Remarkable Optical Properties of the Alkali Metals

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Thin films of alkali metals opaque to visible light are highly transparent in the ultraviolet region. The point in the spectrum at which transparency commences moves toward shorter wave-lengths with decreasing atomic number as follows: Cs 4400; Rb 3600; K 3150; Na 2100; Li 2050A. The transparency continues as far down the spectrum as the investigations have gone (1860A). In this region the phenomenon of plane polarization by reflection is observed. The reflecting powers of these metals for different wave-lengths have been measured. From these measurements and also from the Brewsterian angles for plane polarization, the refractive index of a potassium film has been calculated. The values range from 0.90 at 2147A to 0.50 at 3100A. Since the refractive index is less than unity total reflection takes place, although the critical angle is not sharply defined. Interference maxima and minima in the spectrum of light reflected from a metal film permit a rough determination of the film thickness.

THE optical properties of the metals of the alkali group have been investigated chiefly with reference to the photoelectric effect, their optical constants having been studied in only a few instances and then only in the visible region of the spectrum. Extension of this study into the region of shorter wave-lengths has brought to light the very remarkable fact that, at a certain point in the spectrum, they cease to exhibit the optical properties of metals and acquire those of transparent media, yielding plane polarized light by reflection of ordinary light at a Brewsterian angle, from which their refractive index (and dispersion) can be calculated. A preliminary report of these results was published in *Nature* for April 22, 1933.

As was shown by the writer[1] over fifteen years ago, films of sodium and potassium, deposited on the inner walls of highly exhausted quartz bulbs at liquid air temperature, while completely opaque to visible, were highly transparent to the ultraviolet. The entire spectrum from wave-length 3000 to the limit reached by the quartz spectrograph was freely transmitted in the case of potassium. No additional observations of importance appear to have been made since these experiments and the investigation was taken up again with a view to studying the optical properties of all the alkali metals in a more quantitative manner and over a wider spectral range than in the earlier investigation.

Their high transparency indicated that other interesting phenomena were to be expected.

It is necessary to deposit the films at liquid air temperature, for at higher temperatures a colloidal deposit is obtained, the optical properties of which are quite different from those of homogeneous films.

The films deposited in this way, in the earlier investigation, survived exposure to room temperature for only a few minutes. Minute holes appeared which increased in size rapidly and acquired arborescent forms. The metal finally gathered into invisible drops and the bulb became almost completely transparent. In the present work it soon developed that a certain degree of permanency at room temperature was acquired if before the introduction of the metal, the bulbs were thoroughly degassed by prolonged pumping at high temperature. A potassium film formed under these conditions, of such thickness that the sun's disk was barely visible through it, lasted several days before developing small pinhole leaks. Such a film forms a most useful filter for spectroscopic work as it transmits everything below 3000, reducing the intensity to about one-fourth, while the entire visible and upper ultraviolet is certainly reduced several hundred thousand times.

In some of the bulbs, probably because of imperfect degassing, a potassium film, deposited in the form of a circular disk 2 cm in diameter, when warmed to room temperature contracted

[1] R. W. Wood, Phil. Mag. **38**, 98 (1918).

to a single flattened globule about 1.5 mm in diameter at the center of the circle. It seems surprising that surface tension can draw in a metal having a rigidity of a moderately hard wax. Further investigations along these lines are contemplated.

The bulbs are prepared in the following way. A quartz bulb is blown of the form and size shown in Fig. 1a, with very thin walls, and the
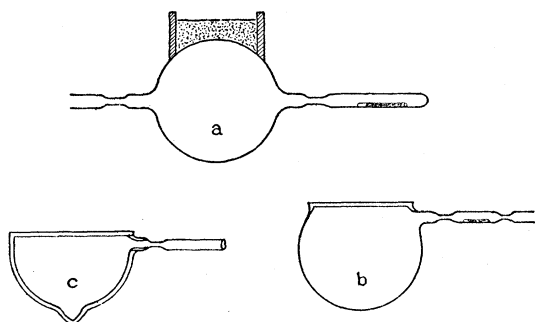

FIG. 1. Forms of bulbs used.

metal introduced into the side chamber either by distillation from a mixture of the chloride with calcium turnings or from the metal contained in a very thin walled tube of about 1 mm bore. A small fragment of the metal should be melted in a tube of about 8 mm bore, closed at the bottom, and a small amount sucked up into a long capillary tube made by drawing out a short piece of thin walled tubing. It is advisable to use a rubber tube for this operation as it is easier to watch the rise of the metal. A number of such tubes can be prepared at one time, closing one end by fusion near the metal and the other by a small lump of soft wax. A piece of the desired length is then cut off with scissors and quickly slipped into the side tube, which should be immediately sealed and the pump started. The exhaustion is best done with a mercury vapor pump with liquid air trap, the bulb being heated up to the constricted portions over a Bunsen flame or in an electric furnace. After a thorough exhaustion the bulb is allowed to cool, the metal distilled into it and the side tube sealed off. The metal should now be driven back and forth from one side of the bulb to the other with a small flame to remove occluded hydrogen. After sealing

off the bulb from the pump a spot is cleaned by a small pointed gas flame and this spot covered by a short piece of fiber tube half filled with infusorial earth (shown in Fig. 1), or other similar incombustible power, covered with a disk of filter paper and then thoroughly saturated with liquid air. The metal is then deposited by local heating of other parts of the bulb with the flame. The thickness of the film is regulated by the area cleaned off. During the operation the capsule can be removed for a few seconds and the opacity observed by viewing a small electric lamp mounted below the bulb.

The point in the spectrum at which transparency commences moves towards shorter wave-lengths with decreasing atomic number, as follows: caesium 4400, rubidium 3600, potassium 3150, sodium 2100, lithium 2050. A little uncertainty is felt about lithium, as some plates indicated that its transparency commenced at about the same point as in the case of sodium, while others indicated a shift towards shorter wave-lengths. Interference introduces an uncertainty as will appear presently.

The transmission spectra of the five metals are shown by Fig. 2, the source of light being an end-on hydrogen tube with its inner wall silvered to suppress the line spectrum by catalyzing the atomic hydrogen. The upper spectrum shows the distribution of intensity with the spectrograph employed, a small quartz instrument with its prism replaced by one of fluorite. The great intensity recorded in the region of longer wave-lengths makes the efficiency of the metal filters in suppressing this part of the spectrum all the more striking. The absorption bands below 1900 are the oxygen bands of the air. A comparison spectrum of the Cd-Al spark is at the bottom of the figure.

Because of underexposure the transparency of the last three metals in the region of shortest wave-lengths is not apparent in these photographs. It is brought out to better advantage in Fig. 3 made with the Cd-Al spark. Here rubidium and potassium show commencement of transmission at the same point, but the point of highest transparency for potassium is shifted to the right. The failure of the last aluminum line, 1860, to appear in the case of lithium has not

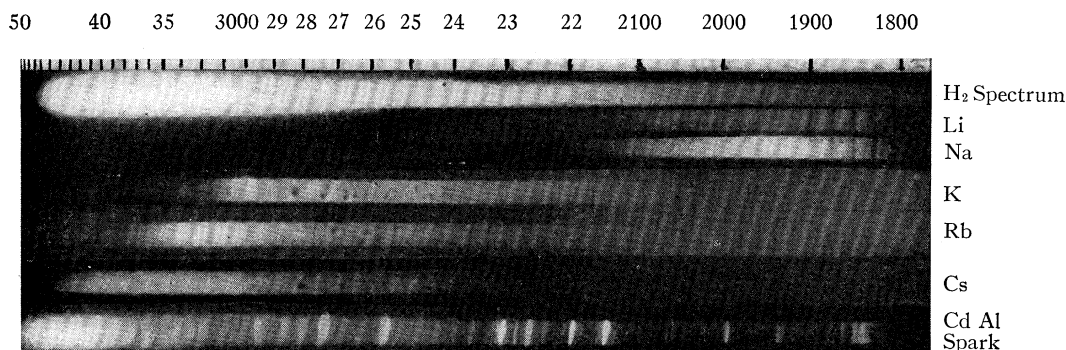50   40   35   3000 29 28 27 26 25 24   23   22   2100   2000   1900   1800

FIG. 2. Transmission by the alkali metals of light from a hydrogen tube.
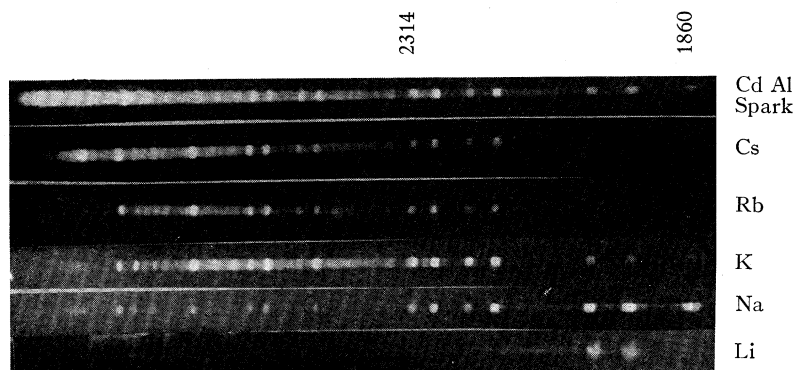

FIG. 3. Transmission by the alkali metals of light from a Cd-Al spark.

been explained but it is certainly not due to absorption by the metal as it appears in other spectrograms. The transparency continues from the points indicated as far down the spectrum as the investigations have gone at the present time, i.e., to about 1860. In the case of caesium there appeared to be indications of a slight increase of absorption at the extreme end of the spectrum. It is clear that we have in these cases a very wide gap between the absorptions due to the free and bound electrons. A somewhat similar but very narrow gap occurs in the case of silver at $\lambda = 3160$, but the transparency in the case of the alkali metals is of a different order of magnitude from that of silver. A film of potassium through which the sun's disk is barely visible (which means a reduction of intensity of perhaps half a million) transmits 25 percent of everything below 3000.

The case of caesium is especially interesting as its region of high transparency begins in the visible violet and films of the proper thickness transmit light of a rich violet color as deep and pure as that transmitted by a strong solution of cuprammonium or dense cobalt glass.

The transmission of potassium is illustrated by Fig. 4a for a film of increasing thickness, the upper spectrum of two seconds exposure made with no film, the following spectra with eight seconds exposure, a candle flame easily visible through the film in the first case and the sun's disk absolutely invisible in the last. It is to be noticed that only a very slight increase in the ultraviolet absorption accompanies this enormous increment in the absorption of visible light. It seemed probable that the high transparency would be accompanied by a very low reflecting power and this was found to be the case, the reflection of potassium, for example, at wave-length 2147 being only 0.003, or 1/10th that of a single surface of fused quartz.

The reflecting powers for different wavelengths for these metals, with the exception of lithium, are shown by the curves in Fig. 5.
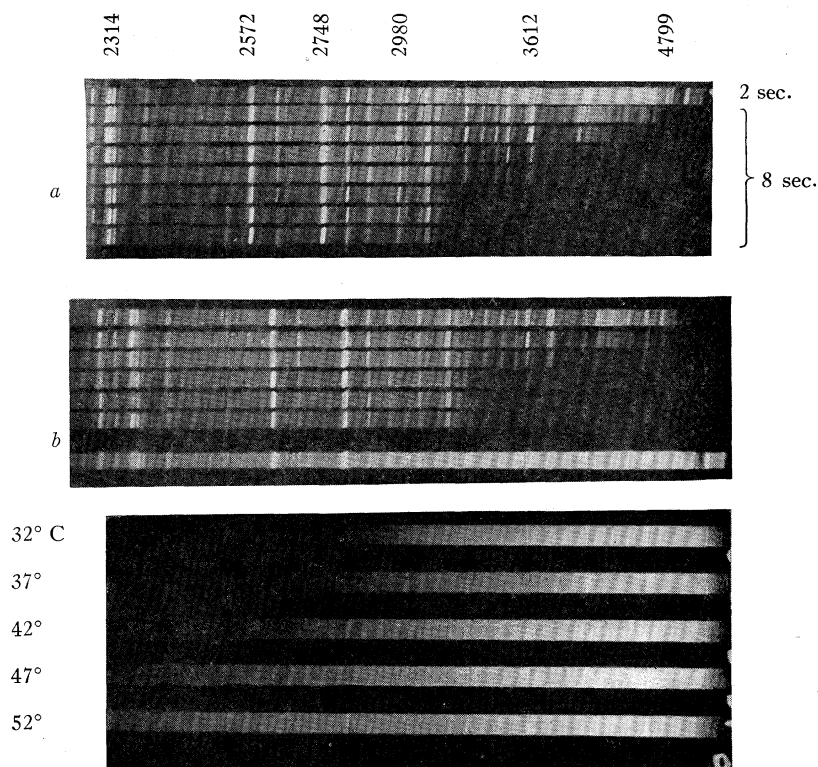
FIG. 4. Transmission of light by various thicknesses of potassium film.

Values higher than 30 percent are not given, as only determinations in the region of low reflectivity were made. This very low reflecting power, combined with high transparency, raised the question as to why the intensity was reduced to one-quarter by transmission through a moderately thin film, while a further considerable increment of thickness produced very little change in the intensity of the transmitted light. The loss evidently occurred at the surface and

FIG. 5. Reflecting power of films of alkali metals and the dispersion curve for potassium.

the only plausible hypothesis appeared to be that there was a surface scattering. The metal surface sometimes showed slight traces of granularity, a faint halo appearing around the reflected image of the spark. A film was accordingly built up with especial care to avoid this condition, the capsule being wet with liquid air every half minute. A series of photographs for increasing thicknesses, with exposures of five seconds each and a final exposure, also of five seconds, with the film cleaned off, is reproduced in Fig. 4b. Comparison of the first spectrum with the last shows very little difference in intensity in the short wave-length region, certainly not a 1 : 4 ratio, as in the case of Fig. 4a where equality was secured with exposures in this ratio.

The reflecting powers for different wave-lengths were determined by forming a very thick film on the inner surface of the quartz bulb, cleaning off the front surface with a small flame and pointing a quartz spectrograph at the image of a Cd-Al spark reflected in the concave metal
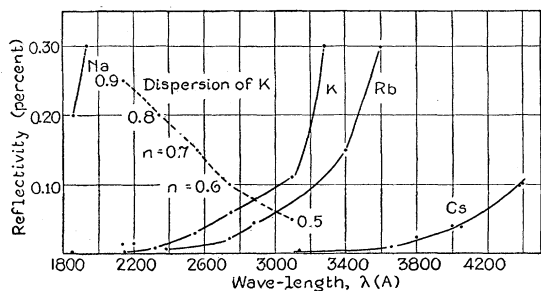
mirror, the spark being close to the slit. A number of exposures of different times were made, after which the film was removed by the flame and the outer surface of the quartz painted with black Duco. A second set of exposures was now made of the reflection from the single surface of quartz. By comparison of these plates the reflecting power of the metal in comparison to that of quartz was determined. After the reflecting power of quartz for the different spectral lines had been computed from the table of its refractive indices, it was easy to determine R for the metal.

From the reflecting powers thus determined, the refractive index of the metal can be determined, as in the case of transparent substances, from the formula $(n-1)^2/(n+1)^2 = R$ in which R is expressed in percent. The rigorous formula could not be used as no measurements of the absorption coefficient have been made as yet. The dispersion curve for potassium obtained in this way is shown (dotted) in Fig. 5.

Certain anomalies, observed at first in the measurements of the reflecting power for different wave-lengths, were suspected to be due to interference between rays reflected from the front and back surface of the metal film, which would be almost certain to occur in the case of a film of such high transparency.

It should then be possible to photograph maxima and minima in the spectrum of the light from a continuous source, as in the case of thin films of glass. Substitution of the end-on hydrogen tube as a source proved the presence of very distinct maxima and minima and a series of spectra were then taken in coincidence, the thickness of the potassium film being slightly increased between each exposure. The cell of infusorial earth was attached to the bulb with a wire and liquid air introduced through a small thistle tube every few minutes as shown in Fig. 6, in which case a bulb with a flat plate as the reflecting surface is represented.

The spectrograms are reproduced in Fig. 7 which shows in a very graphic manner how the interference minima enter the spectrum at the short wave-length end and move gradually along the spectrum as the film thickness increases. As the reflection minima move up the spectrum

they become less well defined, because of increased loss by reflection at the first surface. They cannot be pushed beyond wave-length 3000.
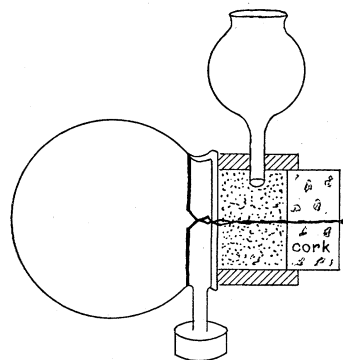

FIG. 6. Arrangement of bulb for interference measurements.

The prediction was now made that these metals would show a Brewsterian angle in the ultraviolet, giving plane polarization by reflection of ordinary light. This was found to be the case, the angle varying with the wave-length, so that it became at once possible to calculate the dispersion from the formula $n = \tan i$, in which i is the polarizing angle.

For the experiments on polarization a quartz bulb of the form shown in Fig. 1b was made by fusing an optically worked circular disk on the end of a tube, inserting a small side tube for exhaustion and introduction of the metal, drawing down (Fig. 1c) and then blowing out, a thin walled bulb as shown. This bulb was mounted on a divided circle with the reflecting inner surface parallel to and over the axis of rotation, Fig. 6. The rays from the image of the spark in the metal mirror were passed through a double image Wollaston prism and focussed on the slit by a short focus fluorite lens. From the relative intensities of the cadmium lines in the two images the completeness of the polarization could be determined, the ratio of exposure times to secure equality being in some cases as 1 : 400.

The Brewsterian angle, in the case of potassium was found to vary with the wave-length, making it possible to determine the dispersion of the metal in the ultraviolet. Considerable trouble was experienced at first due to the fog on the plate caused by the high reflecting power of the metal films in the violet and upper ultraviolet.
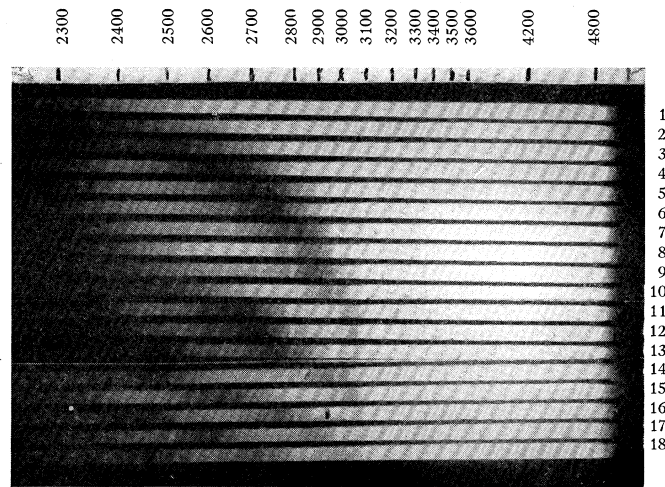
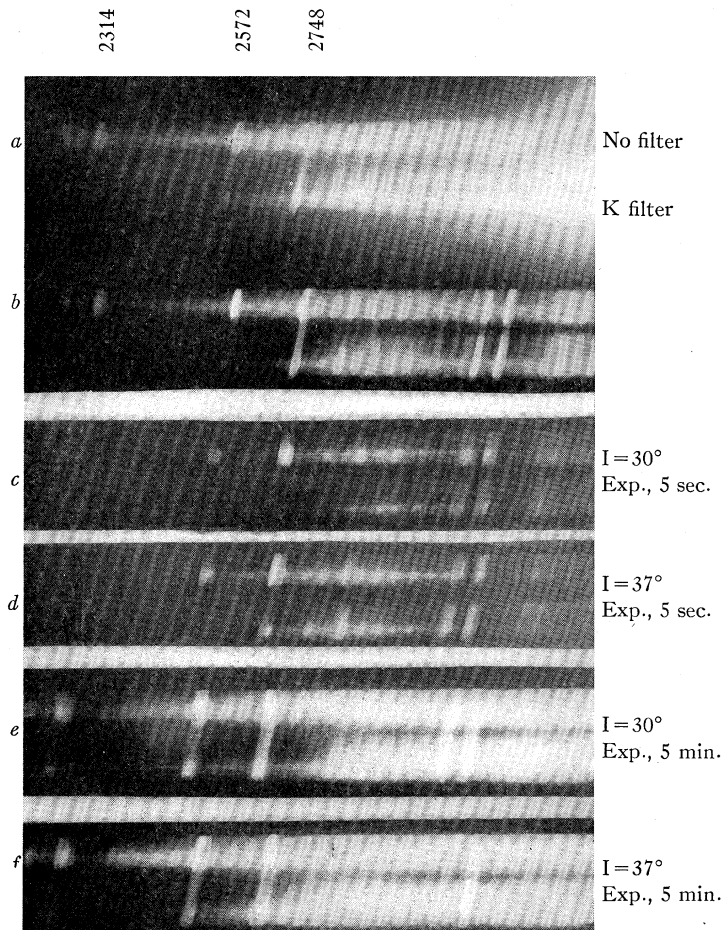FIG. 7. Interference minima by reflection from potassium film of increasing thickness.

FIG. 8. Plane polarization by reflection from potassium.

This was overcome by inserting a second quartz bulb with a fairly thick potassium film in front of the spark as an ultraviolet filter. The advantage gained by the use of this filter is illustrated in Fig. 8, the upper pair of polarized spectra (a) having been made without the filter, the second pair (b) with the filter inserted. The two polarized spectra have equal intensity above 2748 while the lower spectrum is practically absent below this point. The dispersion is illustrated by Fig. 8c and e, which show that the polarizing angle for 2748 is 30°, the intensity of this line in the lower spectrum being about 1/40 of that in the upper. An exposure of five seconds was given for c and five minutes for e to bring out the 2314 line, for which the intensity ratio is 1/10. Figs. d and f show a polarization angle of 37° for 2314, the measured intensity ratio in this case being 1 : 240.

The intensity ratios were measured by giving, say, a five minute exposure to the two spectra, and then making a series of exposures of the brighter spectrum (covering the image of the fainter on the slit) of 1, 2, 4, 8, . . . etc., seconds, picking out the one which matched the fainter spectrum made with the five minute exposure. The results obtained in this way are, of course, not very accurate but the dispersion calculated from the values of the angle i of maximum polarization by the formula $n = \tan i$ agreed surprisingly well with the values obtained from the reflecting power, as shown by Table I.

TABLE I. *Refractive index of potassium film as measured by reflection and by polarizing angle.*

λ	n (from R)	n (from Pol)
2147	0.895	—
2200	.877	0.86
2314	.83	.80
2572	.70	.69
2748	.60	.58
3100	.50?	—

DETERMINATION OF FILM THICKNESS FROM INTERFERENCE BANDS

We can determine the thickness of the metal film from the interference bands shown in Fig. 6 and obtain as well a check on the values of n for the different wave-lengths.

A preliminary calculation showed that the interference bands could not be reconciled with the calculated values of n if reflection from the two surfaces of the metal involved no relative phase change. Since n is less than unity, in every case we are dealing with a reflection from "dense to rare" at the vacuum-metal interface and from "rare to dense" at metal quartz surface. Assuming a phase change of 180° such as we have in the case of a transparent film we have for e the thickness for a minimum $e = 2(n-1)\lambda/4$ in which n is the order of interference, or thicknesses corresponding to 0, $\lambda/2$, λ, $3\lambda/2$, etc., and λ is the wave-length in the metal which can be calculated from the dispersion curve.

If the values of the refractive indices are correctly given, the values of e, the thickness calculated from, say, three interference bands, should agree. For spectrum No. 4, Fig. 5, the minimum comes at 2650, for which $n = 0.65$ giving $\lambda = 4100$ or $e = 2050$A.

For spectrum 6 we have two minima available, at 2200 ($n = 0.87$) and 2750 ($n = 0.6$), the former giving $e = 2530$A, the latter 2300A, a fair agreement under the circumstances.

For spectrum 11, Fig. 7, we have minima at 2300 ($n = 0.83$), 2600 ($n = 0.65$) and a third in the vicinity of 3100, the position of which cannot be accurately determined as it falls in the region of strong reflection and the interference is incomplete. The values for the thickness in this case were 4150 and 4100.

For spectrum 16, $e = 4620$ calculated from the band at 2750 ($n = 0.60$) and $e = 4830$ from the band at 2450 ($n = 0.76$). This last case shows us that with a film of thickness equal to twice the wave-length in air, we have sufficient intensity, after two transmissions, to produce strong interference. In the case of silver a single transmission through a film one-tenth of a wave-length in thickness reduces the intensity to less than 1 percent.

ANGLE OF TOTAL REFLECTION

As the alkali metals function for ultraviolet light as the rarer medium with respect to vacuum, an angle of total reflection is to be expected which can be calculated from the refractive index. Calculations showed that total reflection should occur at an incidence angle of

about 30° for wave-length 2750, at 45° for 2570 and 52° for 2350. A series of spectra of the light of the hydrogen tube reflected at incidence angles included in this range are reproduced in Fig. 4c showing the gradual extension of the spectrum towards shorter wave-lengths with increasing incidence angle. There is, however, no sudden transition in the intensity at a definite wave-length as is to be expected for an imperfectly transparent medium.

The results obtained up to the present time are to be regarded as preliminary only. No determinations have been made as yet of the coefficient of absorption and it is obvious that it is extremely important to investigate the optical constants in the transition region where the extreme opacity passes over into comparative transparency. This investigation will require the development of a technique for the determination of the angles of principal incidence and azimuth in the visible and upper ultraviolet region and preparations for this work are now under way.

50   40   35   3000 29 28 27 26 25 24   23   22   2100   2000   1900   1800

H₂ Spectrum
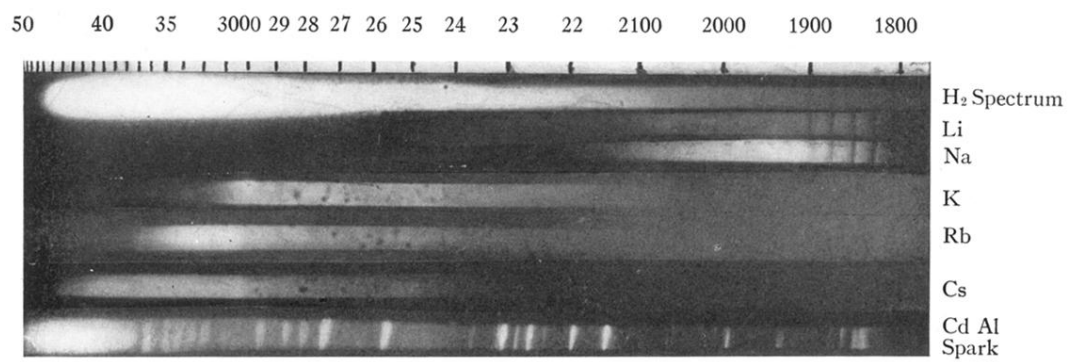Li
Na
K
Rb
Cs
Cd Al
Spark

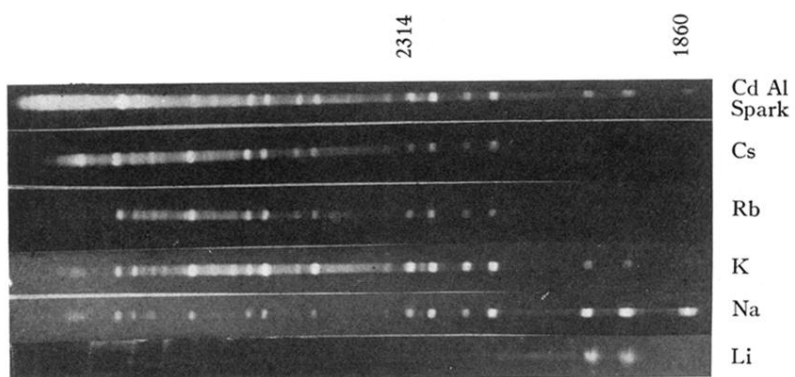Fig. 2. Transmission by the alkali metals of light from a hydrogen tube.

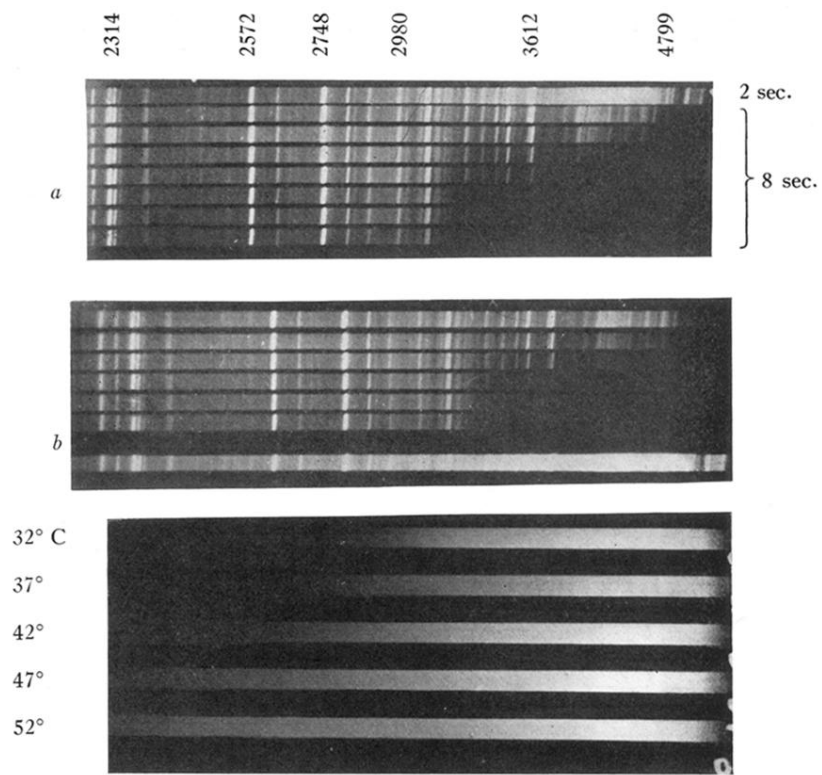FIG. 3. Transmission by the alkali metals of light from a Cd-Al spark.

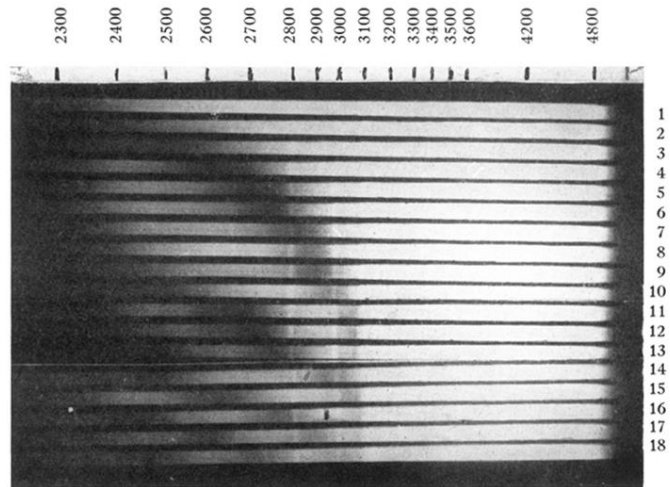FIG. 4. Transmission of light by various thicknesses of potassium film.

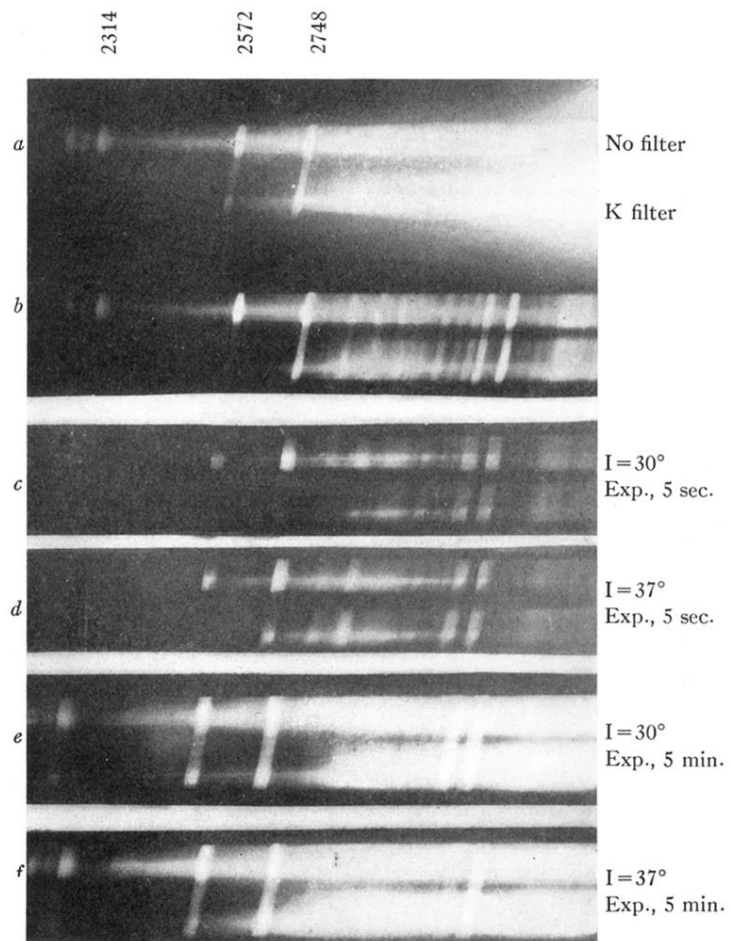FIG. 7. Interference minima by reflection from potassium film of increasing thickness.

FIG. 8. Plane polarization by reflection from potassium.