

March 27, 1945.

J. HILLIER

2,372,422

ELECTRON MICROANALYZER

Filed Feb. 17, 1944

2 Sheets-Sheet 1

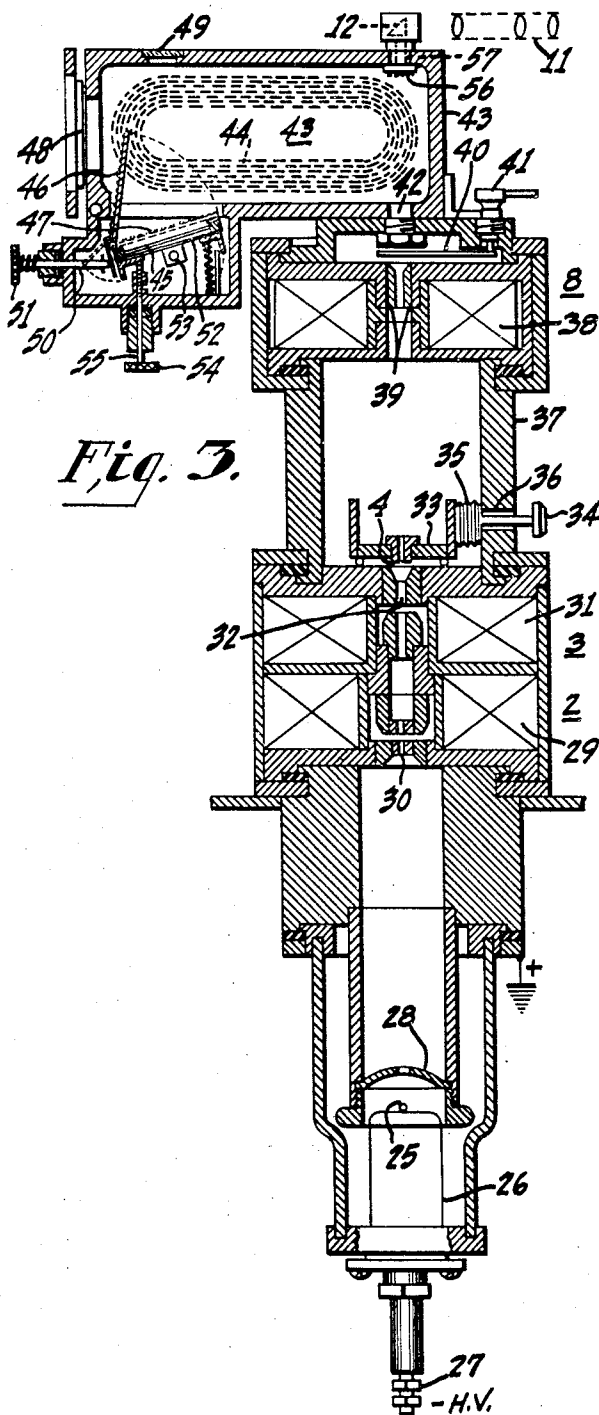


Fig. 3.

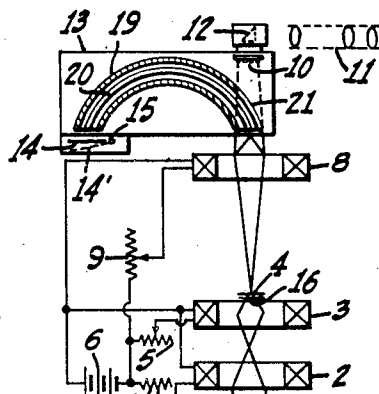


Fig. 2.

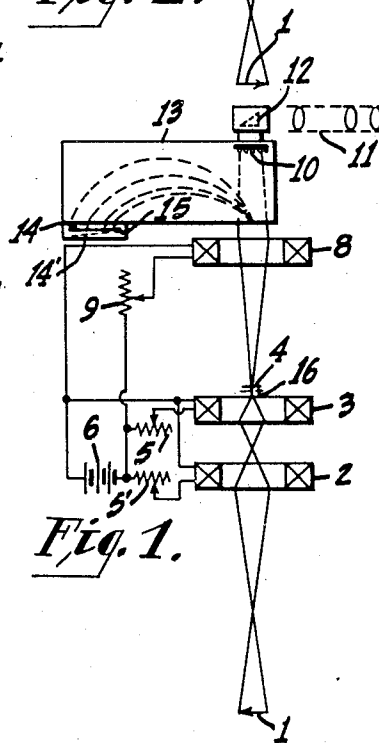


Fig. 1.

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Fig. 5.

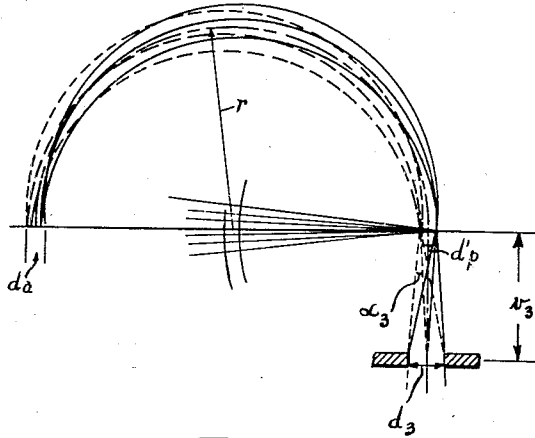


Fig. 6.

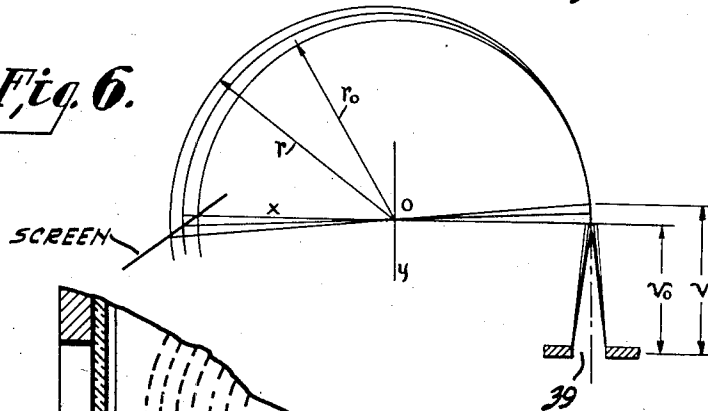
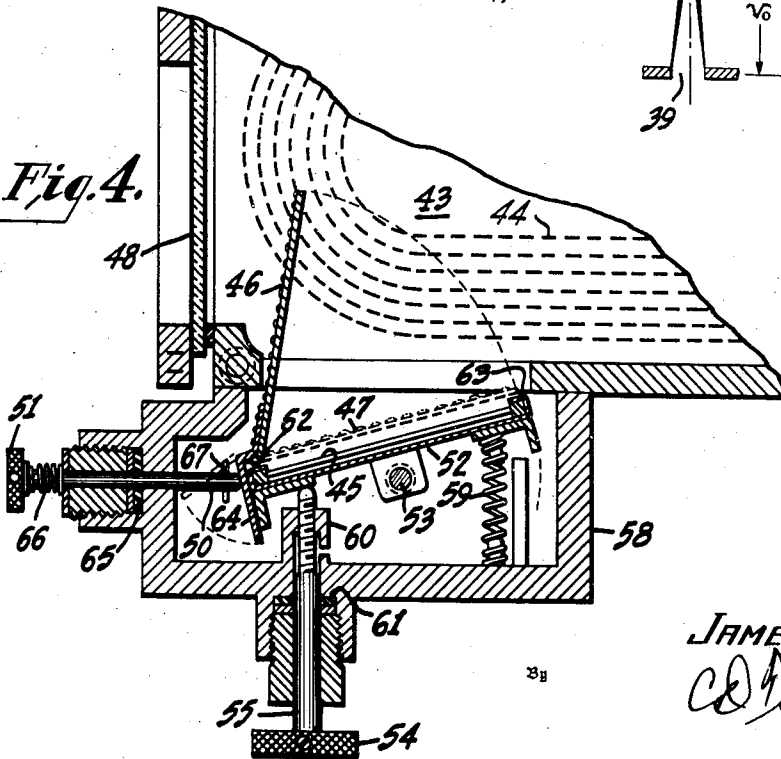


Fig. 4.



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2,372,422

ELECTRON MICROANALYZER

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Application February 17, 1944, Serial No. 522,831

15 Claims. (Cl. 250—49.5)

This invention relates generally to electron optics and more particularly to an improved method of and means for microanalyzing materials by electron irradiation.

The instant invention is an improvement over the two embodiments of an electron microanalyzer described in applicant's copending U. S. application Serial No. 505,572, filed October 8, 1943. Said application discloses and claims devices which provide for the generation of an electron probe, having extremely minute cross-sectional area, which is focused upon a minute area of the electron permeable material to be analyzed. Electrons which are transmitted, or modified, or reflected from the material by the impinging electrons, are subjected to an electric or magnetic deflecting field which deflects the electrons as a function of their velocities. The deflected electrons impinge upon a fluorescent screen for visual observation of the electron velocity distribution pattern, or impinge upon a photographic plate for providing a permanent record of the pattern. Means are included for observing upon an auxiliary fluorescent screen the portion of the specimen upon which the electron probe impinges. Means also are provided for adjusting the position of the material under observation with respect to the axis of the electron probe.

The operation of the electronic microanalyzer is based on the fact that when electrons pass through matter some of the energy of the electrons is transformed into X-ray radiation energy. Since this transformation of energy must take place according to the quantum theory, it can easily be seen that for an electron to excite a photon of the characteristic X-ray radiation of an element it must lose energy in an amount equal to or greater than that contained in the X-ray photon. Thus among the electrons leaving a specimen containing a certain element there will be a predominance of those electrons which have lost an amount of energy equal to or slightly greater than the energy contained in a single photon of the characteristic X-ray radiation of that element. The velocity spectrum of the electrons leaving a point of the specimen will have "lines" corresponding to the important X-ray lines of all the elements contained in the area of the specimen being examined. Electron microanalysis offers several advantages over ordinary methods of microanalysis. Sub-microscopic regions of a specimen can be analyzed without removing the region from the specimen, or without changing it in any way. By means

of the electron microscope associated with the analyzer, the area of the specimen analyzed can be observed so that the relationship of the region examined to the remainder of the specimen can be determined.

The apparatus required for electronically analyzing materials is similar in many respects to the conventional electron microscope. The principal different resides in the fact that electrons which penetrate the substance under observation are subjected to deflecting electric or magnetic fields whereby they are deflected amounts proportional to their velocities before impingement upon the observation screen. In accordance with the teachings of the instant invention, a relatively simple attachment may be provided for conventional electron microscopes to permit microanalysis by electronic methods.

In each of the embodiments of the invention described in applicant's copending application identified heretofore, an electron lens is interposed between the electron irradiated specimen and the uniform deflecting field to provide a focused velocity distribution image on the photographic or fluorescent image screen. Chromatic aberration inherent in all conventional electron lenses thereby provides distortion and poor focus of portions of the electron velocity distribution pattern on the image screen.

The instant invention contemplates correcting for said chromatic aberrations with respect to orientation of the image screen with respect to the normal axis of said lens in accordance with the principles described in detail hereinafter, in order that all portions of the velocity distribution pattern may be correctly focused upon the image screen.

Among the objects of the invention are to provide an improved method of and means for microanalyzing materials permeable to electron irradiation. Another object of the invention is to provide an improved method of and means for electronically analyzing minute specimens of materials. A further object of the invention is to provide an improved method of and means for electronically analyzing materials by subjecting a minute area of the material to electron irradiation, subjecting electrons derived from said irradiated area to the effects of a deflecting field, and indicating the relative velocities of the electrons subjected to said field. Another object is to provide improved means for securing a permanent record of the relative velocities of said electrons subjected to said deflecting field. A further object is to provide an improved method

of and means for correcting for chromatic aberrations in the indications of said electron velocity characteristics. A still further object includes an improved method of and means for subjecting a minute area of a substance to a uniform magnetic field, indicating the relative velocities of electrons subjected to said magnetic field and orienting said velocity indicating means with respect to said field and said electron irradiated substance to correct for aberrations in the electron focusing portions of the system. Another object is to provide an attachment for use with an electron microscope whereby electron velocity measurements may be made upon electrons transmitted by or impinging upon said microscope specimen.

The invention will be further described by reference to the accompanying drawings of which Figure 1 is a schematic diagram of one embodiment thereof, Figure 2 is a schematic diagram of a second embodiment thereof, Figure 3 is a cross-sectional elevational view of a preferred embodiment of the invention according to the schematic diagram of Figure 1, Figure 4 is an enlarged cross-sectional elevational view of the image screen portion of the deflection chamber of the device of Figure 3, and Figures 5 and 6 are ray diagrams showing the electron paths through the deflection chamber. Similar reference characters are applied to similar elements throughout the drawings.

Referring to Figure 1, an electron source 1, which may be provided by a conventional thermionic cathode which is maintained at a relatively high negative potential with respect to an apertured anode electrode, neither of which are shown herein, is imaged by a pair of electron lenses 2, 3 respectively, to irradiate an extremely minute area of an electron permeable object 4. The electron lenses 2, 3, respectively, may be of either the electromagnetic or electrostatic types customarily employed in electron optical apparatus such as, for example, electron microscopes. If electromagnetic lenses are employed, as shown in the drawings, the focus of said lenses may be adjusted by means of series resistors 5, 5' connected between one terminal of each of the magnetic lenses and an energizing current source such as, for example, a battery 6.

A third electron lens 8, which may be energized through a third variable resistor 9 from the battery 6, is disposed coaxially with the first and second electron lenses 2, 3.

The electrons transmitted by the specimen 4 may be selectively subjected to a magnetic field within a deflection chamber 13. The magnetic field will cause the transmitted electrons to follow substantially semi-circular paths and impinge upon an image screen or photographic plate 14. The magnetic field within the deflection chamber 13 will deflect the electrons different amounts determined by their respective velocities whereby a velocity distribution pattern will be provided upon the image screen 14. The focus of the pattern is controlled by varying the current through the third lens 8 by adjusting the resistor 9.

In order to correct for the inherent chromatic aberration in the third electron lens 8, which causes distortion or poor focus of the electron velocity distribution image upon the image screen 14, the screen is pivoted at 15, or is otherwise adjusted, so that it may be oriented as shown by the dash line 14', in accordance with the principles explained in detail hereinafter by reference to Figures 4, 5 and 6.

Adjustment of the energizing current applied to the third electron lens 8 will permit observation of the irradiated area of the specimen 4 by effectively transposing the image of the electron source 1 from the specimen 4 to the point indicated by the arrow 16. The highly magnified shadow image of the object 4 thus produced is further magnified and projected on the fluorescent screen, (or photographic plate) at 10, by means of the third lens 8. The image upon the small fluorescent screen 10 may be observed conveniently by means of a conventional light microscope 11 operating, if desired, in conjunction with a prism 12.

It should be understood that the magnetic field within the deflection chamber 13 may be established in any desired manner. It should also be understood that the electron lens system described may be modified in any known manner to provide a suitable electron probe of convenient cross-sectional area for irradiation of the specimen 4.

Figure 2 is similar in all respects to Figure 1 with the exception that an electric field is substituted for the magnetic field within the deflection chamber 13 of the device of Figure 1 for deflecting the electrons derived from the specimen 4 in accordance with their relative electron velocities. In order to provide relatively long electron paths through an electric field, two arcuate hemi-cylindrical concave electrodes 18, 19, separated by an air gap 20, are disposed in co-operative relation to provide an arcuate tubular electric deflecting element which will cause the deflected electrons to impinge upon the screen 14 to provide a velocity distribution pattern thereon. A small aperture 21 in the wall of the deflecting electrode 19 coincidental with the axis of the electrons derived from the specimen 4 permits a portion of the transmitted electrons to be focused upon the small fluorescent screen 10, when the deflecting electrodes 18, 19 are de-energized, for observation of the electron irradiated area of the specimen 4 by means of an externally disposed light microscope 11 and prism 12, as described heretofore in Figure 1.

Figure 3 is a preferred embodiment of the device described in Figure 1 constructed according to conventional electron microscope practice. The electron source includes a thermionic cathode 25 which is supported by a high potential insulator 26 and connected to a terminal 27 which is maintained at high negative potential. An apertured anode electrode 28, which is maintained at a high positive potential with respect to the thermionic cathode 25, provides an electron beam having relatively high electron velocity. The first electron lens 2 is illustrated as a conventional electromagnetic electron microscope lens including a winding 29 having a pole piece aperture 30. The second electron lens 3 forms a unitary structure with the first electron lens 2 and includes a second winding 31 and a second pole piece aperture 32.

The specimen 4 is supported by a conventional specimen supporting element 33 which may be adjusted with respect to the electron beam axis by an external adjusting knob 34 operating through a conventional bellows joint 35 which is sealed around an aperture 36 in the outer wall 37 of the supporting structure. The third electron lens 8 may be similar to the first and second electron lenses 2, 3, respectively, and includes a third winding 38 and a relatively large pole piece aperture 39. A main shutter 40, operated

by an externally controlled knob 41, is interposed between the third electron lens 8 and an aperture 42 in the wall of a deflection chamber 43 which is secured to the supporting structure of the third electron lens.

A magnetic deflection winding 44, disposed external to the deflection chamber 43, provides a magnetic field therein for deflecting electrons entering the aperture 42 and for causing them to impinge upon a photographic plate 45 for providing a permanent record of the deflected electron pattern. The photographic plate 45 may be removed from the deflection chamber 43 by means of an air lock or any other structure customarily employed in conventional electron microscopes. A hinged fluorescent screen 46, pivoted adjacent one edge of the photographic plate 45, may be rotated effectively to provide an auxiliary shutter to cover the plate 45 and alternately for providing a visual image of the electron velocity distribution pattern. The visual image on the fluorescent screen, when in the position 47, shown in dash lines, may be observed through either of the windows 48, 49 in the walls of the deflection chamber 43. The fluorescent screen 46 may be lifted by means of a spring-actuated plunger 50 which is terminated outside the deflection chamber by a knob 51. Similarly, the plate holder 52 for the photographic plate 45 is pivoted at 53, and is adjustable by means of a second knob 54 which actuates a second plunger 55 threaded into the bottom of the deflection chamber. The structure of the pivoted plate holder and hinged fluorescent screen are described in greater detail hereinafter by reference to Figure 4 of the drawings.

The main shutter 40 is opened by turning the shutter adjusting knob 41, to permit observation of the electron irradiated area of the specimen 4 upon the auxiliary viewing screen 56 by means of the prism 12 and light-microscope 11. When the magnetic field is established within the deflection chamber 43 by energization of the magnetic winding 44, the velocity distribution pattern may be observed through the windows 48, 49, upon the hinged fluorescent screen 46 when it is in the position indicated by the dash lines 47. The main shutter 40 then may be closed to prevent electrons entering through the aperture 42 and the fluorescent screen-auxiliary shutter 46 rotated to its vertical position, as indicated in the drawings. The main shutter 40 then may be opened for a desired interval to expose the photographic plate 45.

Referring to Figure 4, the deflection chamber 43 opens into a photographic plate enclosure 58 which may be opened in any conventional manner to provide access to the photographic plate 45 for removal and replacement thereof. The photographic plate 45 is supported by a plate holder 52 which is pivoted on a bearing 53 to permit angular adjustment of the plate with respect to the deflection chamber 43. A spring 59 interposed between the wall of the enclosure 58 and the plate holder 52 provides constant pressure of the plate holder against the end of an adjusting plunger 55 which is threaded into a bushing 60 in the wall of the enclosure 58. A packing bushing 61 adjacent the threaded bushing 60 provides an effective air seal for the plate adjusting plunger 55. The adjusting plunger 55 is provided with a control knob 54 situated below the plate enclosure 58.

The fluorescent screen-auxiliary shutter 46 is secured by a hinge 62 to one edge of the plate holder 52. A stop 63 adjacent the opposite edge

of the plate holder permits the fluorescent screen to lie parallel to the photographic plate 45 and act as an auxiliary shutter therefor. An extension 64 on the hinge 62 engages with the screen adjusting plunger 50 which is terminated in an external screen adjusting knob 51 and is sealed into the side of the plate enclosure 58 by means of a second packing bushing 65. A second spring 66 disposed between the screen adjusting knob 51 and the second bushing 65 permits the fluorescent screen 46 to occupy normally the position 47 parallel to and covering the photographic plate 45. A stop 67 retains the plunger 50 in a neutral position against the tension of the second spring 66.

It will be seen that, regardless of the position of the photographic plate 45 as determined by the adjustment of the plate adjusting knob 54, the neutral position 47 of the fluorescent screen 46 always will be adjacent and parallel to the plate 45. However, the screen adjusting knob 51 may be depressed against the tension of the spring 66 to lift the fluorescent screen from the photographic plate, regardless of the position of the plate.

When the fluorescent screen 46 is in its neutral position covering the plate, it may be observed through a window 48 sealed in the adjacent end of the deflection chamber 43. Alternately, it may be observed by means of an external light image magnifying device, not shown, through a second window 49 disposed in the top wall of the chamber.

The desirability of adjusting the position of the photographic plate as explained heretofore will be apparent from the ray analyses described with reference to Figs. 5 and 6. It should be understood that, once the plate is adjusted to a particular lens system, no further adjustment is necessary, notwithstanding variations in specimens and the velocity of the specimen irradiating electron probe. Therefore, in practice, the photographic plate position may be initially adjusted and locked in position for a particular electron optical system.

It should be understood that the velocity analyzer may, if desired, comprise an attachment for a conventional electron microscope. The attachment would comprise the deflection chamber 43 including the deflecting field generating means, the two fluorescent screens 46, 56, the photographic plate 45, the light microscope 11, 12, and all actuating members therefor. As an attachment the casing 43 of the deflection chamber would be complementarily formed to fit the housing of the third, or projection, electron lens of the microscope, and the attachment unit would be interposed between said third lens and the final image screen of the microscope.

The primary purpose of the limiting aperture 39 situated in the third lens of the embodiment of the invention shown in Fig. 3 is the control of the resolving power of the electron velocity analyzing system. Figure 5 is a ray diagram showing the trajectories of the electrons leaving the third lens aperture 39 and passing through the homogeneous magnetic field analyzer. It should be pointed out that this differs somewhat from the conventional velocity analyzing systems in that the beam entering the analyzer is in the form of a narrow cone instead of a collimated sheet. Thus, the diagram shown represents only those rays which are traveling in the plane of symmetry of the system. The maximum width

of the image line produced in the analyzer is given by the expression

$$(1) \quad d_a = d_p' + 2r(1 - \cos \alpha_3)$$

where d_p' is the diameter of the probe at the entrance position of the analyzer, r is radius of the circular paths of the electrons in the analyzer and α_3 is the angular aperture of the beam entering the analyzer. In this expression

$$(2) \quad r = 3.37V^{1/2}H$$

and

$$(3) \quad \alpha_3 = d_3/2v_3$$

where V is the velocity of the electron beam expressed in electron volts, H is the strength of the homogenous magnetic field of the analyzer expressed in gauss, d_3 is the diameter of the limiting aperture in the plane of the third lens at the entrance position of the analyzer, and v_3 is the distance between the center of the third lens 8 and the focal point of the electron beam.

If we express the resolving power of the system by the ratio $\Delta V/V$ we have the relations

$$(4) \quad \Delta V/V = 2\Delta r/r = (d/r) + 2(1 - \cos \alpha_3)$$

Since, in the practical case under consideration d_p' is negligible and α_3 is small we can write

$$(5) \quad \Delta V/V = \alpha_3^2$$

For $d_3 = 1.0$ mm. and $v_3 = 50$ mm. Equations 3 and 5 give $1/10,000$ as the calculated resolving power of the system. The experimental resolving power measured under the same conditions has been established at $1/6,000$. The discrepancy between the measured and calculated resolving powers of the instrument has not yet been investigated. The width of the line at the position of the photographic plate is given by the expression

$$(6) \quad 2\Delta r = r\alpha_3^2$$

For the practical case in which $r = 80$ mm. and $\alpha_3 = 10^{-2}$ radian the line width is immediately seen to be 8 microns. Such a line can be recorded satisfactorily on Eastman medium lantern slide emulsion.

These simple expressions for the resolving power of the system can also be used to determine the degree of stability required in the magnetic analyzing field. From (7) we can write

$$(7) \quad \Delta V/V = 2\Delta H/H = 2\Delta i_a/i_a$$

where i_a is the current in the coil windings producing the magnetic analyzing field. Thus to achieve a resolving power of $1/10,000$ the magnetic field and hence the exciting current must not vary by more than $1/20,000$ i. e. 0.005% during the exposure time.

The accelerating potential of the incident electrons must not vary by more than $1/10,000$ i. e. 0.01 percent during the exposure time. The stability requirements of the first, second and third lenses of the system are almost the same as those for the projection, objective and condenser lenses respectively, of a conventional electron microscope and hence will not be discussed here.

Figure 6 is a ray diagram demonstrating the effect of the chromatic aberration of the third lens. In the diagram three sets of rays corresponding to 50, 53 and 56 kilovolts are drawn. It is necessary to place the photographic plate in the right position if the entire velocity distribution is to be obtained in focus at the same time.

The proper position for the photographic plate can be determined from the following expressions:

$$(8) \quad x = r \cos \frac{(v-v_0)}{r} + (r-r_0)$$

$$y = r \sin \frac{(v-v_0)}{r}$$

$$(9) \quad v = uV/(ku + V)$$

$$(10) \quad r = k_1 V^{1/2}$$

where x and y are the coordinates of the emulsion position at which electrons of velocity corresponding to V electron-volts will be accurately focused. The origin is taken at the center of the circular path corresponding to the minimum electron energy to be recorded. k and k_1 are constants while u is the distance of the specimen from the third lens, and v and v_0 are distances between the center of the third lens 8 and the focal points of the electron beams of different predetermined electron velocities. In Fig. 6 the plate position has been plotted using the parameters of the experimental instrument. It also can be seen from (8), (9) and (10) that the optimum position of the plate does not depend on the velocity of the incident electrons for which the instrument is adjusted.

Thus the invention described comprises a method of and means for providing improved electron velocity distribution patterns in an electron microanalyzer by properly orienting the pattern image screen to correct for chromatic aberration in the electron lens employed for focusing said pattern. A modification of the invention comprises an attachment for a conventional electron microscope to provide electron velocity analyses of electrons irradiating and permeating the microscope specimens to determine thereby the composition of said specimen.

I claim as my invention:

1. In an electron microanalyzer including means for providing an electron probe having extremely minute cross-sectional area, means for supporting an object, means for irradiating said object by said electron probe, an electron sensitive screen responsive to electrons from said object, and means interposed between said screen and said object means providing a field for deflecting said electrons as a function of their velocity, the improvement comprising means orienting said screen with respect to said deflecting field for correcting for chromatic aberrations of said interposed means.

2. In an electron microanalyzer including electron beam generating means and electron beam focusing means for providing an electron probe having extremely minute cross-sectional area, means for supporting an object substantially permeable to electron irradiation, means for irradiating said object by said electron probe, an electron sensitive photographic screen responsive to electrons from said object, and means interposed between said screen and said object means including means providing a field for deflecting said electrons as a function of their velocity, the improvement comprising means orienting said screen with respect to said deflecting field for correcting for chromatic aberrations of said interposed means.

3. Apparatus of the type described in claim 1 including means disposed within said deflecting means selectively providing a visual image of said screen.

4. Apparatus of the type described in claim 1

including a fluorescent screen, and means for imaging said object on said fluorescent screen for observing said electron probe irradiation of said object.

5. Apparatus of the type described in claim 1 including a fluorescent screen, means for imaging said object on said fluorescent screen for observing said electron probe irradiation of said object, and means for optically magnifying said image on said fluorescent screen.

6. Apparatus of the type described in claim 1 including externally adjustable means for orienting said object with respect to said electron probe.

7. In an electron microanalyzer including means for providing an electron probe having extremely minute cross-sectional area, an object substantially permeable to electron irradiation, means for irradiating said object by said electron probe, an electron lens for focusing electrons transmitted by said object, an electron sensitive screen responsive to said focused electrons from said object, and means interposed between said screen and said object means providing a field for deflecting said electrons as a function of their velocity, the improvement comprising means orienting said screen with respect to said deflecting field for correcting for chromatic aberrations of said electron lens.

8. In an electron microanalyzer including means for providing an electron probe having extremely minute cross-sectional area, means for supporting an object substantially permeable to electron irradiation, means for irradiating said object by said electron probe, an electron sensitive screen responsive to electrons from said object, and means interposed between said screen and said object means including means providing a magnetic field for deflecting said electrons as a function of their velocity, the improvement comprising means orienting said screen with respect to said deflecting field for correcting for chromatic aberrations of said interposed means.

9. In an electron microanalyzer including means for providing an electron probe having extremely minute cross-sectional area, means for supporting an object substantially permeable to electron irradiation, means for irradiating said object by said electron probe, an electron sensitive

screen responsive to electrons from said object, and means interposed between said screen and said object means including means providing an electrostatic field for deflecting said electrons as a function of their velocity, the improvement comprising means orienting said screen with respect to said deflecting field for correcting for chromatic aberrations of said interposed means.

10. The method of electron microanalyzing a material comprising generating an electron probe of minute cross-sectional area, electron irradiating said material by said electron probe, subjecting electrons derived from said object to a field to deflect said electrons as a function of electron velocity, focusing said deflected electrons to form a velocity distribution image, correcting for chromatic aberrations in said focused electrons, and indicating the relative velocities of said focused and corrected electrons.

11. Apparatus of the type described in claim 1 including means for indicating the relative velocities of said deflected electrons.

12. An electron velocity microanalyzer attachment for an electron microscope having an electron projection lens including an evacuable chamber adapted to be mounted upon said microscope adjacent said lens to receive electrons focused by said lens, means for establishing a substantially homogeneous electron deflecting field within said chamber for deflecting said electrons as a function of their velocities, and an electron sensitive screen disposed within said chamber responsive to said electrons deflected by said field.

13. Apparatus of the type described in claim 12 including a fluorescent screen, and means for selectively interposing said fluorescent screen between said lens and said image screen for providing a visual image of said deflected focused electrons.

14. Apparatus of the type described in claim 12 including an electron image screen for the electron microscope image focused by said lens.

15. Apparatus of the type described in claim 12 including means for orienting said electron sensitive screen with respect to said lens for correcting for electron aberrations in said lens.

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