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A ONE-DIMENSIONAL FOCUSING CRITICAL ANGLE REFRACTOMETER FOR MASS TRANSFER STUDIES

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ABSTRACT

A focusing critical angle refractometer has been constructed to measure the one-dimensional refractive index profile inside the glass wall of a liquid container. The instrument displays a graphic image of the entire refractive index profile.

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Interferometric and schlieren optical systems have long been used in the study of refractive index fields. They offer convenient methods for observing large regions with high resolution in short times. The images formed provide detailed graphic displays of the refractive index fields under study. The techniques suffer from an intrinsic disadvantage: they form images from light which has passed through the entire experimental region and, therefore, contains information only on the integral (average) refractive index (or refractive index gradient) traversed. In addition, the refractive index gradients cause distortions in the image.

In mass transfer studies, where the refractive index profile near the cell wall is different from that in the center of the cell, it is desirable to augment interferometric refractive index measurements by a refractive index profile measured next to the cell window, in order to correct for refractive index variation in the direction of light propagation. The critical angle refractometer described here was constructed for this purpose, but it may also be used as a separate experimental tool.

CRITICAL ANGLE REFRACTOMETERY

Snell's Law (Eq. 1) relates the angle of refraction θ_k at which light passes through a mdeium of refractive index n_k to the angle of incidence θ_i and the corresponding external refractive index n_i.

$$n_i \sin \theta_i = n_k \sin \theta_k \tag{1}$$

The medium k need not be in direct contact with the external medium i as long as all media in between are joined by parallel interfaces. The angle θ is measured from the line perpendicular to all of the interfaces.

If the refractive index of one of the layers is so low that Eq. 1 cannot be satisfied (sin θ cannot exceed 1.0), light is totally reflected at the layer. The largest angle of refraction for transmitted light is the critical angle of refraction. It is determined by the lowest refractive index region traversed. Even when the critical angle is not exceeded, a part of the incident light is reflected.

Critical angle refractometers determine the refractive index of the medium of lowest refractive index in the optical path by measuring the critical angle. Figure 1 shows the reflected and transmitted light beams and images observed in the telescope of an Abbe refractometer.[1,2] The images are formed by illuminating a pair of optical reference prisms, bounding the medium to be measured, with diffuse monochromatic light and observing the transmitted or reflected light. The lowest angle of totally reflected light (Fig. 1a), or the highest angle of transmitted light (Fig. 1b), appear as the boundary between an illuminated region and a dark region. The reflected image is of low contrast because light at angles below the critical angle is partially reflected. The transmitted image is of lower intensity but higher contrast and should, therefore, be used whenever possible. The boundary between the two regions is parallel to the axis of the critical angle.[3] If the measured medium in the Abbe refractometer is not of uniform refractive index, the line indicating the critical angle will be blurred. Such local refractive index variations can be resolved by two approaches: 1) limiting the illuminated area of the medium to obtain a measurement representative of one point in the sample, 2) imaging the medium to obtain localized measurements. The instrument described here limits the illuminated area in one direction and focuses in the other direction to provide a display of refractive index vs distance, for the observation of a one dimensional refractive index field.

A ONE-DIMENSIONAL FOCUSING REFRACTOMETER

A one-dimensional focusing refractometer, using cylindrical optics, has been developed for use in conjunction with a Mach-Zehnder interferometer in convective mass transfer studies. The instrument (Fig. 2) was designed to measure refractive index profiles just inside the glass wall of an electrolytic mass transport cell.

A diagram of the instrument (Fig. 3) shows collimated light from a mercury vapor light source A, directed by a mirror E, into a cylindrical lens on the prism assembly F, G.[4] The cylindrical lens, with vertical axis, converges the light in a wedge to a vertical vertex line which is located at the interface between the glass wall G and the observed medium J. The part of the light which is reflected leaves the prism assembly through a cylindrical lens with horizontal axis and enters the camera lens H. The camera lens is focused at infinity so that the horizontal angle of the light leaving the prism is displayed as horizontal displacement on the film. The cylindrical lens, located at its focal distance from the line of measurement, in combination with the camera lens, images the line of measurement on the film in the vertical direction.

The wedge of incident light, which strikes the line of measurement, includes all critical angles to be measured. The smallest angle of totally reflected light, a measure of local refractive index, appears as a boundary between a dark and a light region on the film. Thus, the refractive index profile along the line of measurement is graphically recorded in the image. Figure 4 shows such an image of a refractive index profile formed at a diffusing boundary between two solutions.

A diagram of the light reflection and refraction at the observed interface helps to explain how the image is formed. Figure 5 shows the interface B between the glass wall G and the liquid medium J. The liquid medium is assumed to contain a diffusion boundary similar to the one observed in Fig. 4, with refractive index increasing in the downward direction. A wedge of incident light A is converging to a vertical apex line on the interface and results in the reflected light bundles C and the refracted bundles D. Planes 5 in incident and reflected bundles represent light which is incident on the entire interface above the critical angle and is therefore totally reflected. Planes 1 to 4 represent light which is totally reflected only over part of the interface.

With increasing angle of incidence (plane 1 to 4), partial transmission occurs at increasingly lower locations of the interface, corresponding to increasing refractive index of medium J. Partial transmission below the critical angle of incidence results in a decreased intensity of the reflected light; the critical angle is recognized by an abrupt change in the reflected intensity. The refracted light D (not used in this instrument) shows an angle of refraction which decreases in the downward direction.

Calibration of the instrument is illustrated in Fig. 6. Refractograms of solutions of known concentration have been photographed. It can be seen that the horizontal displacement of the transition line between partial and total reflection (a measure of the critical angle) is very nearly a linear function of concentration. Thus, refractive index profiles, such as the ones shown in Fig. 4, can be quantitatively interpreted.

REFRACTIVE INDEX GRADIENT NORMAL TO PRISM FACE

A complication arises when the instrument is used to measure the interfacial refractive index in a medium in which the refractive index decreases with increasing distance away from the prism (glass wall). In this case, light of low angle of incidence which is transmitted by the interface may exceed the critical angle in a region at some distance from the prism and be totally reflected. If there is no refractive index gradient in the direction perpendicular to the line of measurement but normal to the measured interface, the refractive index corresponding to the return of the light incident at a particular angle can be calculated from Snell's law (Eq. 1). In order for this returning light to affect the critical angle measurement, the light must return to the interface at a location which allows it to be accepted by the focusing optics.

The location of the returning light may be found by solving the equation of light deflection (Eq. 2).[5]

$$\frac{d^2y}{dx^2} = \frac{1}{n(y)} \left(1 + \frac{dy}{dx}^2\right) \frac{dn}{dy} \qquad (2)$$

y(x) describes the path of the light, with refractive index n being a function of the distance y from the observed interface. If the light is incident on the observed interfact at x = 0, y = 0 and continues into the observed medium (which has an interfacial refractive index of n_k) at an angle θ_k in the +x, -y direction, a solution for the case of a linearly decreasing refractive index is

$$y - y_0 = \frac{n_k \sin \theta_k}{\frac{dn}{dy}} \left(\cosh \left(\frac{dn}{dy} (x - x_o)/(n_k \sin \theta_k)\right)\right) \qquad (3)$$

where $y_0 = -\frac{n_k}{\frac{dn}{dy}}$. The light penetrates into the solution to point x_0, y_p where

$$y_p = y_0 (\sin \theta_k - 1) \qquad (4)$$

and re-enters the reference prism at x_r where

$$x_r = 2\, y_0 \sin \theta_k (\cos^{-1} (\csc \theta_1)). \qquad (5)$$

The angle of the returned light equals the angle of the incident light.

The light which returns to the interface from within the solution may be eliminated by spatial filtering. Thus, the refractive index profile next to the glass wall can be measured. Alternatively, the light returning to the interface may be used to study the refractive index profile in the y direction.

CONCLUSION

A critical angle refractometer has been constructed for use in mass transfer studies. The instrument is designed to measure a one dimensional refractive index profile parallel to a glass wall. It is capable of resolving concentration difference on the order of 10^{-4} molar (10^{-5} refractive index units) and distances of 0.02 mm. The images formed are not distorted by refractive index gradients as are the images formed from light rays which have passed through a refractive index field. The instrument has been used in conjunction with a Mach-Zehnder interferometer[6] in electrochemical mass transfer studies.

ACKNOWLEDGMENTS

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REFERENCES AND NOTES

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2. G. E. Fishter, in Applied Optics and Optical Engineering, R. Kingslake, ed., (Academic Press, New York, 1967) Vol IV, Part I, Ch. 10.

3. The transition line is actually an arc of the critical angle circle when diffuse illimination is used, as it is with the Abbe and dipping refractometers. The complete circle is most commonly seen when a swimmer looks up from under water. Light is transmitted from the air above inside the circle limited by the critical angle and reflected from within the water beyond. The transmitted light shows a wide-angle effect displaying the entire air space above within the critical angle circle.

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FIGURE CAPTIONS

Fig. 1 Abbe refractometer patterns

A. illuminating prism

B. measured medium

C. refractometer prism

a) Pattern seen in reflection, a low contrast boundary between totally reflected light and partially reflected light. The critical angle is the lowest angle of total reflection.

b) Pattern seen in transmission, a high contrast boundary of the partially transmitted light. The critical angle is the highest angle of transmitted light.

Fig. 2 Focusing refractometer for observing refractive index gradients through the glass wall of a mass transfer cell (top view).

A. water cooled mercury light source and collimating optics

B. mirror

C. cylindrical converging lens with vertical axis on the input end of the prism assembly

D. calibration cell attached to the aligning plate

E. cylindrical focusing lens with horizontal axis on the output end of the prism assembly

F. motor driven camera with 500 mm lens focused at infinity (Nikon F)

Fig. 3 Schematic of focusing refractometer (top view)

A. mercury vapor light

B. dichroic interference filters passing 5460Å

C. collimating lenses

D. pinhole spatial filter

E. mirror

F. contact prism assembly with converging cylinder lens on right and focusing cylinder lens (horizontal axis) on left

G. glass wall of cell

H. 500 mm camera lens focused at infinity

J. electrolyte with refractive index profile in the vertical direction

The optical contact between the prism F and the glass wall G is made by introducing methylene iodide between the pieces. When the optical contact is broken, total reflection occurs at the prism face and the light follows the dotted path to 1/2 mm spaced horizontal reference lines etched on the back of the prism (under "F").

Fig. 4 Refractograms from the focusing refractometer of the boundary between water and 1.0 molar copper sulfate at two different times after the boundary was formed. a) 0 min b) 3 min. The concentration is indicated on the horizontal axis. The separation between the marks on the vertical axis is 1 mm.

Fig. 5 Reflection and refraction at an interface with a vertical refractive index gradient.

A. incident light

B. interface between medium G (glass wall of cell) and medium J (electrolyte with refractive index variation in vertical direction)

C. reflected light

D. refracted light

For any angle of incidence of light (planes 1-5) the angle of reflection is the same as the angle of incidence but the angle of refraction varies with the refractive index.

Fig. 6 Calibration of the focusing refractometer. Critical angle line on the film plane marked for solution concentrations indicated in the right column.

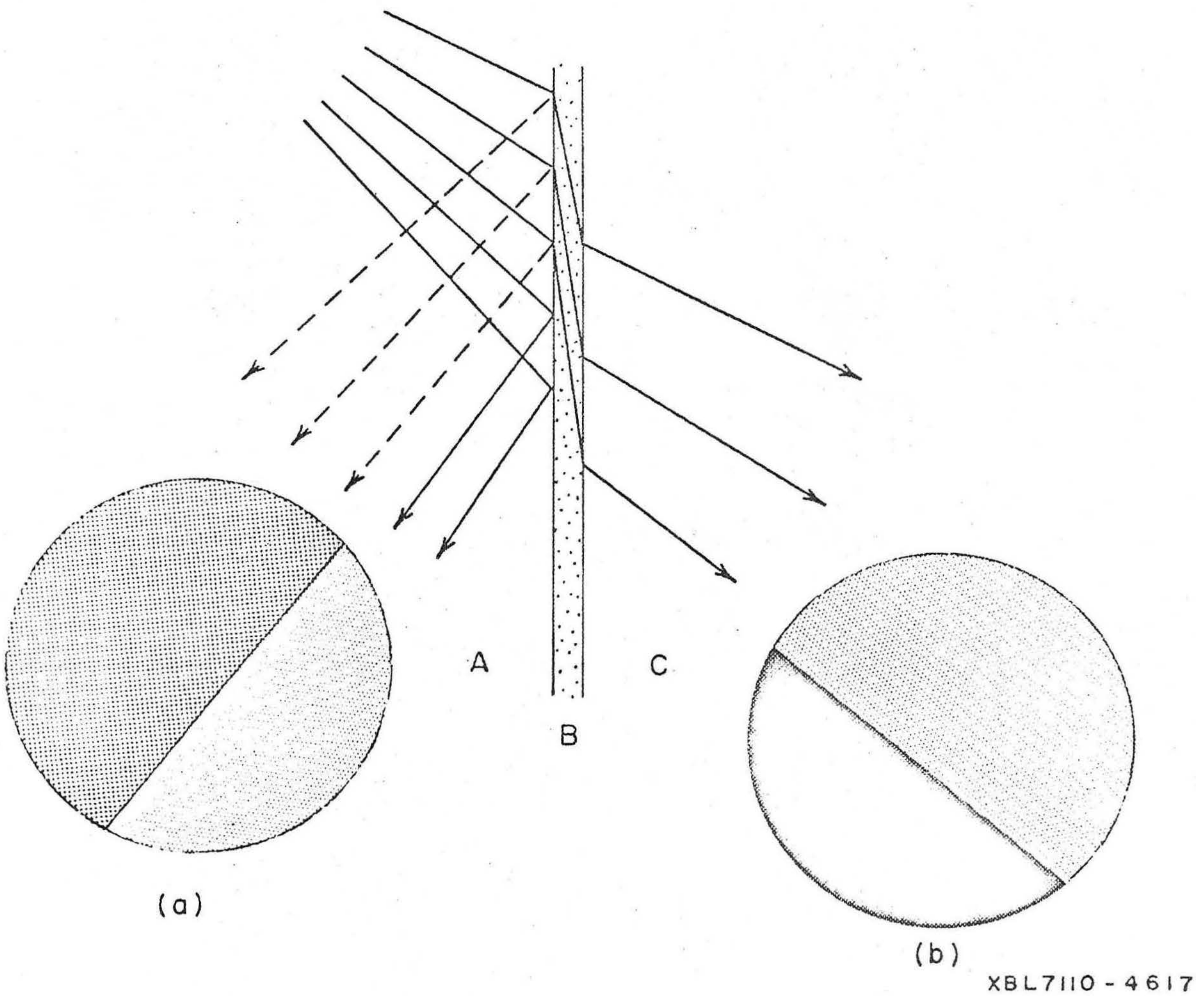

Fig. 1

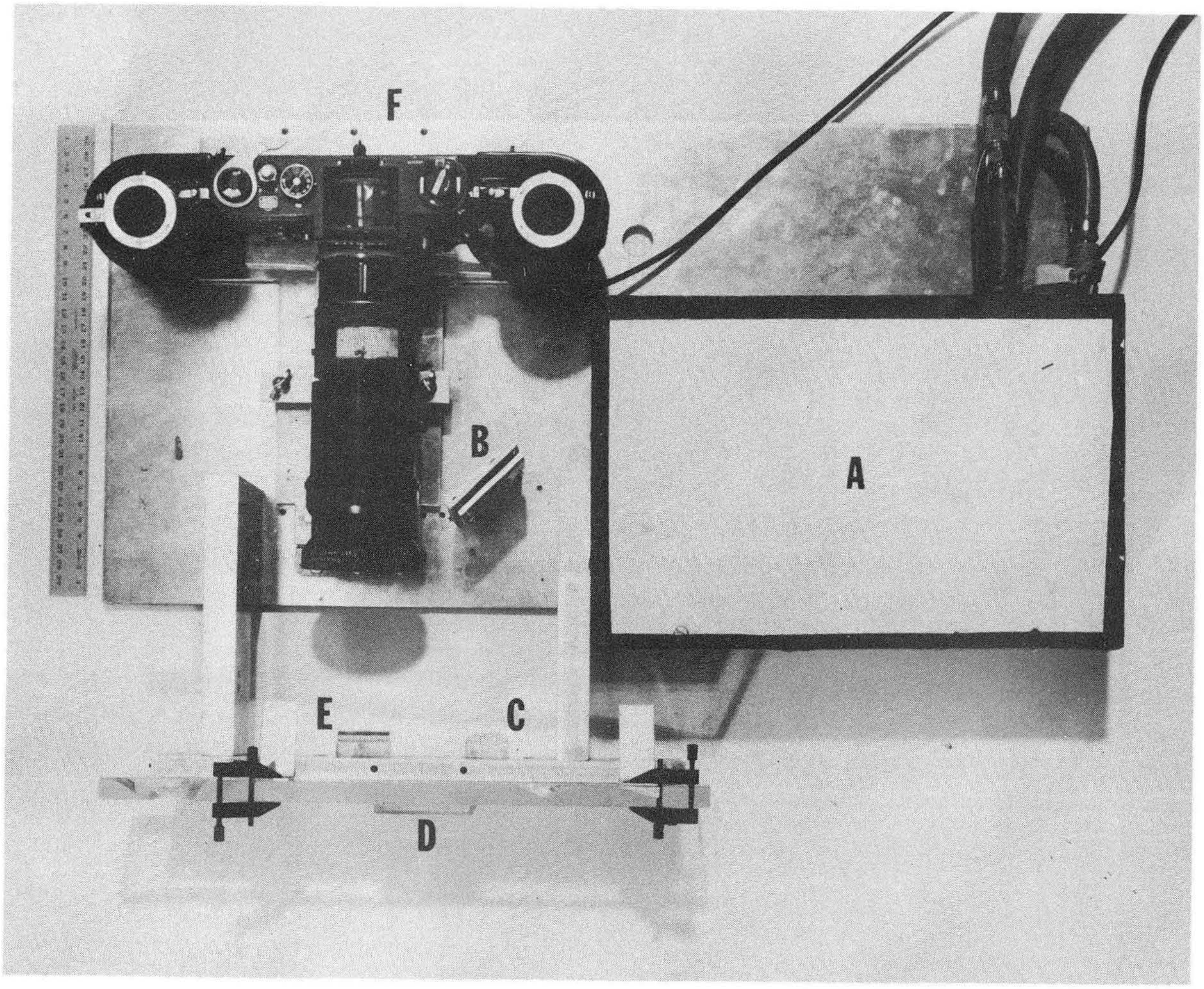

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Fig. 2

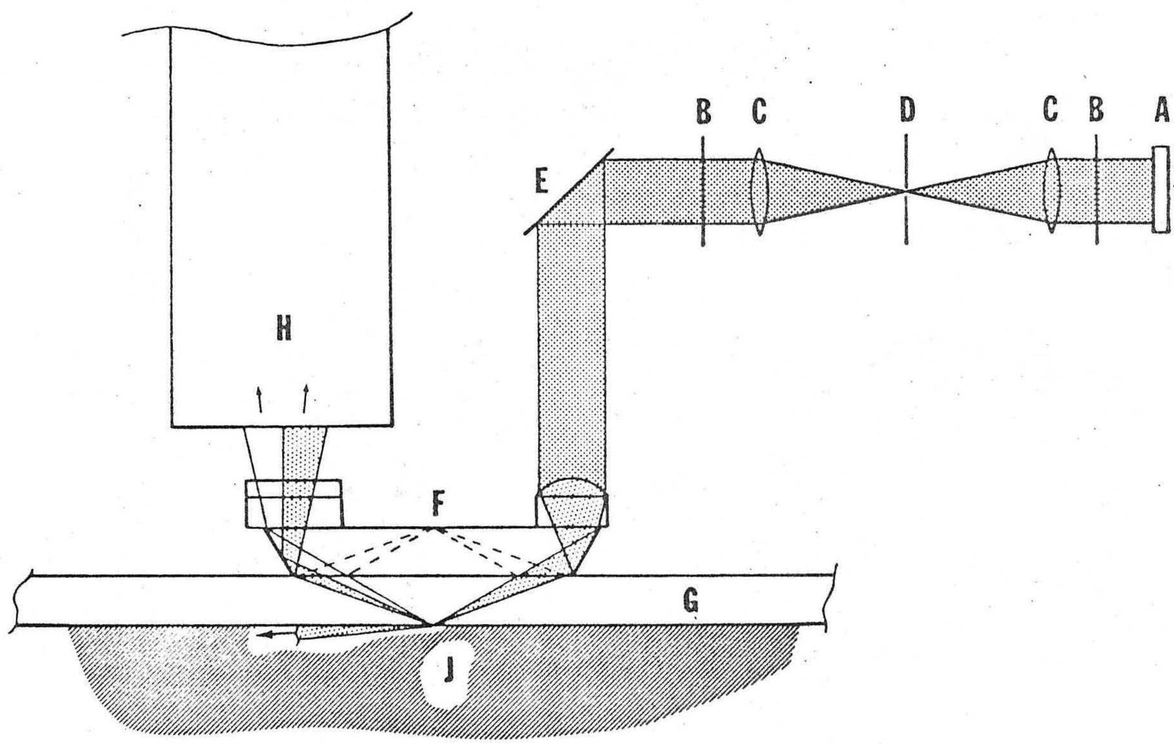

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Fig. 3

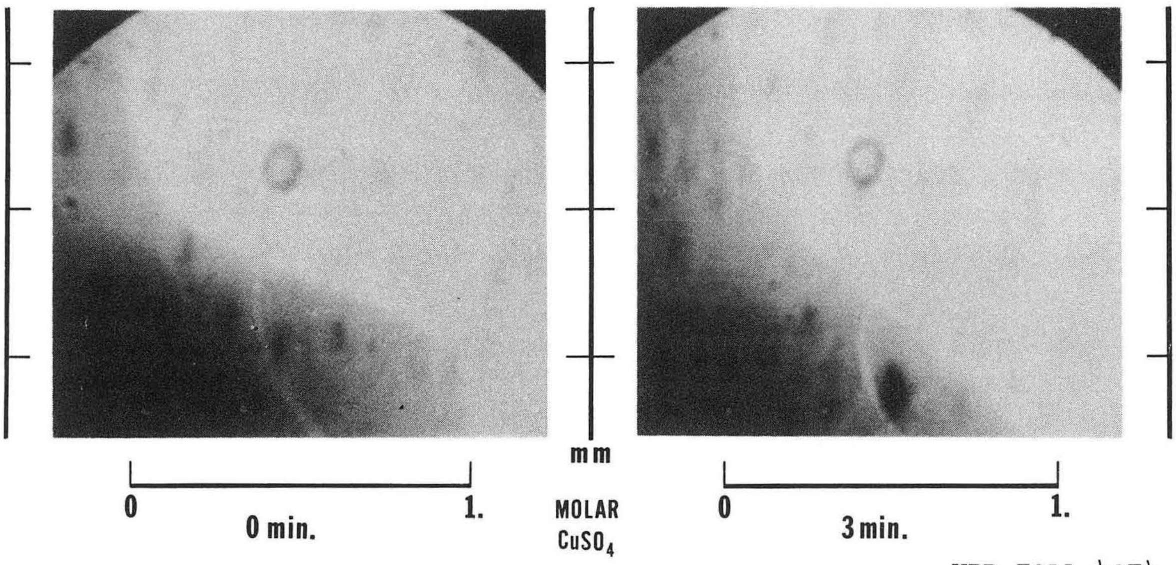

Fig. 4

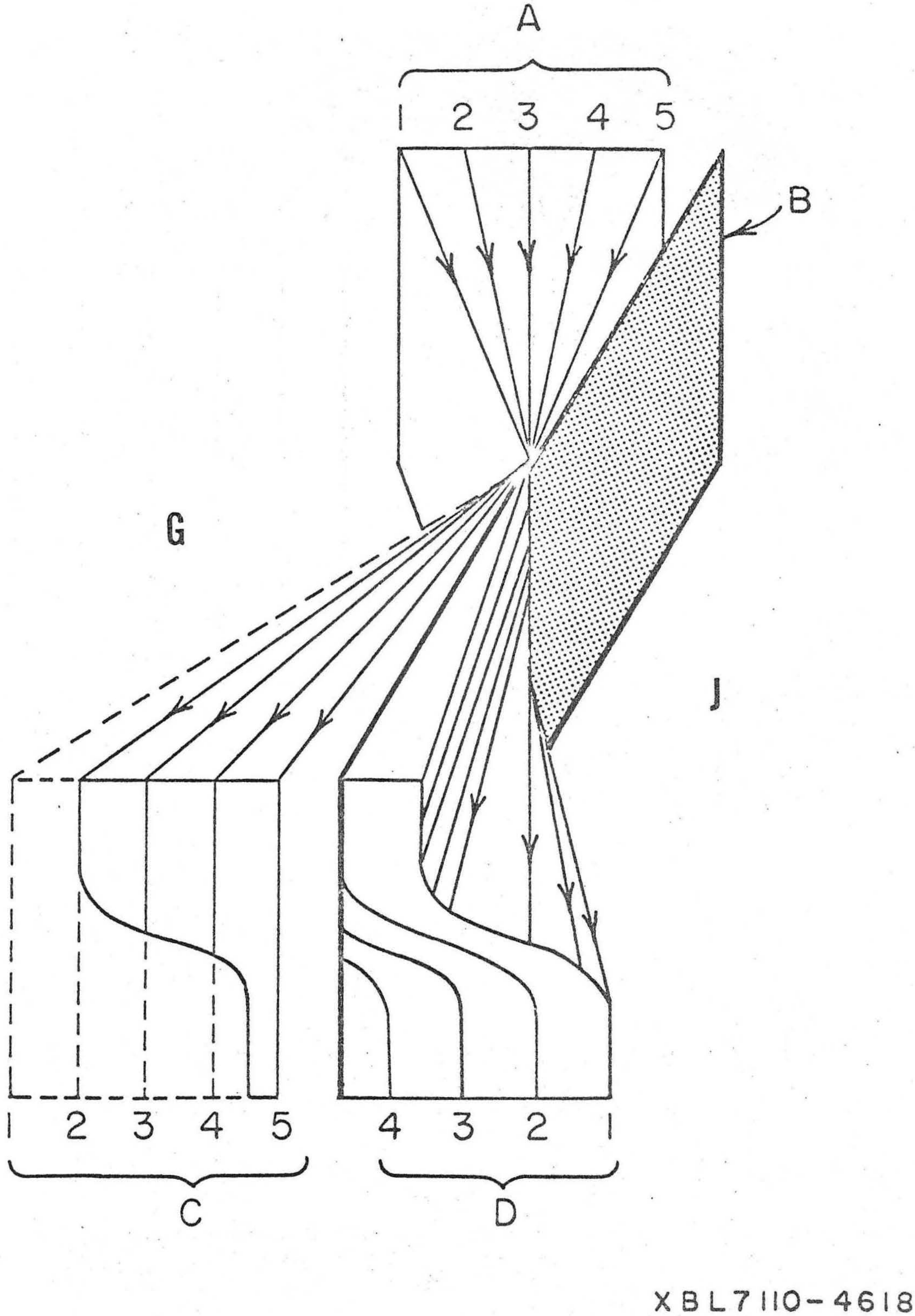

Fig. 5

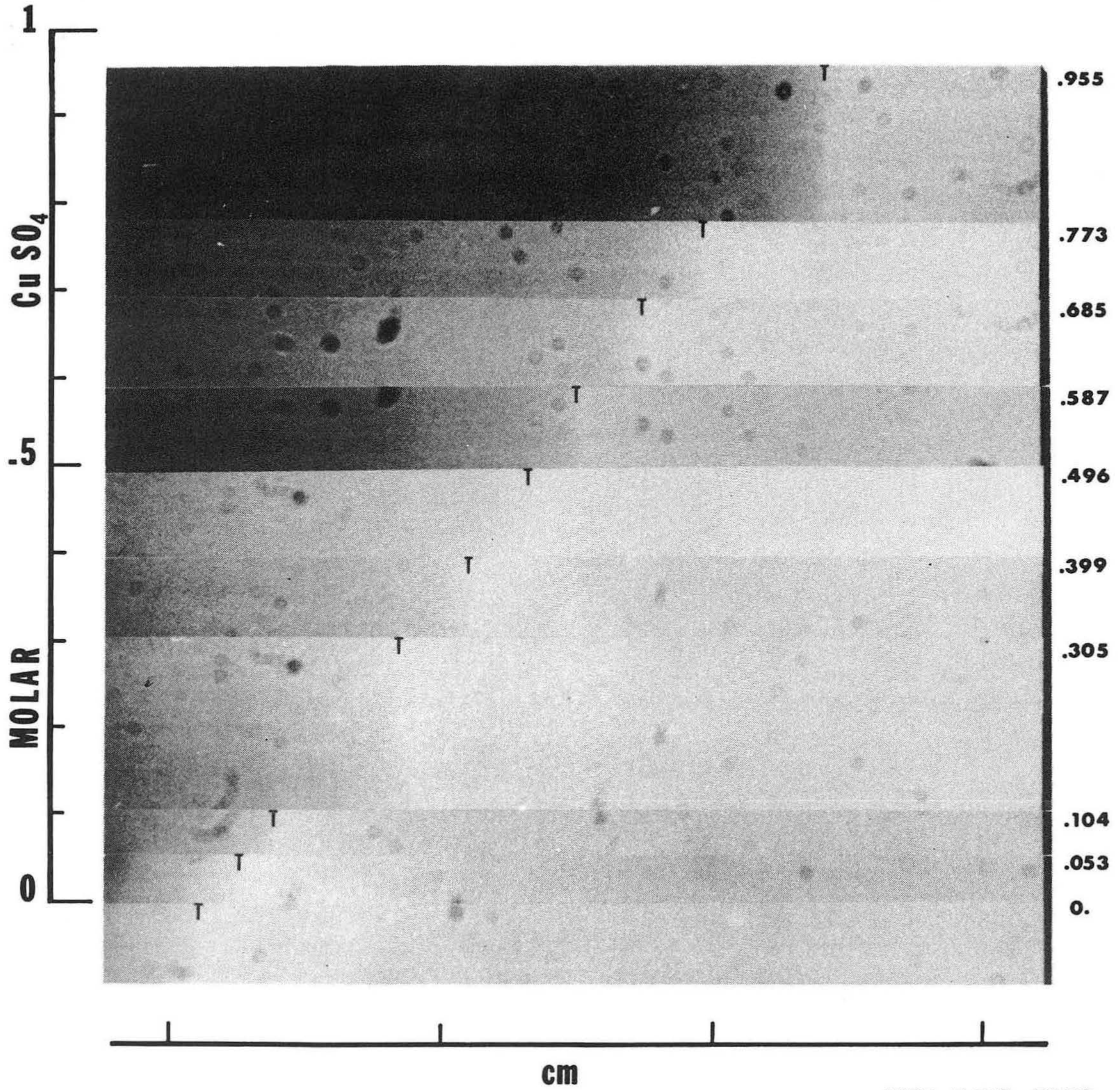

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Fig. 6

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