GEOLOGIE EN MIJNBOUW VOLUME 47 (6), p. 415-422 1968

THE TPD ELECTRON PROBE X-RAY MICRO ANALYZER

L.A. FONTIJN[1], A.B. BOK[1] and J.G. KORNET[1]

SUMMARY

The article describes an electron probe X-ray micro-analyzer specially designed for mineralogical investigations and constructed for the Department of Mining Engineering of the Technological University, Delft. A miniature magnetic lens is used in the electron optics making it possible to employ a standard Leitz polarization microscope. The specimen can be rotated around the microscope axis and translated in two orthogonal directions.

INTRODUCTION

The principle of the method is already widely known: an accurately focused electron beam is directed at a particular point on the surface of a sample whose chemical composition it is desired to ascertain. Owing to the small diameter of the electron spot, which is in the order of 1 μm, and the slight depth of electron penetration into the specimen, which is likewise in the order of 1 μm, a very small volume of material is irradiated by the electron beam. The X-ray spectrum includes the characteristic radiations of the various elements at the point of impact of the electron probe. Spectographic analysis of this X-ray spectrum permits the concentrations of these elements to be determined. The spot nature of the analysis is a refinement on chemical analysis by X-ray fluorescence and a more direct method of obtaining quantitative measurements.

In the microprobe, the required size and shape of the iron shrouded objective lens always limit the freedom of design for both light and X-ray optics. The various philosophies behind these limitations have resulted in a wide variety of microprobes. The TPD microprobe uses a miniature magnetic lens as the objective lens. The electron optics are scaled down, providing space for a good polarization microscope (Leitz), which is of particular importance for work on mineralogy. The light and electron optical system axes are separated, the electron optical axis being inclined at 45° to the horizontal specimen plane. This inclined position of the electron optics in theory permits any take-off angle of the X-rays to the specimen plane. In the TPD microprobe two Philips Norelco spectrometers allow a take-off angle of 30° owing to their being placed upside down.

The main design features of the TPD microprobe are:

1. The use of a standard Leitz microscope mounted entirely outside the vacuum, permitting observation of the specimen during X-ray analysis. Resolution is 1 μm and polarization facilities are included.
2. The electron optical axis is inclined at 45° to the horizontal specimen plane, enabling the electron beam to clear the light objective and maintaining a short working distance in the miniature magnetic lens. Defocusing due to the skew illumination is corrected.
3. The X-ray take-off ranges from 0°...60° and may be extended to 90° if the light optics are omitted. Owing to the smallness of the miniature lens, the spectrometers and detectors may be mounted at an azimuthal angle of 300° around the electron probe.
4. The specimen holder fits on a cross-table mounted on a turn-table so that the specimen can be translated in x, y directions and rotated around the turn-table axis, which coincides with the microscope axis.

Besides a complete microprobe system built for the Department of Mining Engineering of the Technological University, Delft, the same electron and light optics as used in the apparatus have been placed on a Philips Norelco Probe at the Analytical Chemical Laboratory of the State University, Utrecht.

[1] Institute of Applied Physics TNO-TH, Delft.

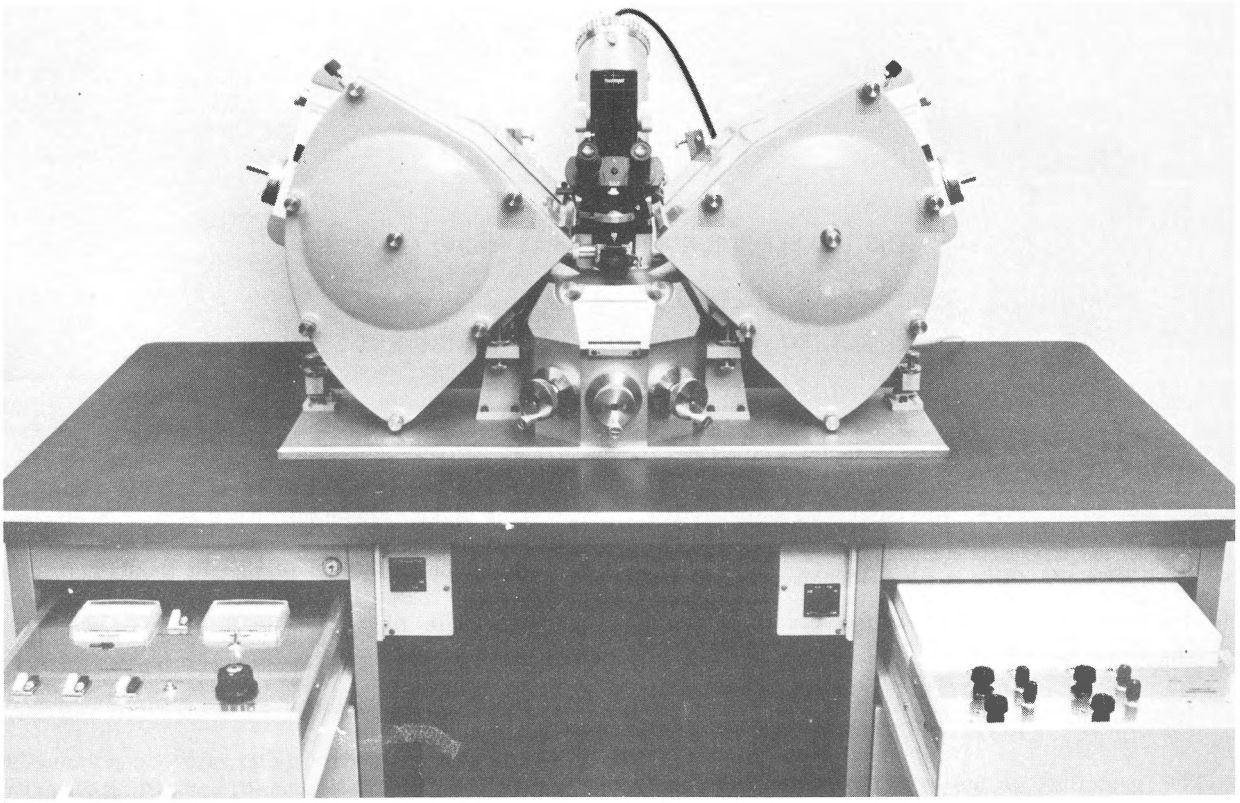


Fig. 1 - General view of the TPD microprobe, with at the left: vacuum system, at the right: lens currents regulation.

DESCRIPTION OF THE MICROPROBE SYSTEM

The microprobe consists of four main parts: electron optics, light optics, X-ray optics and specimen movements system. These four main parts will be described first and then the further equipment with reference to photographs and drawings.

Electron optics

The electron optical axis, inclined at 45° to the horizontal specimen plane, is determined by the fixed positions of the anode and the miniature magnetic lens. Otherwise the electron optics are conventional and consist of the following parts:

(a) a triode-type electron gun is used to accelerate the generated electrons, with a standard filament 0.125 mm in diameter. All electron gun adjustments are possible without breaking the vacuum, including:
1. adjustment of filament height relative to the Wehnelt cylinder;
2. centring of filament in the Wehnelt opening;
3. centring of Wehnelt-cylinder and filament relatively to the fixed anode.

The electron gun H.T. supply is variable between 4 and 50 kV, while the Wehnelt tension can be changed with resistors in the H.T. supply. In order to obtain maximum gun performance, measurements of brightness were made. Special attention was paid to the vacuum conditions in the gun chamber for reasons of filament life.

(b) The condenser lens has an iron circuit in order, together with the objective lens, to obtain adequate geometrical demagnification (max. 250 x) of the gun cross-over. To avoid deflection defects by a change in lens excitation owing to misalignment of the pole pieces, the upper pole piece can be centred.
The beam-limiting apertures are positioned between the condensor and objective lens in a rotatable holder and are easy to change.
The scanning coils, a double deflection system, are mounted outside the vacuum system around a brass tube between the aperture holder and the miniature lens. The stigmator and correction deflection coils are just above the objective lens.

(c) The objective lens is a miniature magnetic lens constructed for operation up to 50 kV. It was tested on an electron optical bench. As regards its spherical aberration coefficient, close agreement was obtained between calculated and measured values. At ten times demagnification

1 microscope height control
2 Philips X-ray spectrometer with mica cristal; take-off angle 30°
3 adapter fo, camera
4 Leitz polarization microscope
5 binocular viewing head
6 Bertrand lens
7 analyzer
8 polarizer
9 objective lens
10 vacuum seal for microscope
11 contact ring for absorbed electron signal
12 vacuum chamber door
13 specimen holder
14 knob of specimen rotation around the microscope axis
15 part of the 2 orthogonal x-y traverses
16 centring adjustment
17 polarizer
18 specimen height control knob
19 transmitted light attachment
20 table top
21 vacuum connection to oil diffusion pump
22 miniature magnetic lens with coil for defocusing correction
23 stigmator and correction deflection coils
24 scanning deflection coils
25 beam limiting aperture holder
26 aperture
27 fluorescent screen
28 condenser lens
29 pole piece centring
30 aperture
31 anode
32 Wehnelt cylinder
33 filament
34 electron gun
35 high-tension cable
36 gun-earth contact

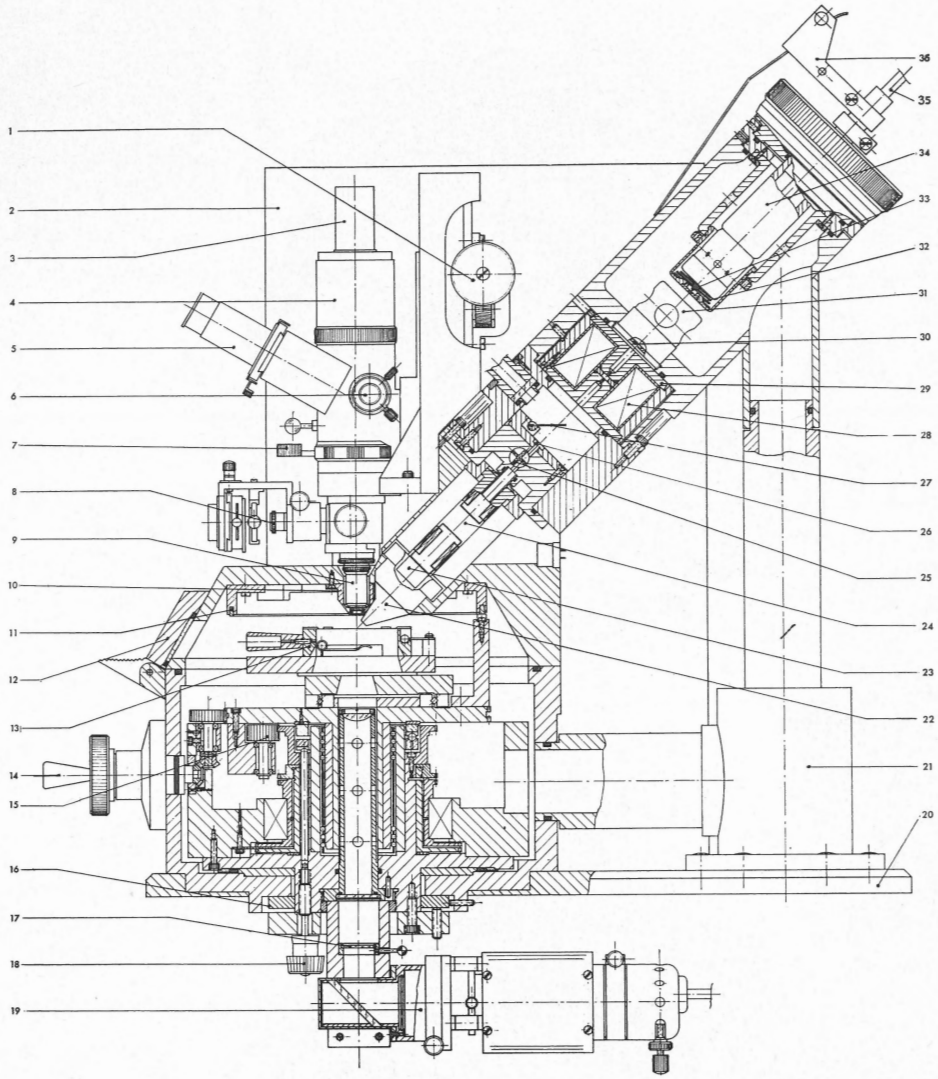


Fig. 2 - Cross-section of the TPD-microprobe.

the value was $Cs/f^3 = 3.5 \times 10^{-3}$ mm^{-2} ($\pm$ 15%). Cs is the spherical aberration coefficient and f the focal length. The Cs value in the instrument is 40 mm. A first order stigmator, placed above the lens, is necessary to correct astigmatism. When the specimen is scanned by the electron beam, defocusing of the electron spot due to skew illumination is corrected with an extra layer of windings around the main coil of the miniature lens. As the scanning coils are mounted outside the vacuum, they can easily be rotated so that defocusing occurs in one scanning direction.

In order to obtain the right variation of lens excitation to correct defocusing, the deflection coils for the direction in the plane of the electron optical axis and the normal on the specimen plane are connected in series with the extra windings on the miniature lens. This gives a good first order approximation for correcting defocusing. By induction in the copper jacket of the miniature lens, a frame frequency up to 10 Hz is usable for defocusing correction.

Light optics

The light optics are a Leitz refractive polarization microscope. This is completely outside the vacuum system, a glass plate forming a vacuum seal between the objective lens and the specimen. The microscope axis is perpendicular to the specimen surface. The specimen can be observed during X-ray analysis by transmitted or reflected light from the probe side. By using the different objective lenses and eyepieces, magnification can be chosen in the range from 50 to 500 x. The field of view is

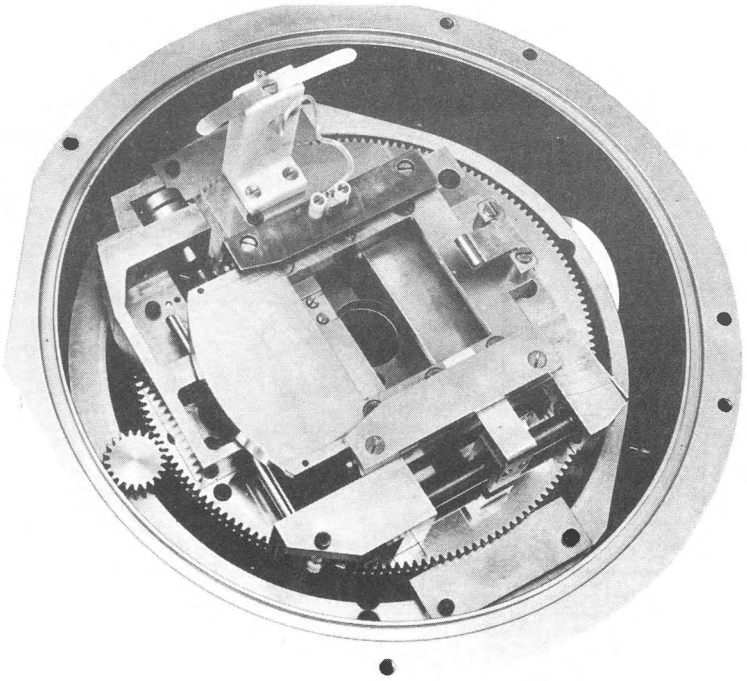


Fig. 3 - The specimen movements system. Rotation at every point of the specimen (not shown) is possible. Translation in two orthogonal directions of the specimen on the turn-table.

at least 600 μm. The microscope assembly includes a binocular viewing head, camera tube, polarized light attachments and facilities for using illumination filters. The objective lenses are the same as used in the Leitz universal turn-table microscope. For our purpose these have the advantage of a large free object distance of about 15 mm.

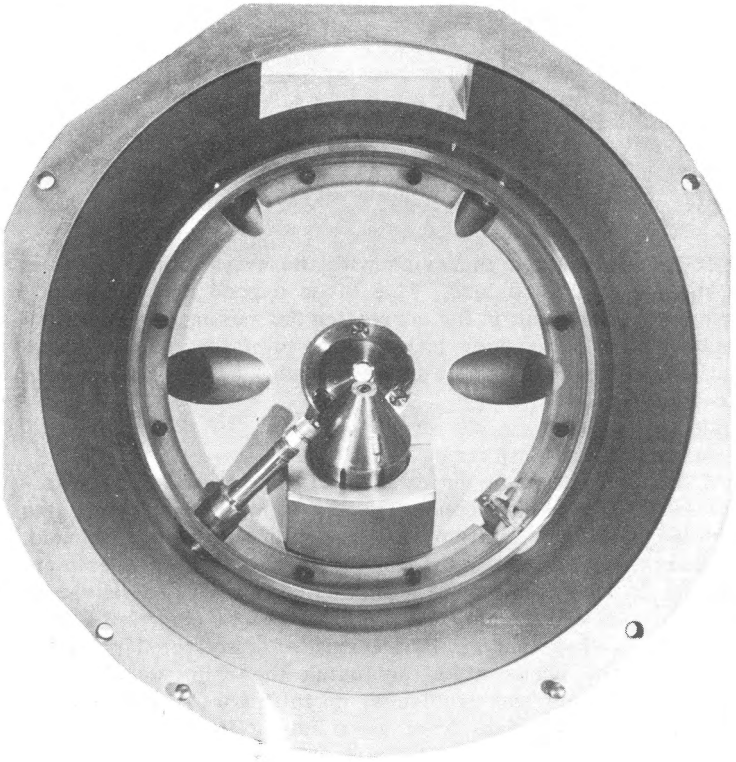
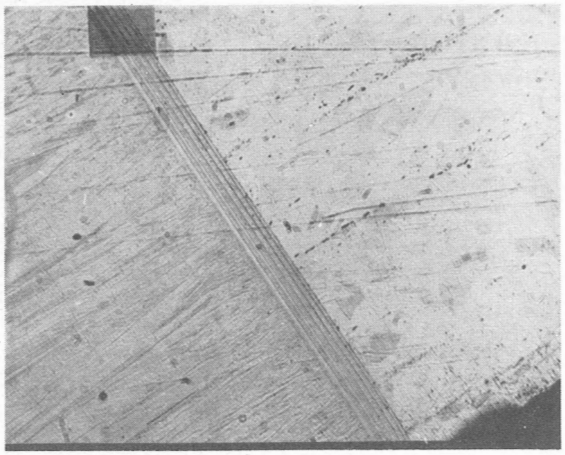
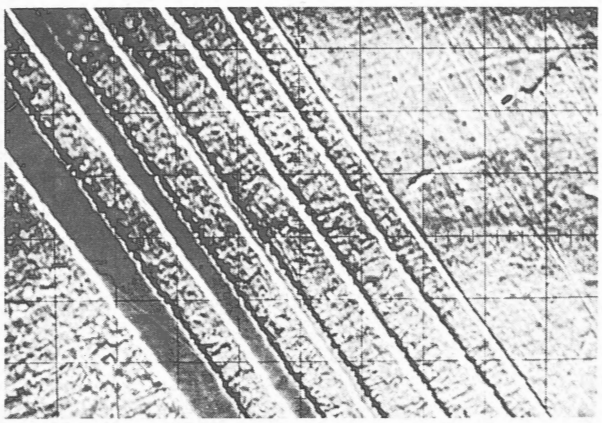


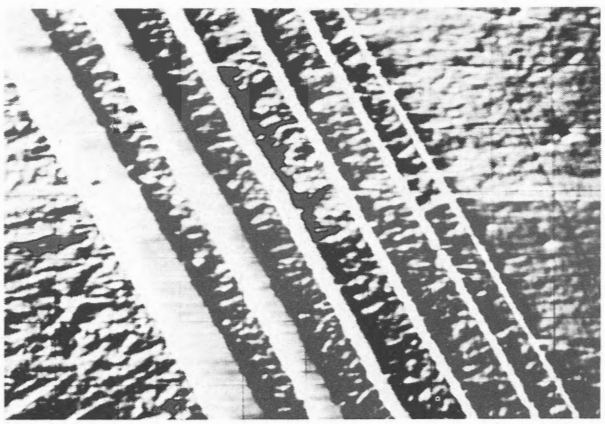
Fig. 4
Top plate of the specimen chamber seen from the specimen side. In the centre is the holder with a glass plate acting as a vacuum seal for the microscope. Opposite the opening for specimen changing, a part of the miniature objective lens can be seen. Two large openings for passing the generated X-rays to both Philips X-ray spectrometers. An electron backscatter detector and a feed-through of the specimen current are positioned in two of the four remaining openings.



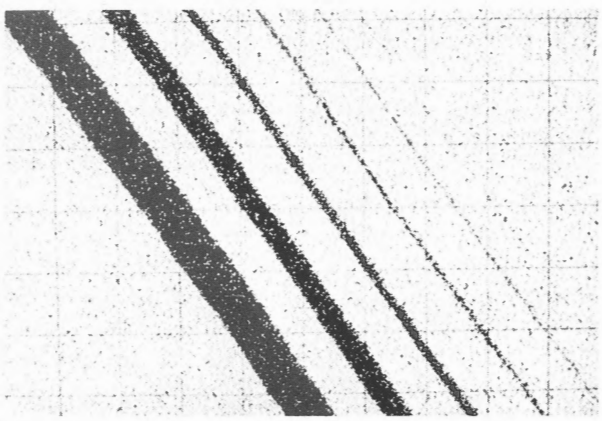
a



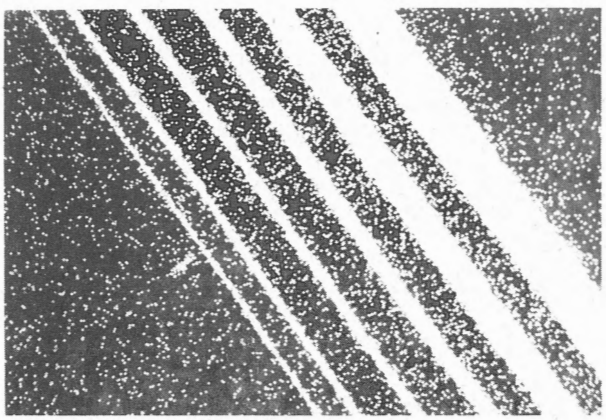
b



c



d



e

Fig. 5 - Results with a Cu-Ni sandwich; 19 kV; 0.1 μA sample current
a) Light optical image sample
b) Absorbed electron image
c) Backscattered electron image
d) CuKα image
e) NiKα image

X-ray optics

An X-ray take-off angle of 30° is obtained in this apparatus with a Philips Norelco spectrometer placed upside down. Normally, this spectrometer allows for an X-ray take-off angle of 15°. The maximum take-off angle will be about 60° owing to the dimensions of the objective lens in the polarization microscope. Left and right Philips Norelco spectrometers are used.

Specimen movements system

To obtain full benefit from the polarization microscope and the fullest possibility of scanning the specimen with the electron probe, the microprobe specimen table permits the same movements as with a normal polarization microscope. They include manual rotation of the specimen around the light optical axis and two orthogonal traverses on the turn-table. The space available for specimens and standards is 50 x 50 x 15 mm^3. Specimen holders can be provided for different sample sizes. The specimen movements system is constructed so that if a perfectly flat glass plate is mounted in the specimen holder, the vertical displacement of the specimen over its whole area is less than 5 μm; the specimen remains within the focal depth of the light microscope objective lens and, with a stationary electron beam, within the focal depth of the miniature lens. The axis of the turn-table can be centred in the specimen chamber. The position of the specimen can be varied vertically within 0.6 mm. These adjustments are necessary to ensure that the fixed electron optical axis and the rotation axis intersect on the specimen plane. The microscope axis is afterwards centred on the axis of the turn-table of the specimen movements system. To hold the specimen at a fixed height, the microscope can be fixed in its lowest position.

Construction of this ideal specimen movements system with the cross-table on the turn-table has been made possible by using concentric toothed wheels and two differentials for both orthogonal traverses.

The vacuum system is automatic for convenience in operation. Electro-pneumatic valves are used to avoid strong magnetic fields in the vicinity of the electron optical column.

Standard Philips electronic measuring panels are used for measuring the generated X-rays, in combination with the Philips Norelco spectrometers. A modified Norelco beamscanner is used for displaying electron and X-ray images.

A Brandenburg E.H.T. power supply is used and the very stable lens power supply is our own design.

For meaningful light-element analysis with a suitable crystal, carbon contamination in the vicinity of the electron spot is reduced by an air-inlet anti-contamination device. Fully focusing X-ray spectrometers can be used by readapting the electron optics and the specimen chamber top-plate. An instrument combining an electron probe X-ray analyzer and a scanning electron microscope is possible by using a stereo-scan accessory. This accessory consists of an extra condenser lens, which can easily be fitted in the electron optics for adequate geometrical demagnification and a sensitive wide band detector for measuring the small number of secondary electrons.

THE THEORY OF ELECTRON SCATTERING AND X-RAY GENERATION

Because almost all theoretical considerations and experiments relate to a normal incident electron beam, a relation must be found between the skew and the normal incident electron beam position with quantitative analysis. It should be noted that the distribution of the X-rays will be rotationally symmetrical about the electron spot in a homogeneous matrix, but the distribution of the backscattered electrons will then be non-symmetrical.

Three important effects modifying X-ray generation must be considered: absorption of X-rays by the specimen, fluorescence contributed by the continuous and characteristic X-rays, and the atomic number effect, which accounts for the fraction of electrons backscattered and the depth of electron penetration. In the inclined electron beam position, the total fraction of electrons backscattered is increased, causing a smaller production of X-rays in the specimen. But as electron penetration below the specimen surface is slighter, this results in less absorption of X-rays. In these conditions, the total X-ray intensity measured may increase.

Absorption correction of X-ray peak intensities can be obtained with the Duncumb and Shields modification of Philibert's absorption equation:

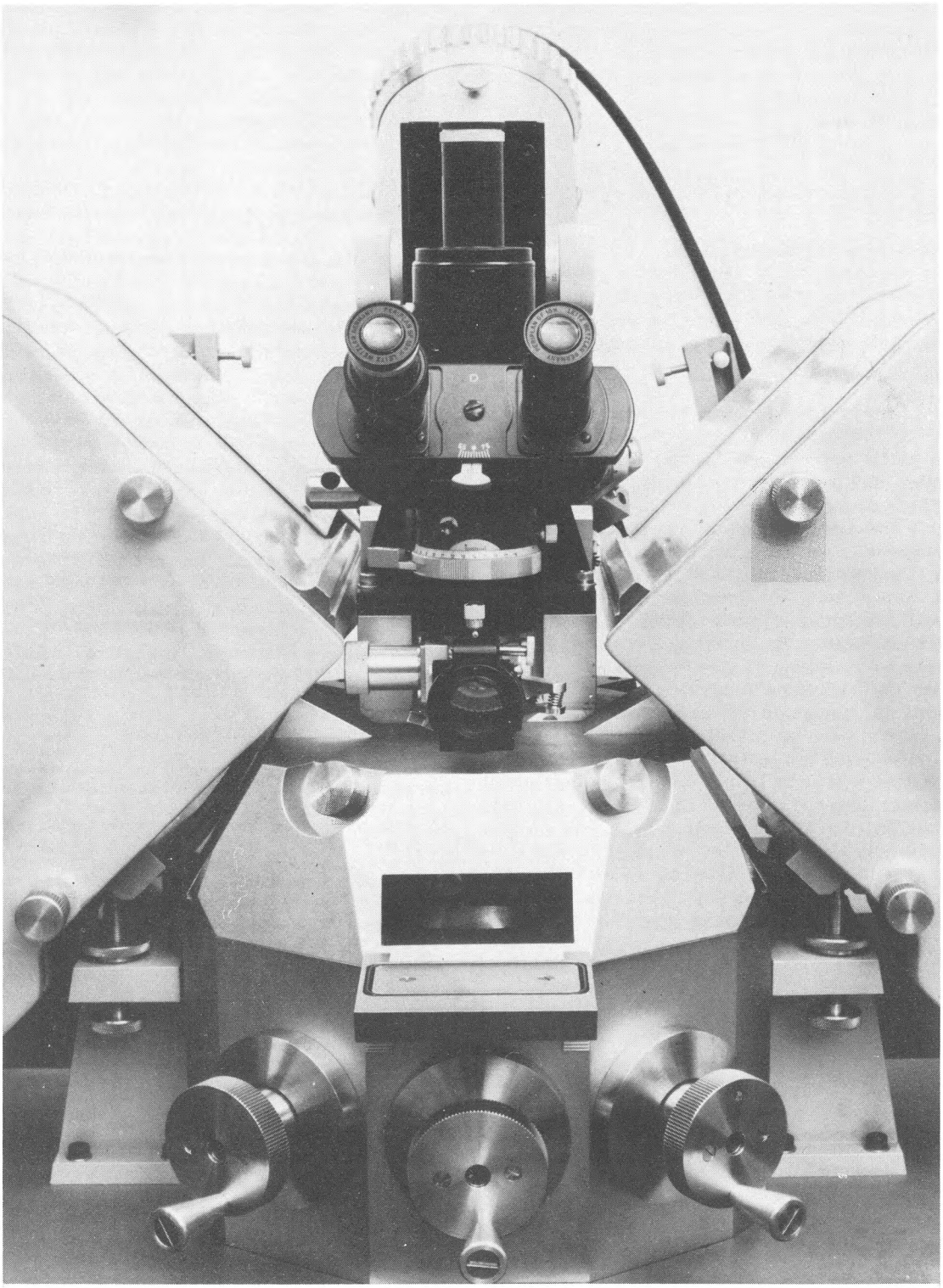
$$\frac{1}{f(\chi)} = \left(1 + \frac{\chi}{\sigma}\right)\left[1 + \left(\frac{h}{1+h}\right)\frac{\chi}{\sigma}\right]$$

in which $\sigma = \dfrac{2.39 \times 10^5}{V^{1.5} - V_k^{1.5}}$

and $h = \dfrac{1 \cdot 2A}{Z^2}$

V = beam acceleration voltage
Vk = critical excitation potential
A = atomic number
Z = atomic weight.

Electron probe X-ray micro-analyzer. Detailed view of the specimen chamber with controls for two orthogonal traverses and rotation of the specimen.



x for the inclined electron beam on the specimen can be found with a formula based on the assumption that the distribution of excitation in the direction of the incident beam is the same as that with depth for normal beam incidence

$\chi = \frac{\mu}{\varrho} \operatorname{cosec} \Theta \sin \alpha$

Θ = take-off angle

α = angle between electron beam and specimen surface.

$\frac{\mu}{\varrho}$ = mass-absorption coefficient

One can also apply the formula proposed by Bishop, obtained from the results of Monte-Carlo calculations and checked by using Green's data for the variation of f( ) curves with incident angle

$$\chi = (\frac{\mu}{\varrho}) \operatorname{cosec} \Theta \cdot (1 - 0{,}5 \cos^2 \alpha)$$

Under our conditions $\alpha = 30^{\circ}$ and $\Theta = 45^{\circ}$, the difference between these two formulas for χ being only a small percentage. Another small advantage with the inclined electron beam position is the analysis of elements closer to the specimen surface owing to the smaller vertical penetration depth of the electrons.

The fluorescence contribution as regards the direct X-ray emission generated in the electron spot will decrease slightly owing to the shorter penetration below the surface resulting in less fluorescence radiation excited by the direct emission towards the specimen surface. The fluorescence emission is generated on average at a depth six times greater than the direct emission. This means that for quantitative analysis the fluorescence correction procedure can be the same for both inclined and normal electron beam positions.

The inclination of the electron beam has a slight effect on the atomic number correction, which is due to the variation of electron deceleration and backscatter properties of the elements. This is determined by the fraction of electrons backscattered from the specimen and the appropriate electron energy distribution for this inclined electron beam position at the average mass concentration of the specimen. Experimental and theoretical investigations of electron backscattering are necessary for proper atomic number correction.

For quantitative analysis with an inclined electron beam of 45° it will be possible to proceed as with a normal incident electron beam to determine the emission function of the characteristic X-rays with depth.

In this way the absorption correction can be found with the known techniques of variation of X-ray take-off angle, tracer method, specimen inclination or with Monte-Carlo calculations. Another possibility of quantitative analysis is to use standards whose composition is close to that of the specimen.

Although the correction procedures for the normal incident electron beam position are not yet reliable enough for general use, transformation of the correction procedures in the normal case to the inclined electron beam position, as described above, can be used in the first instance.

The first results obtained with the electron and light optics are given. They relate to a scan of the stationary electron beam over a Cu-Ni sandwich. There are six tracks of Ni with thicknesses of 10, 5.6, 3.1, 1.7, 0.9 and 0.4 μm respectively. The 5th order CuKα radiation in a Philips spectrometer with a take-off angle of 30° was used for detection.

REFERENCES

For further general information on microprobe analysis: Conference Books on X-ray optics an X-ray micro-analysis.

1. Third International Symposium, Stanford 1963, Academic Press.
2. Fourth International Symposium, Paris 1966, Hermann.
3. The electron microprobe. Proceedings of the symposium sponsored by the electrochemical Society, Washington 1964, J. Wiley & Sons.