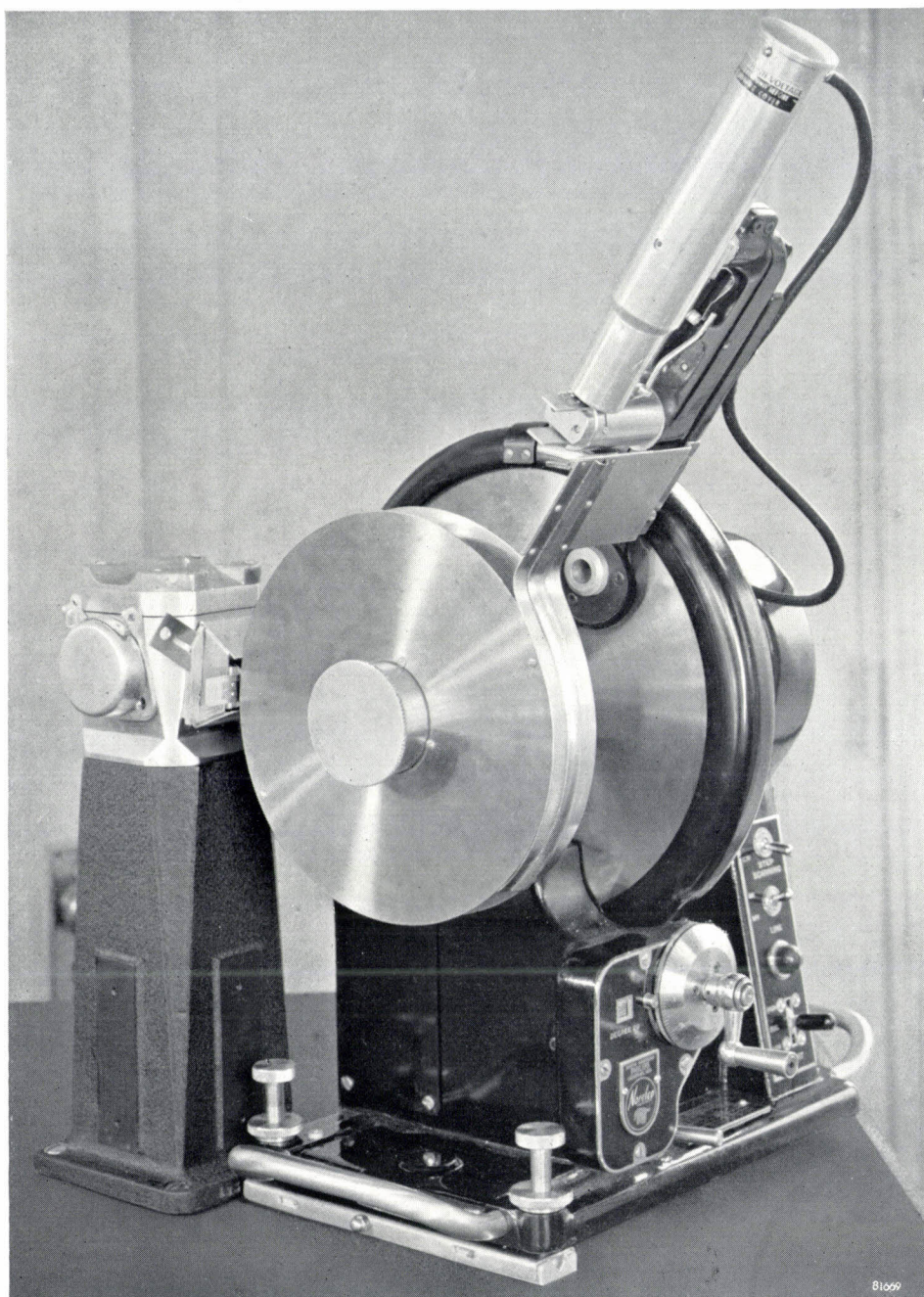


Fig. 3. The "Norelco" Geiger counter goniometer. The Geiger counter tube rigidly mounted on the scanning arm of the goniometer is seen at the top of the photograph. A handle for manual scanning and dials for reading degrees and fractions of degrees diffraction angle 2θ are seen near the base of the instrument.

Arrangement of X-ray tube and goniometer

For the sake of clarity we start with the last point, though this improvement was obtained by rather straightforward measures, and is not necessarily the most important for all users of the instrument.

In normal photographic diffraction techniques it has been common practice for a long time to use an X-ray tube with four windows so that four diffraction cameras can be operated simultaneously. The running time of the tube and the time of the operator are thus more usefully employed. *Fig. 4* shows

the arrangement. It should be noted that the windows of the X-ray tube may be divided into two pairs which transmit beams of different cross-section. The line-shaped focus produced on the target of the X-ray tube (10 mm \times 1.6 mm in the "Norelco" tube) is viewed at a small glancing angle to the target surface, since at a smaller apparent size it will exhibit a higher X-ray brilliance. Through the two opposite windows looking in the *long* direction of the focus at a glancing angle of say 6° , a small, approximately square focus of 1.6 \times 1.6 mm will be

seen, whereas the two remaining windows looking at the same glancing angle in the direction *perpendicular* to the line focus will offer a long and very thin apparent focus, of e.g. $10 \text{ mm} \times 0.16 \text{ mm}$.

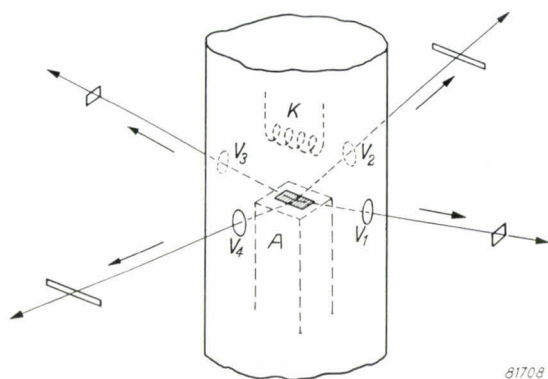


Fig. 4. Arrangement for using four diffraction devices simultaneously with a four-window X-ray tube. Through one pair of windows (spot focus windows V_1, V_2) the source is seen as a small square surface, through the other pair as a very narrow line (line-focus windows V_3, V_4). (In reality the anode A is positioned above the cathode K .)

Using the "line-focus" windows a large part of the focus area will remain unused in filling the narrow collimator system of a usual Debye-Scherrer camera with radiation, whereas when using the first mentioned "spot-focus" windows, radiation of the full focus area may be employed. The spot-focus windows

are therefore better suited for photographic cameras such as the Debye-Scherrer and single crystal goniometers, and the line-focus windows for focussing cameras such as the symmetrical back-reflection and crystal monochromators.

In the old X-ray spectrometer both the X-ray tube and the goniometer circle, along which the Geiger counter tube travels, were mounted in a horizontal position and the X-ray optics of the arrangement was based on the employment of a "spot-focus" window (cf. the article quoted in ¹).

In the new instrument, on the other hand, the X-ray tube is mounted with its axis vertical and the Geiger counter tube scans in the vertical plane, thus offering geometrical conditions favorable for using four windows, according to fig. 4. Moreover, the X-ray optics of the present design is based on the use of a line-focus window, thus leaving the two spot-focus windows available for photographic devices. Finally, the former spectrometer for the sake of simplicity and economy contained an air-cooled X-ray tube rated for only 35 kV, 125 W; the basic diffraction unit employed with the new instrument, is equipped with a normal water-cooled X-ray diffraction tube rated for 50 kV, 800 W (copper target), which produces a high X-ray intensity, sufficient for the photographic recording of weak diffraction lines.

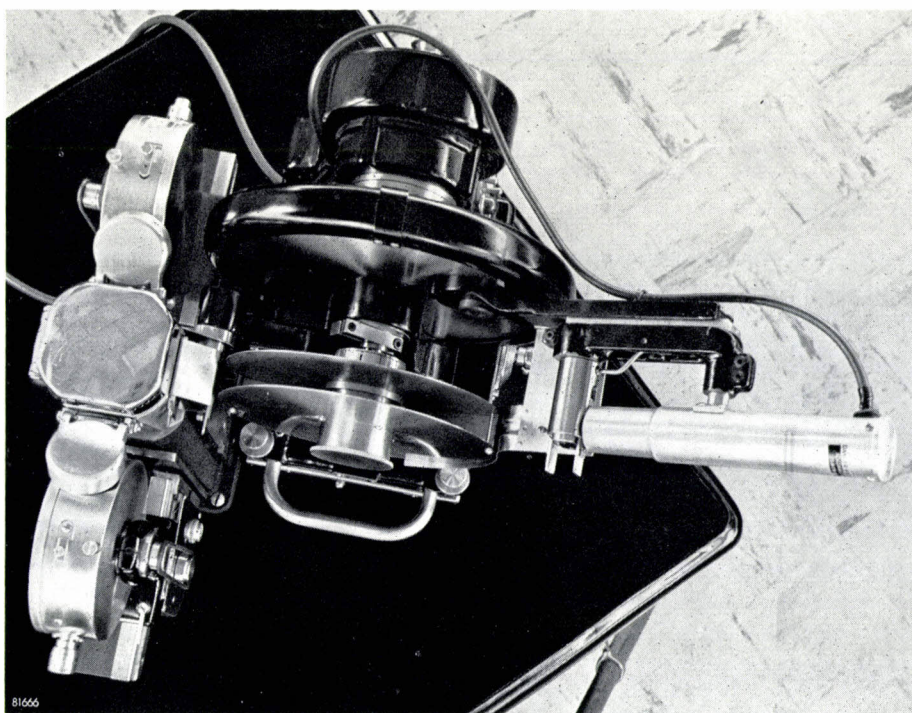


Fig. 5. Top view of basic diffraction unit, with three diffraction devices in simultaneous operation. On the left the anode end of the X-ray tube may be seen; on either side of it are two "Norelco" powder diffraction cameras; to the right is one of the new Geiger counter goniometers. Opposite the fourth window of the X-ray tube (i.e. to the far left in the photograph) another diffraction instrument can be placed.

The photograph *fig. 5* demonstrates the practicality of a simultaneous use of all four windows. In this instance one Geiger counter goniometer is used on one of the line-focus windows and two Debye-Scherrer cameras on the spot-focus windows; the fourth place is vacant.

The new X-ray optics, which is an essential innovation of the design, will presently be discussed at some length, but first it should be briefly explained how the high angular range of the diffractometer is achieved.

The high angular range

In the old instrument the angular range was limited mechanically since the movement of the Geiger counter tube beyond angles of $2\theta \approx 90^\circ$ was impeded by the anode end of the X-ray tube cover. With a water-cooled X-ray tube, as employed in the present diffractometer, the total anode surface required for cooling is rather small, so that the tube cover can be made to extend only slightly beyond the focus. This permits the Geiger counter tube to continue its travel to $165^\circ 2\theta$.

The increased X-ray tube rating again is essential for providing this facility, as the diffraction lines at these high angles (back reflection lines) are usually very weak.

It should be mentioned incidentally, that the useful X-ray intensity is raised not only by increasing the rating of the X-ray tube, but also by providing the tube with mica + beryllium windows instead of the formerly used Lindemann glass windows³⁾. The transmission of different types of windows is indicated in *Table I*. It is seen that the transmission of mica 0.012 mm thick is about 86% for the CuK α -line (1.54 Å) which is used in most cases. The transmission of a complete window consisting of such a sheet of mica and a thin beryllium plate is about 83%. A Lindemann window 0.25 mm thick transmits only 61% of CuK α . For a softer radiation which must be used in some diffraction investigations, e.g. CrK α radiation, the advantage of the mica + beryllium window becomes even more important.

The vacuum tight mica + beryllium windows are relatively cheap and easy to fabricate, making four-window X-ray diffraction tubes an economic proposition.

Table I. Calculated transmission (%) of different types of window for X-rays of different wavelengths.

Window	X-ray spectral line		
		CuK α	CrK α
Lindemann glass	0.5 mm	38	5
Lindemann glass	0.25 mm	61	22
Mica	0.012 mm	86	66
Beryllium	0.12 mm	96	90
Mica 0.012 mm + Be 0.12 mm		83	60

³⁾ The use of a mica entrance window in the Geiger counter tube to give a very high sensitivity has been described in the article quoted in¹⁾, where the application of mica exit windows for the X-ray tube was anticipated. A description of one type of X-ray tube (contact therapy tube) equipped with a mica + beryllium window was given in Philips tech. Rev. **13**, 75-77, 1951/52.

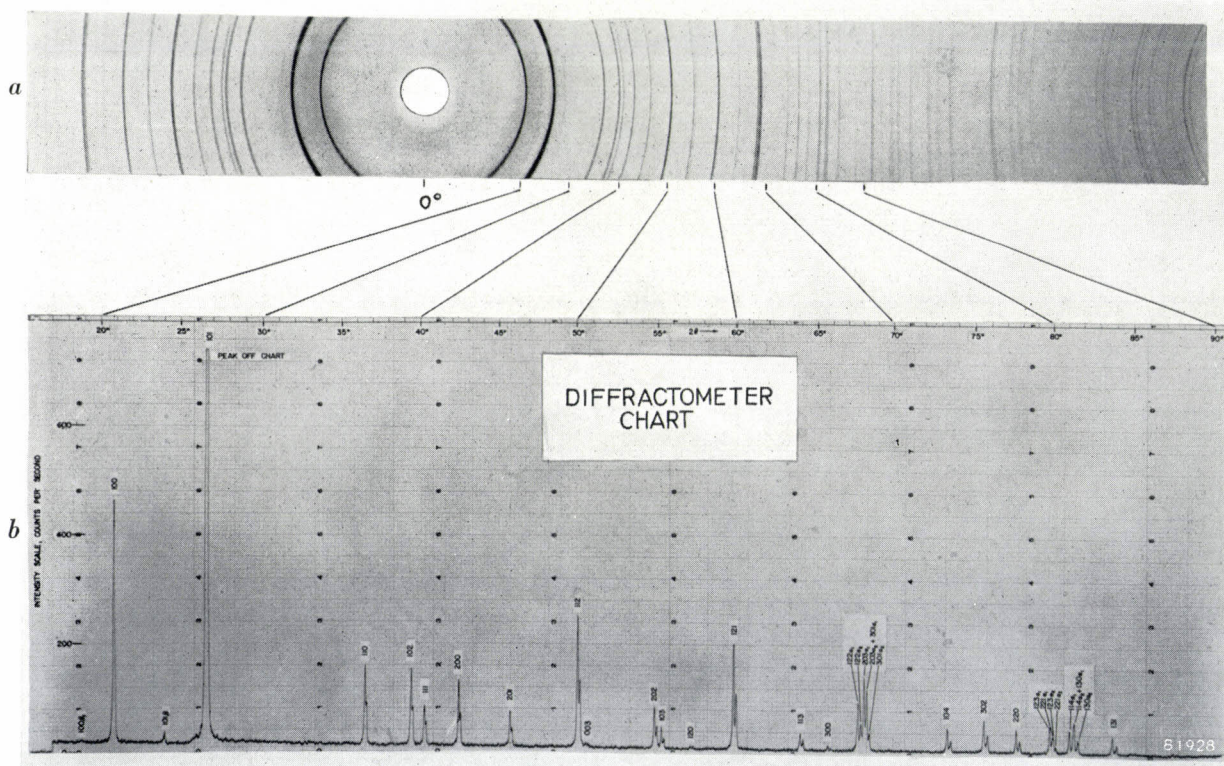


Fig. 6. *a*) X-ray diffraction pattern of quartz powder photographed with a 114.6 mm diameter Debye-Scherrer camera. Filtered CuK α radiation, 40 kVp, 20 mA, exposure time 2 hours. *b*) Automatically recorded chart obtained with the new Norelco X-ray diffractometer using the same X-ray tube conditions. Recording time 4.8 hours.

X-ray optics of the instrument

Perhaps the most notable improvement obtained in the diffractometer is its very high resolution, i.e. the extreme sharpness of the diffraction lines recorded. When using $\text{CuK}\alpha$ radiation and recording the diffraction pattern of a well crystallized powder specimen (whose diffraction lines have a very small natural width) with a receiving slit of about the same width as the source, the width at one half peak height of the recorded $\text{K}\alpha_1$ lines is about $0.1^\circ 2\theta$ in the front reflection region. The separation of the two lines produced by the $\text{CuK}\alpha_1$ and $\text{K}\alpha_2$ radiations, which in normal photographic techniques can be seen only at rather large diffraction angles ($2\theta > 110^\circ$) is visible at about $2\theta > 30^\circ$ in the diffractometer recordings, cf. fig. 6.

This high resolution is primarily obtained by reducing the geometrical width of the X-ray source: the focus of the X-ray tube measuring $10 \text{ mm} \times 1.6 \text{ mm}$ is viewed at an angle of about 3° to the

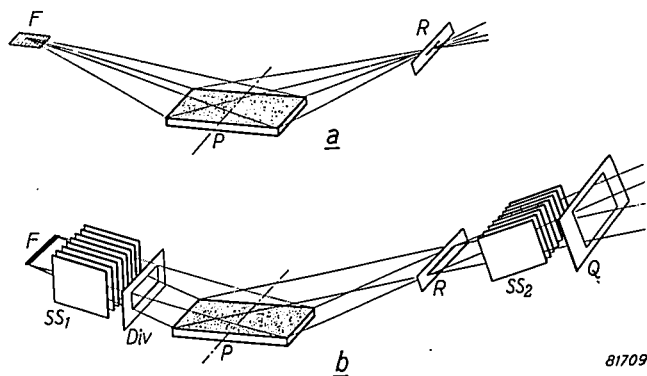


Fig. 7. *a*) X-ray optics of the former instrument (the "spectrometer" described in ¹⁾). A "spot-focus" source F is used. The receiving slit R must be rather short in order to get a narrow recorded line profile when scanning. P = flat specimen. *b*) X-ray optics of the new instrument. A "line-focus" source F is used. The receiving slit R has the same length as the source. This is made possible by the use of the parallel slit systems SS_1 and SS_2 , in conjunction with a chlorine quenched Geiger counter tube, as explained in the text. Div = aperture limiting slit, Q = scatter eliminating slit.

target surface perpendicularly to its length (i.e. a "line" X-ray tube window is being used as stated above). The effective source width with this arrangement is 0.08 mm as against 0.2 mm in the old spectrometer. Fig. 7 serves to illustrate the difference between the former and the present method.

The substitution of the effective line-source in fig. 7*b* for the spot-source in fig. 7*a* was made possible by two new elements in the design, viz. the introduction of a Geiger counter tube containing chlorine as a quenching agent and the insertion of two "parallel slit systems" in the X-ray beam as

shown in fig. 7*b* and fig. 8. Let us first consider what would happen if the parallel slit systems were omitted. The long effective X-ray source may be regarded as a large number of point-sources aligned in a horizontal direction parallel to the axis of the specimen and of rotation of the counter tube.

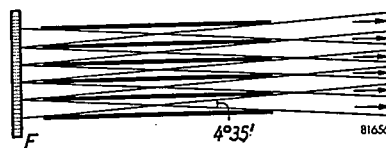


Fig. 8. Parallel slit system consisting of a number of molybdenum foils 0.025 mm thick, transmitting X-rays directed parallel to the foils and suppressing rays entering obliquely. F = focus. (The effect may be compared to that of the well-known Potter-Bucky grid for suppressing scattered radiation in X-ray diagnostics.)

Considering a number of imaginary vertical planes perpendicular to the axis of the goniometer, each point-source in its own vertical plane will give rise to a pattern of very narrow diffraction spots. In fact, however, owing to the horizontal divergence of the X-rays emitted from the focus each point-source will produce horizontal diffraction lines and thus contribute to the patterns in the planes of all the remaining point-sources. As these lines are shaped as ring sections (with a curvature largest for angles 2θ approaching 0° and 180° , as is well-known from Debye-Scherrer photographs, cf. fig. 6*a*), the superposition of the contributions of the aligned spot-sources would result in considerable asymmetric line broadening as illustrated in fig. 9. This is avoided by the insertion of the two parallel slit systems, each of which consists of a number of thin (0.025 mm) molybdenum foils placed in the X-ray beam in such a way that the narrow spaces between adjacent foils may be regarded as the above-mentioned imaginary planes. Each individual spot of the line

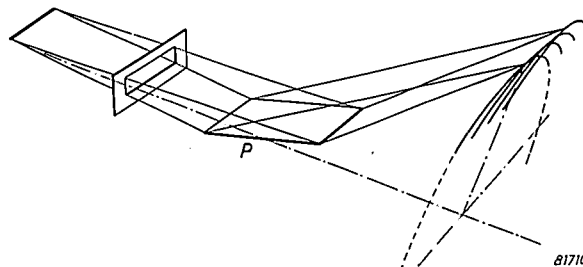


Fig. 9. If the parallel slit systems in fig. 7*b* are omitted, each point of the line source in a given specimen position produces a diffraction line of its own, covering the whole length of the counter window and being curved as a ring with its centre of curvature in the $0^\circ 2\theta$ direction. The curved lines of all source points are integrated to form a broadened asymmetric line of asymmetric profile.

source is now substantially prevented from contributing radiation outside its "own" plane, as these oblique radiations are strongly absorbed on their long path through the foils; the horizontal divergence of rays in each system is restricted to the very small value of $4^\circ 35'$, resulting in the very sharp lines demonstrated by fig. 6b. Even at small diffraction angles ($2\theta = 5$ to 10°), where the curvature of lines is rather pronounced, the measured line profiles still have a high symmetry; see fig. 10.

The Geiger counter tube positioned with its window opposite a diffraction line will indicate the line intensity by integrating the X-ray energy received along the length of the line (parallel to the axis of rotation of the specimen). This is where the

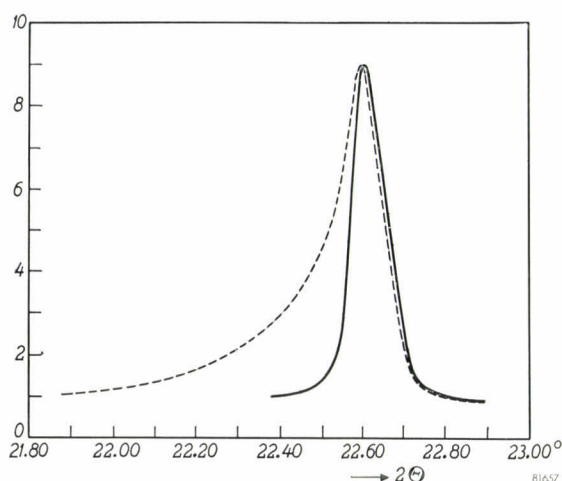


Fig. 10. Profile of a diffraction line measured with the Geiger counter diffractometer, without the parallel slit systems (broken line) and with the parallel slit systems (full line).

second factor mentioned above, i.e. the addition of chlorine to the gas filling of the counter tube, enters the picture. The tubes formerly used contained argon for absorbing the X-ray quanta (and giving rise to photo-electrons) and methylene bromide as a quenching agent. These tubes had a rather limited "sensitive volume": only those quanta that passed within about 1.5 mm from the axial anode-wire had a high probability of being counted. Hence the integration was effectively accomplished over only a 3 mm length of the line. Reflections from the whole specimen height (10 mm) were nevertheless included in this integration owing to the rather large horizontal divergence permitted. With the X-ray optics of the goniometer illustrated in fig. 7b, however, the limitation of the line length to 3 mm at the entrance of the Geiger counter tube would mean that reflected rays emanating from the ends of the specimen surface are not detected and that the ends of the X-ray source do not contribute to the integrated line intensity. It is an essential feature of the revised

X-ray optics that the chlorine counter tubes possess a much larger sensitive volume, covering the complete 10 mm width of the beam in the goniometer (fig. 11): this ensures that full use is made of the

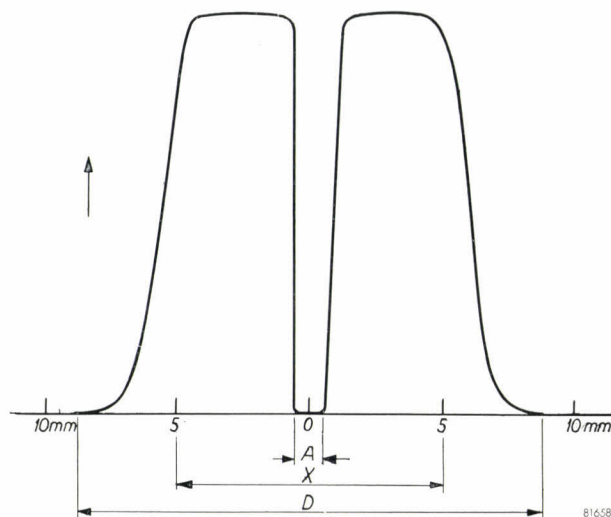


Fig. 11. Radial distribution of sensitivity (in arbitrary units) of chlorine-quenched Geiger counter tube (type 62019). A = width of the axial anode wire and bead. X = width of X-ray beam when using the new X-ray optical system. D = inside diameter of the Geiger tube.

focus as well as of the specimen area (the latter is important for good averaging of the crystallite reflections).

The chlorine counter tubes also offer other advantages: for example, a very long life, a rather low working voltage and a long "plateau", but we shall not dwell on these points in this article⁴). A photograph of the counter tube in its present form is reproduced in fig. 12.

Although the Geiger counter tube in its present form has excellent characteristics as a radiation detector, other types of detectors have been developed for use in the diffractometer, viz. special forms of the proportional counter and the scintilla-

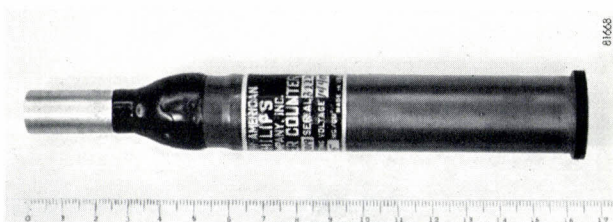


Fig. 12. The Geiger counter tube, type 62019, used in the "Norelco" diffractometer. The end window where the X-rays enter the tube (in a direction parallel to the tube and its axial anode wire) is made of mica 0.012 mm thick. The gas filling consists of argon to a pressure of approximately 55 cm Hg with a few mm Hg chlorine as a quenching agent. The operating voltage is 1400 to 1500 volts, the plateau is at least 300 volts long.

⁴) See N. Warmoltz, Geiger Müller counters, Philips tech. Rev. 13, 282-292, 1951/52.

tion counter. Both of them have the advantage of a very short "dead time", allowing counting at rates many times higher than with the Geiger counter. Moreover, they offer the possibility of pulse height discrimination, which in some cases may be useful. An example is the X-ray diffractometry of radioactive samples, where the background caused in the diffraction pattern by the radioactivity can be reduced very effectively when using a scintillation counter⁵⁾. The latter has a higher quantum efficiency than all other radiation detectors (nearly 100%) for the wavelengths normally used in X-ray analysis.

It is interesting to compare the old and the new instrument from the viewpoint of the number of counts per second obtained for a given diffraction line. It should be pointed out that with a given real focus area a crystallite of the specimen "seeing" the whole focus will receive the same radiated energy per second regardless whether the focus is viewed from its broad or from its narrow side and whatever viewing angle is chosen⁶⁾ (within certain limits). This well known basic fact would mean in our case that the increased resolution would not entail a sacrifice of line intensity except in so far as the horizontal divergence of the rays has been somewhat decreased, permitting a crystallite to see only part of the focus. This loss, however, is amply made good by the much higher radiation output per cm² of the focus (higher specific loading of the focus made possible by the water-cooling).

The goniometer; alignment procedure

In order to obtain full profit from the high resolution achieved it was necessary to ensure that diffraction angles could be measured with adequate accuracy. A large goniometer radius was therefore chosen (radius 17 cm instead of 13 cm with the former instrument⁷⁾), resulting in a large dispersion of the diffraction pattern. At the same time a completely new mechanical design was adopted for the goniometer, enabling the setting and direct reading of the Geiger counter tube position to an accuracy of $0.01^\circ 2\theta$ or better.

⁵⁾ T. R. Kohler and W. Parrish, X-ray diffractometry of radioactive samples, to be published in Rev. sci. Instr. Cf. also: J. Taylor and W. Parrish, Absorption and counting efficiency data for X-ray detectors, also to be published in Rev. sci. Instr.

⁶⁾ This is due to the fact that the impinging electrons penetrate only very slightly into the target whereas the X-rays produced at a depth where the electrons are stopped emerge from the target practically unimpeded even in directions nearly parallel to the target surface. Thus from all directions (in front of the target) the same volume of target material is seen to contribute to the radiation. See for example Philips tech. Rev. 3, 261, 1938.

⁷⁾ It should be remembered that most diffraction cameras have diameters of 5.7 or 11.4 cm. Increasing the radius beyond 17 cm did not seem desirable because of increasing air absorption for long wavelengths and air scatter; moreover, at 17 cm, the size of the instrument is still reasonable.

A cross-section drawing of the goniometer is shown in fig. 13. It consists essentially of a precision 10" worm wheel and worm drive (W_1 and W_2). The wheel carries the Geiger counter tube rigidly attached to it in a radial position. The main dial permitting direct reading of 2θ to 0.01° is fixed on the worm, complete dial revolutions being registered by a subsidiary gear and a mechanical counter. This accuracy is achieved by "cold working" the wheel and permanently loading the worm against it⁸⁾. The specimen under investigation, which is made in the shape of a flat plate 20×10 mm (P in fig. 13), is placed in a holder carried by a hollow shaft positioned within the hollow bearing of the worm wheel and coupled to the latter by a set of accurate herringbone gears. These rotate the specimen at exactly one-half the angular speed of the Geiger tube arm.

To ensure the above-mentioned accuracy of the diffraction angle measurements, the zero angle position of the goniometer must be set to a precision of better than $0.01^\circ 2\theta$. This is achieved as follows. A narrow slit or pin-hole is placed in the specimen holder (fig. 14a). The reference or banking surface of the holder contains the specimen rotation axis, which is made in the factory to coincide with the goniometer axis to better than 0.01 mm. The goniometer arm is turned slowly in 0.01° steps across the X-ray beam transmitted by the slit or pin-hole. The position of maximum intensity thus found is the zero angle position, provided the slit was placed

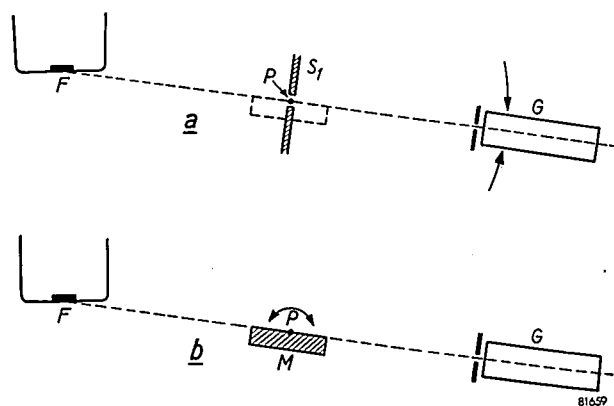


Fig. 14. Alignment and calibration procedure for the goniometer. a) A narrow slit S_1 is placed at the specimen rotation axis P . The Geiger counter tube G is turned to the position in which the largest intensity of the direct X-ray beam transmitted by S_1 is recorded (F = focus of X-ray tube). This is the zero angle position of the goniometer.

b) A flat machined piece of metal M is fastened on the specimen holder and rotated so that maximum intensity of the direct X-ray beam is received by the Geiger counter tube in its zero angle position. The specimen reference plane is then exactly parallel to the zero angle direction, and the exact ratio 1:2 of specimen angle and counter tube angle is obtained when scanning.

⁸⁾ This process is conducted in such a way that the resultant surface hardening almost eliminates further wear.

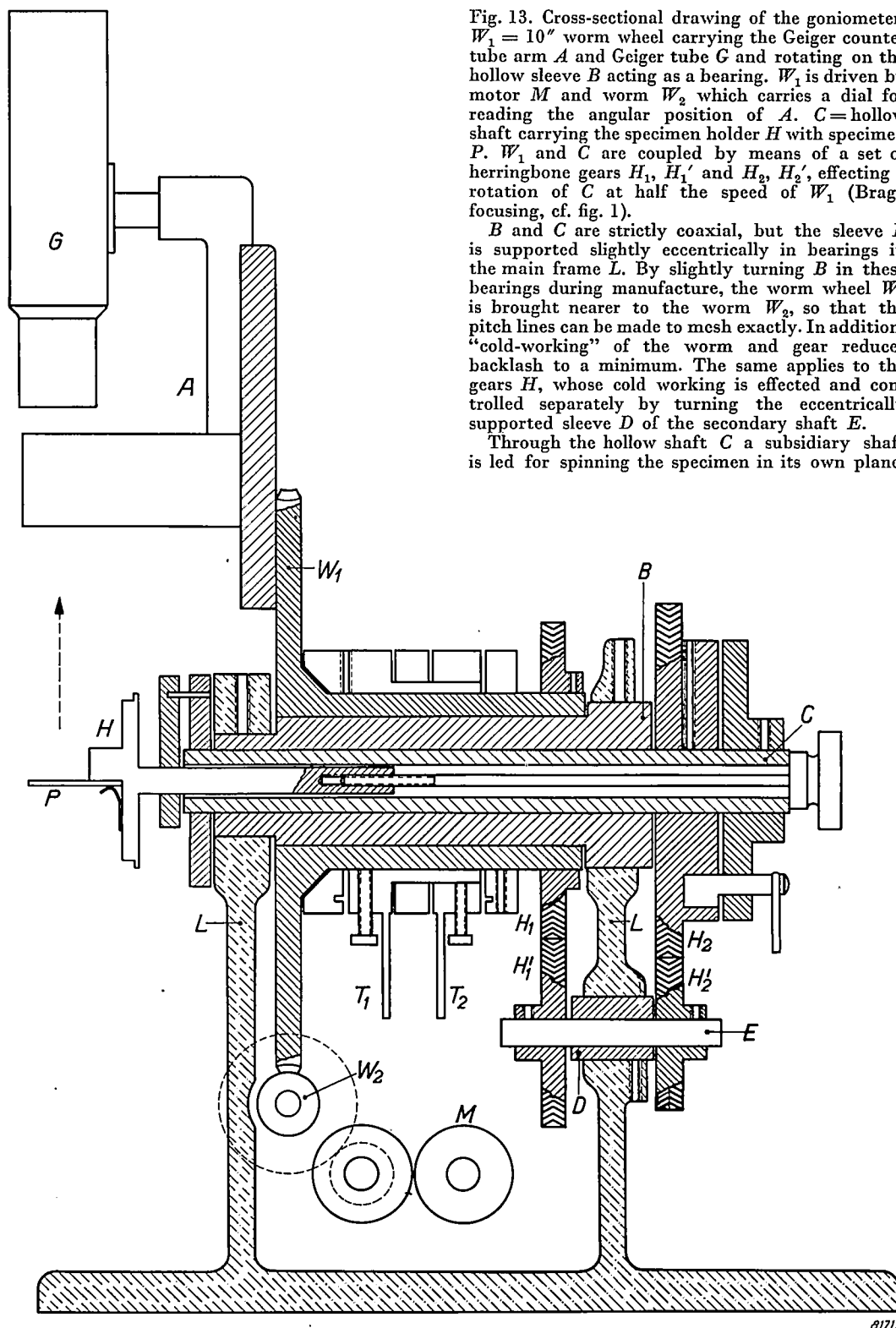


Fig. 13. Cross-sectional drawing of the goniometer. $W_1 = 10^\circ$ worm wheel carrying the Geiger counter tube arm A and Geiger tube G and rotating on the hollow sleeve B acting as a bearing. W_1 is driven by motor M and worm W_2 which carries a dial for reading the angular position of A . C = hollow shaft carrying the specimen holder H with specimen P . W_1 and C are coupled by means of a set of herringbone gears H_1, H_1' and H_2, H_2' , effecting a rotation of C at half the speed of W_1 (Bragg focusing, cf. fig. 1).

B and C are strictly coaxial, but the sleeve B is supported slightly eccentrically in bearings in the main frame L . By slightly turning B in these bearings during manufacture, the worm wheel W_1 is brought nearer to the worm W_2 , so that the pitch lines can be made to mesh exactly. In addition, "cold-working" of the worm and gear reduces backlash to a minimum. The same applies to the gears H , whose cold working is effected and controlled separately by turning the eccentrically supported sleeve D of the secondary shaft E .

Through the hollow shaft C a subsidiary shaft is led for spinning the specimen in its own plane.

exactly on the goniometer axis. The unavoidable error in the placing of the slit is compensated by repeating the procedure with the specimen holder revolved through 180° . The mean value of the two maximum intensity positions read is the true zero angle position. With the arm in this position, the dial is unscrewed and reset to 0.00° .

When this has been done, the specimen holder in this goniometer position must be adjusted so that the surface of the flat specimen will be exactly parallel to the zero angle direction, in order that this surface on scanning will always be oriented at *exactly* one-half the angle of the Geiger counter tube arm (cf. fig. 1). This so-called 2:1 setting is

performed (with the goniometer arm set at 0.00°) by placing a flat machined piece of metal in the specimen holder (fig. 14b), and rotating the holder by means of a micro-adjustment until maximum intensity of the direct X-ray beam is obtained.

As was mentioned above, the reference surface of the specimen holder is manufactured so that it coincides with the goniometer axis to better than 0.01 mm. If diffraction occurs only at the specimen surface, which is approximately the case for a strongly absorbing material, and if the specimen were removed only 0.075 mm from the axis of rotation, the peak positions of the diffraction lines would be shifted $0.045^\circ 2\theta$ at $2\theta = 45^\circ$.

Relative line intensity measurements

Since the Geiger counter method of recording X-ray diffraction patterns (unlike the film method) requires point-by-point measurements, the intensity of the primary X-ray beam must be highly stabilized to make relative measurements of the diffracted intensity reliable. The X-ray generator of the basic diffraction unit employed now operates on full wave rectified voltage enabling more reliable regulation than the previous instrument with a self-rectifying X-ray tube. Long term stabilization to better than 0.2% for both voltage and current of the X-ray tube is obtained by use of an electronic voltage regulator and a feedback type current regulator⁹⁾.

Intensity measurements for weak lines are facilitated by the wavelength response of the argon-filled Geiger counter tube, as was discussed in the article quoted above¹⁾; the background intensity of the diffraction pattern due to the short wavelength continuous radiation is detected with a relatively low efficiency, resulting in a low and even background, comparing very favorably with that of photographically recorded patterns, for equal line peak height. The recording and measuring of weak lines is further improved by the higher intensity of the water-cooled X-ray tube. It is important to note that better accuracy of the intensity measurement is achieved also for *strong* diffraction lines, owing to the full wave rectification. It is well known that for the comparison of high and low line intensities, the non-linear response of the Geiger counter tube, which is caused by the "dead-time" after every recorded count, is a fundamental limitation. By using full wave instead of half wave rectified voltage across the X-ray tube, with the same total number of quanta arriving

in a random fashion at the Geiger counter tube the average time-separation of two quanta will be doubled, thus diminishing the influence of quanta arriving in "dead time" periods and hence shifting the non-linearity effect to higher intensities (twice the former limit).

If line intensities in different 2θ regions have to be measured, the differences of illumination of the 20 mm width of the specimen rotating in the fixed primary beam must be taken into account. With a beam of angular aperture 1° in the scanning plane, the 20 mm specimen width is just covered when the specimen is positioned at $17^\circ 2\theta$. As the angle increases, only part of the specimen is illuminated. This does not affect the relative line intensities, provided the sample is of sufficiently uniform reflecting power over its whole surface. For accurate measurements we have found it useful to rotate the specimen in its own plane (at moderate speed, e.g. 77 rev/min) in order to smooth out the statistical fluctuations obtained even with crystallites smaller than $20\ \mu$ in the specimen. Such a rotation is performed by means of a subsidiary shaft led through the hollow specimen holder shaft (C in fig. 13) of the goniometer and driven by a motor placed at the rear of the instrument. In this way congestion around the specimen is avoided and enough clearance is provided for mounting high or low temperature specimen chambers or other accessories.

In order to make use of the whole specimen surface in the back reflection region, where line intensities are very low, the angular aperture of the primary beam is increased to 4° by inserting a larger aperture-limiting slit. On the other hand, for small Bragg angles, $2\theta < 17^\circ$, smaller apertures must be used, so that the beam does not exceed the specimen width. (This is desirable even when line intensities are not to be measured, in order to avoid excessive scattering. With very small apertures, down to $5'$, it is thus possible to measure diffraction angles corresponding to lattice spacings up to about $90\ \text{\AA}$, using $\text{CrK}\alpha$ radiation.) The divergence slits, as well as the other slits shown in fig. 7b, are designed for maximum reproducibility and convenience by having *fixed* apertures. All slits are constructed of molybdenum, for high X-ray absorption and good mechanical strength.

Scanning of the pattern; counting methods

It will be remembered that due to the random arrival of quanta the accuracy of the line intensity measurement depends on the total number of counts recorded by the Geiger counter tube when traversing

⁹⁾ The Eindhoven version of the diffractometer employs a specially designed basic diffraction unit (type PW 1010) containing a more elaborate stabilization device.

the angular region of the diffraction line¹). In order to conform to specific accuracy requirements, different counting methods can be adopted. With the simplest method, which is used for most routine analyses, and for recording charts as in fig. 6b, the pattern is continuously scanned and the average current intensity produced by the current pulses of the Geiger tube is measured. Automatic scanning is accomplished by driving the goniometer by a fractional horsepower electric motor (*M* in fig. 13). A contact on the main worm shaft of the goniometer with a cam for 0.5° intervals in 2θ actuates a degree marking pen on the strip chart recorder. The accuracy of the recorded line intensities depends on the scanning speed. Through the use of changeable spur gears, scanning speeds (in either direction) of $1/8$, $1/4$, $1/2$, 1 or 2° per min can be selected. A wider receiving slit is used for scanning at higher speed in order not to lose too much in intensity. Owing to the high X-ray intensity of the tube the accuracy is fairly good even at the highest scanning speed. The chart reproduced in fig. 6b was recorded at medium speed ($1/4^\circ$ /min); the recording took about 5 hours.

The same method can be employed for investigating only small parts of a diffraction pattern. Use is then made of adjustable upper and lower limit stops provided on the goniometer (T_1 and T_2 in fig. 13) for stopping or reversing the scanning motion.

For higher accuracy, manual point-by-point plotting of a chart, using the so-called fixed count method, is sometimes desired. In this case a discontinuous stepwise movement of the goniometer is substituted for the continuous scanning movement. The mechanism causing this stepwise movement is shown in fig. 15. It can be adjusted to advance the Geiger counter tube in steps from 0.01° to $0.05^\circ 2\theta$. This type of scanning motion is required also for the recording *counting rate computer*, a device developed to combine the advantages of fully automatic operation and high accuracy in a wide range of intensities.

For the sake of completeness a fourth method of obtaining data from the goniometer should be mentioned, viz. the integrated area measurement. This method and the other methods mentioned above will be described in detail in a subsequent article. All the circuits necessary for measurements according to these methods are contained in the cabinet shown on the right of fig. 2. The conversion from one method to another can be done simply and quickly by means of tap switch selectors.



Fig. 15. Mechanism for stepwise movement of the goniometer arm. The goniometer arm rotates through 0.25° for each revolution of the shaft geared directly to the motor. For the stepwise movement this shaft is fitted with a wheel with 25 triangular-shaped teeth which is advanced one tooth at a time by a pin on the driving member on the motor shaft. With one pin on the driving member one revolution of the motor shaft advances the goniometer by $0.01^\circ 2\theta$, with two pins 0.02° , etc. The driving member can accommodate up to 5 pins (see driving member in the foreground). Indexing is achieved by a spring loaded roller which falls between the teeth of the wheel.

Summary. The "Norelco" X-ray diffractometer, which has now been commercially available for some years, is a completely re-designed version of the Geiger counter X-ray spectrometer formerly described in this Review. The new version incorporates an improved resolution of diffraction lines ($\text{CuK}\alpha_1\text{-}\alpha_2$ separation visible at $2\theta > 30^\circ$), better accuracy in the measurement of diffraction angles (readings to 0.01° in 2θ) and of relative line intensities, and a higher diffraction angle range (up to $2\theta = 165^\circ$). These improvements are due to the use of a new X-ray optical system together with a normal basic diffraction unit having a high-powered water-cooled X-ray tube with mica-beryllium windows, and to the design of a high precision mechanical Geiger counter goniometer. The new X-ray optics is based on the use of a line-focus source. Owing to this feature and to a vertical arrangement of the X-ray tube and goniometer circle, it is possible to use two goniometers and two normal photographic powder diffraction cameras simultaneously with the four window X-ray tube of one basic diffraction unit. Scanning speeds varying from $1/8^\circ$ to 2° per minute can be selected; alternatively an automatic stepwise movement of the goniometer is possible. Apart from automatic recording, either continuously or point-by-point, the electronic circuits developed for the instrument permit the application of special counting methods. The various counting and recording methods will be described in a following article.