TRANSMISSION CHARACTERISTICS IN THE VISIBLE SPECTRAL REGION OF THE QUINALIZARIN AND BERYLLIUM-QUINALIZARIN COMPLEX IN N/4 SODIUM HYDROXIDE SOLUTION

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ILLUSTRATIONS

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INTRODUCTION

A chemical method of analysis for beryllium was developed recently in Bureau of Mines laboratories, In this method,, quinalizarin (1-2-5-8 tetrahydroxyanthraquinone) in N/4 NaOH is used as a colorimetric titration reagent. This solution has a reddish-purple color, whereas the solution containing equivalent amounts of beryllium and the dye is rather blue. In the titration procedure, standard quinalizarin solution is added to the unknown beryllium sample and to two standard beryllium samples of different but known concentrations. Then adjustments in concentrations of BeO in the two known and of quinalizarin in all three are made until the red-violet shade of the unknown is halfway between that of the two knowns. The amount of BeO in the unknown is calculated from the known BeO content of the solutions between which it lies. It is extremely difficult to distinguish the slight differences in shade of these solutions without the use of a proper light filter, especially when the concentration is over 0.1 mg, of BeO, so a study was made of the transmission characteristics of quinalizarin in N/4 NaOH and of the corresponding beryllium complex to determine what filter would give the most contrast.

ACKNOWLEDGMENT

We take pleasure in acknowledging our indebtedness to S. F. Ravitz, who suggested this problem, to M. R. Howcroft for the preparation of the solutions studied, and to E. V. Potter for helpful-suggestions concerning the work.

APPARATUS

In most-investigations of this kind nearly any type of spectrometer can be used satisfactorily. In this case, however, the color of the solutions begins to fade immediately after preparation, and there is a marked change in appearance at the end of 10 minutes. Thus, only instruments that can determine the absorption characteristics of the solutions throughout the desired spectral range in a very short time are applicable.

A Baird grating spectrograph was used. The light source was a line-filament galvanometer lamp. The optical system, besides the photographic plate and the grating, consisted of a 200-micron slit, a filter, and a plane-convex lens (F 5.3) adjusted so that a moderately sharp image of the lamp filament appeared at the grating. The solution being investigated was contained in a 5-cm. glass absorption cell supported just in front of the slit.

It is obviously desirable to have a light source with equal energy distribution throughout the visible region, and also, if possible, to use a photographic plate having more or less uniform response over this same range. A tungsten incandescent lamp operated under ordinary conditions, so that its color temperature is in the neighborhood of 2,800º K., yields a relatively low radiant-energy output below a wave length of about 0.55 micron, but the relative amount of energy radiated in the lower wave length range can be increased by raising the temperature of the filament to about 3,300º K. Also, a filter that absorbs strongly in the red region can be used to give more uniform spectral distribution of energy. There is some objection to the first procedure, as the life of the lamp is greatly reduced. The second procedure increases the exposure time required, but this can be remedied to a certain extent by using a thinner absorption cell. For our work, the latter procedure was followed, the Corning glass filter, Daylite No. 5900, being satisfactory. Eastman I-F plates were employed because of their good response over nearly the entire visible region.

PLATE CALIBRATION

As the photographic plate density is not proportional to light intensity, especially at low intensities, it was first necessary to calibrate the plates to obtain the true relationship between light intensity and plate density. The gamma of any given class of photographic plates varies with wave length; hence, when a broad wave-length band is under investigation it is necessary to obtain a series of calibration curves, each curve being identified with a particular wave length. The difference in wave length between any two consecutive curves should be such that these two serve for the intervening region without gross error.

To eliminate variations between plate emulsions, a group of plates having the same emulsion number was selected, and members of this group were used in all subsequent work. As all the solutions of quinalizarin and the complex are prepared in N/4 NaOH, the absorption cell was filled with this solution and used for plate calibration. Variations in plate exposure were obtained by means of a rapidly rotating step-sector having seven different but accurately known angular apertures. The exposures were timed accurately for 4 minutes. All plates were developed for 5 minutes at 18º C. in Eastman D-19 developer. As the group had the same emulsion number and the development process was the same for each plate, it was assumed that the average calibration for a pair of plates would serve for the lot. After processing and identifying wave lengths by means of an iron spectrogram placed on the plate for this purpose, density measurements were made continuously across each band with a Leeds and Northrup recording densitometer. The density of blackening D for particular wave lengths obtained from the densitometer was then plotted against the logarithm of the relative exposure or effective light intensity I determined by the angular openings in the step sector. This group of curves was used later in determining the transmission characteristics of the solutions. Brode[3] has pointed out that errors resulting from the application of the sector method are small. Although the plates did not have a uniform density throughout the visible wave length range, the above procedure proved adequate for our needs.

EXPERIMENTAL PROCEDURE

Specified volumes of standard BeO and standard quinalizarin solutions having a 1-to-1 equivalent were measured from burettes into a 100-ml. calibrated flask and brought up to volume with N/4 NaOH solution. Solutions so prepared were poured into the absorption cell, and a four-minute exposure was made at once. The color of solutions of beryllium-quinalizarin complex faded somewhat, but not too much, in this time interval. Solutions of quinalizarin without any beryllium also were prepared and spectrograms taken. In all of these tests the step-sector was omitted.

After processing and wave-length identification, density measurements were made along each spectrogram. For given wave lengths, $\log_{10} I$ was read from the corresponding plate calibration curve. T, the transmission can then be calculated as T = I. The percent transmission, or transmittancy, is equal to T x $100/T_0$ where T_0 is the transmission of the original solution (N/4 NaOH in this case) and is taken as 100 in our procedure; the transmittancies are thus obtained directly.

RESULTS

The results of these tests for both standard quinalizarin and the beryllium-quinalizarin complex are shown in figure 1. Curves A, B, and C are for 1 ml., 2 ml., and 3 ml. of standard quinalizarin in N/4 NaOH solution, respectively. The corresponding curves for the beryllium-quinalizarin complex solutions containing, respectively, 1 ml., 2 ml., and 3 ml. of each of the standard BeO and quinalizarin solutions are shown as A', B', and C'. It is readily seen that there is no very marked difference in the transmission characteristics of these solutions.

Tests were then made varying the relative amounts of the standard BeO and quinalizarin solutions. Three mixtures were used, each containing l ml. of quinalizarin with 0.7, 1.0, and 1.5 ml. of the BeO solutions, respectively. The transmissivities, or percent transmission values, were so nearly alike that the separate curves could not readily be distinguished, and an average curve is shown in figure 2 as curve D. Curve E was obtained with appreciable excess of quinalizarin, a solution containing 1 ml. of quinalizarin and 0.5 ml. of BeO being used. These results show that it is not possible to distinguish between a neutral solution and one close to it from transmittancy curves. However, with a proper filter, the eye can discern a difference,

It is noted from the curves in figure 1 that the change from quinalizarin to the beryllium-quinalizarin complex increases the percentage transmission in the blue region by approximately 3 percent, whereas it decreases that of the red region by about 12 percent. This is not a marked effect, and perhaps none is to be expected. A standard beryllium solution containing 0.100 mg. of BeO per ml. is equivalent to

[3] Brode, W. R., Chemical Spectroscopy: John Wiley & Sons, New York, 2d ed., 1943, pp. 110-113.

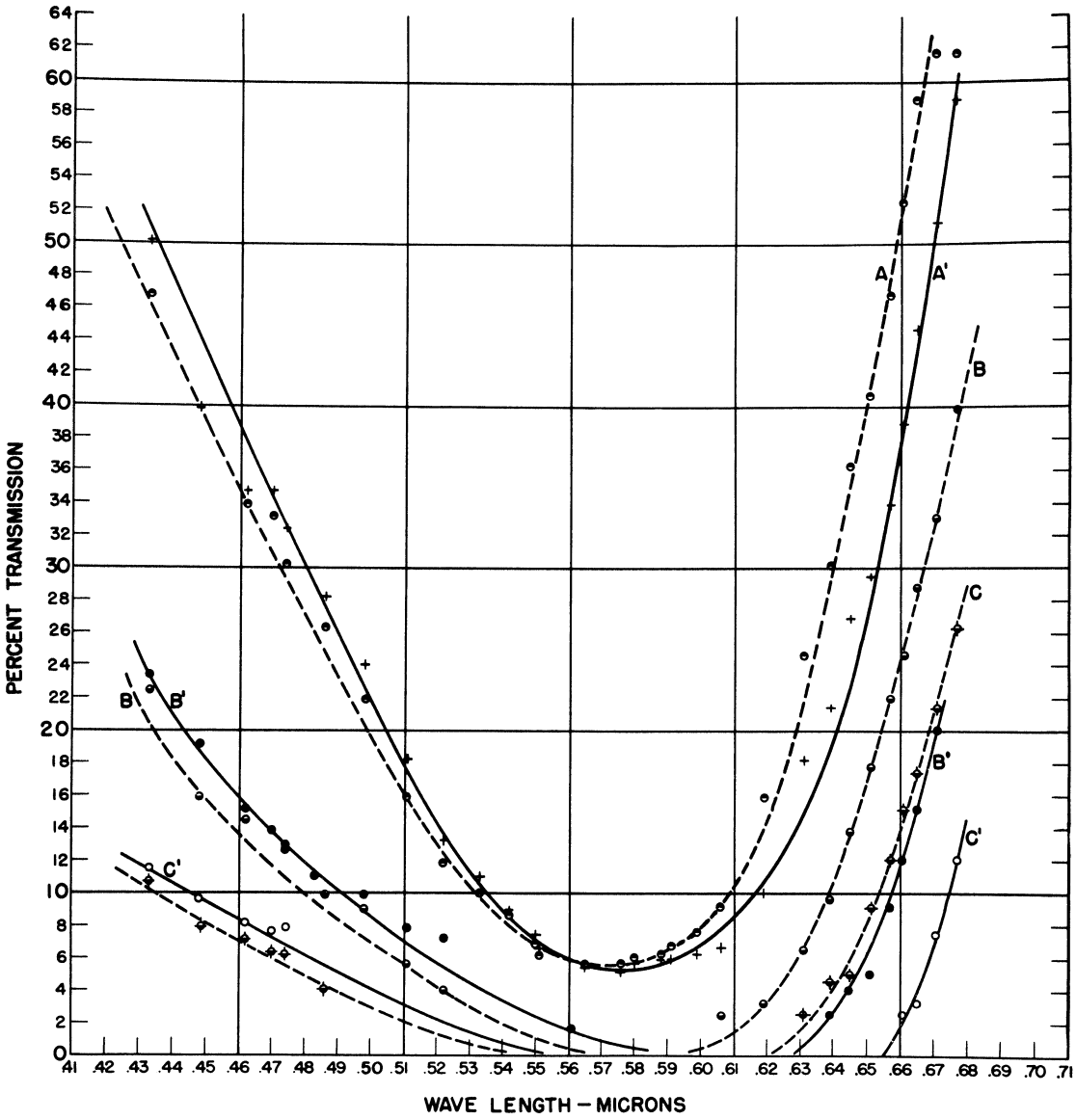


Figure 1. - Transmission characteristics of quinalizarin and Be-quinalizarin complex in N/4 NaOH solution.

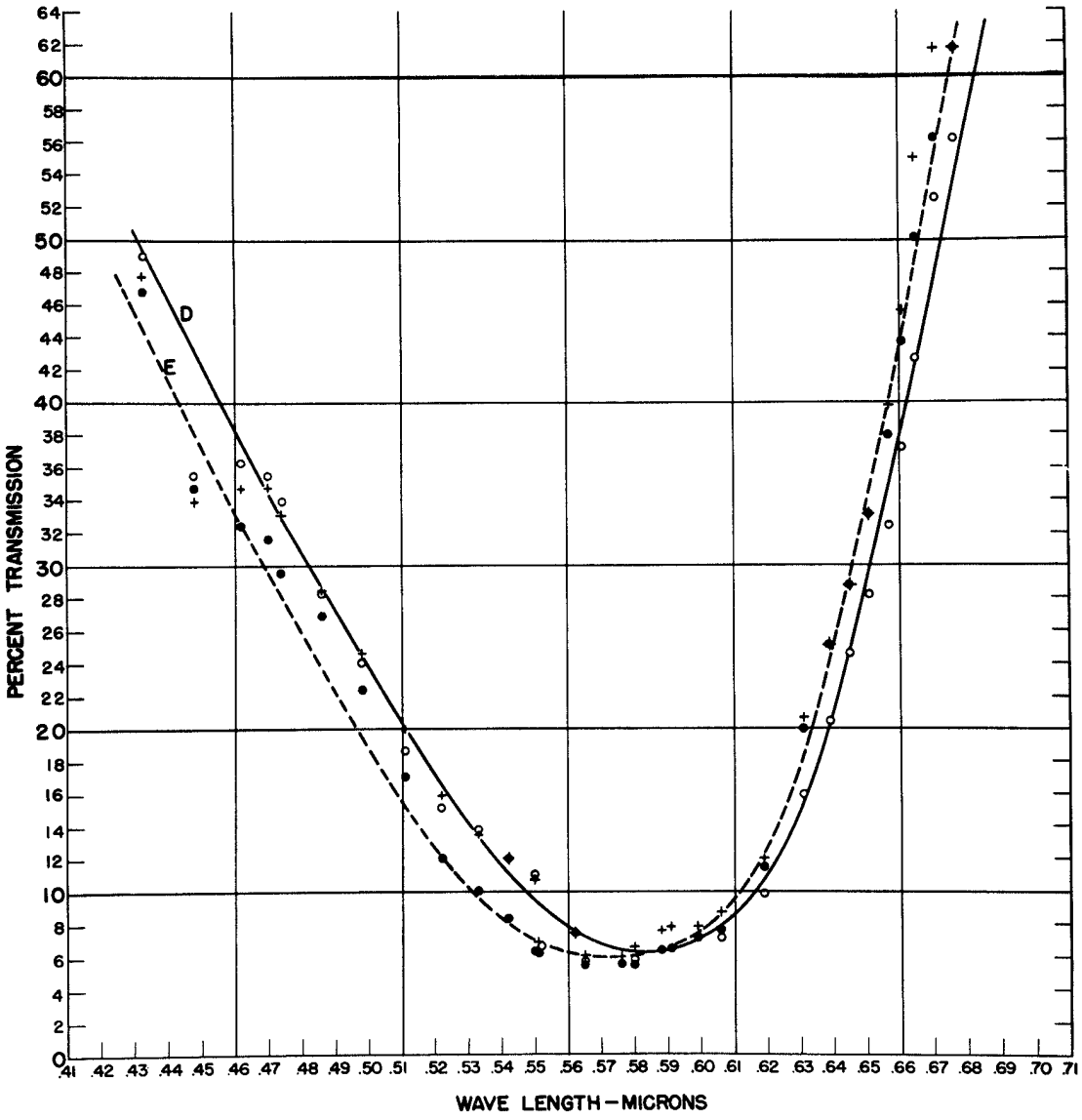


Figure 2. - Transmission characteristics of quinalizarin and Be-quinalizarin complex in N/4 NaOH solution.

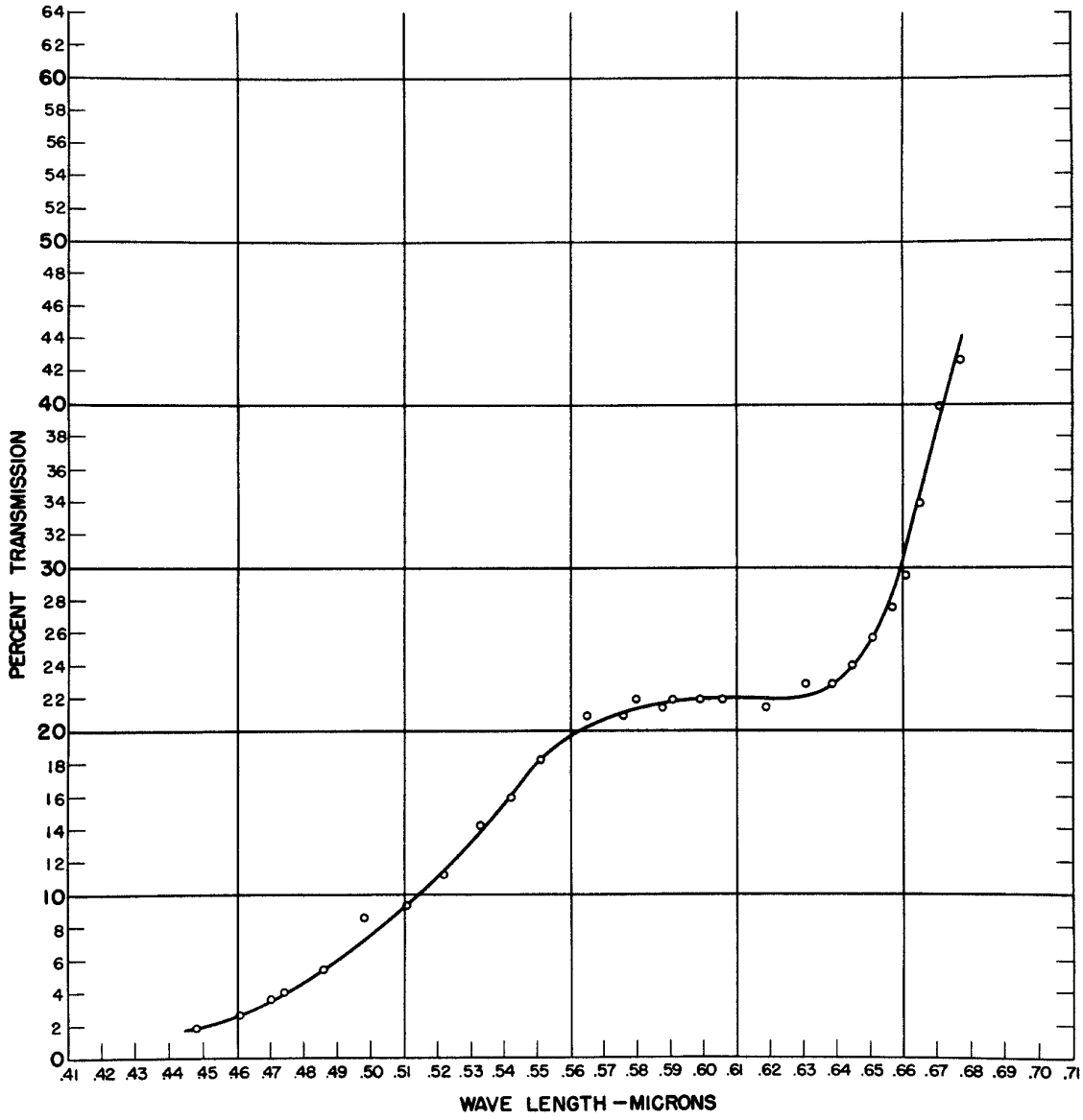
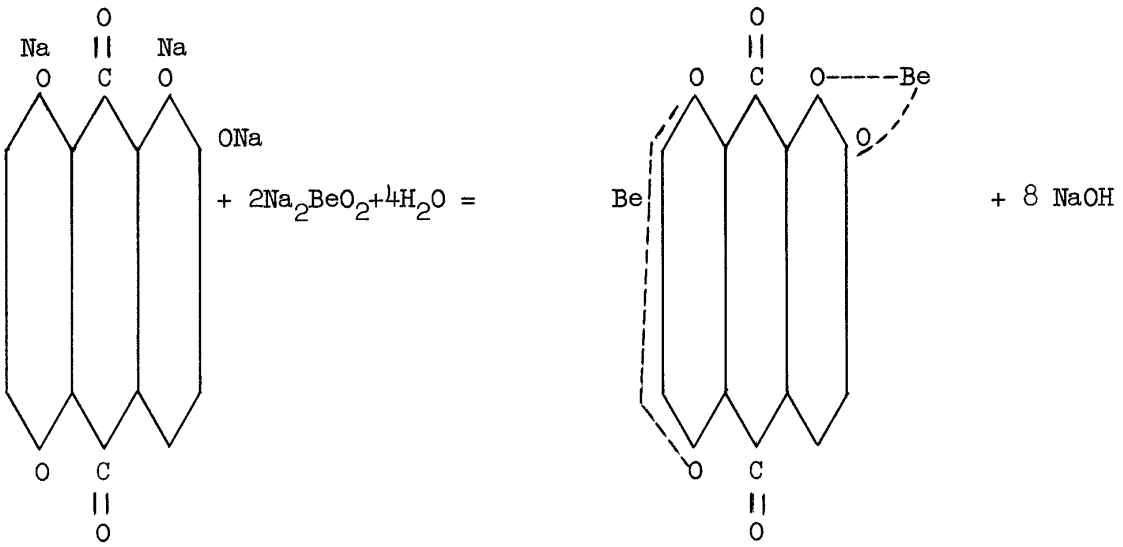


Figure 3. - Transmission characteristics, combined filters.

a solution containing 0.544 of quinalizarin per ml. The mol. ratio is thus 2 BeO:1 quinalizarin. Both solutions are prepared in N/4 NaOH. The probable reaction is



If this reaction is correct, the only change is the substitution of bivalent beryllium atoms for monovalent sodium atoms without any change in the structure of the organic group. There is some shift in the distribution of the resonance energy, however.

With the addition of quinalizarin to a beryllium-quinalizarin complex solution, the color becomes more of a red-violet. To aid the eye in detecting the increase in intensity of the red radiation, it would be better to filter out the wave lengths below about 0.55 micron. Yellow filters such as Corning Nos. 3421, 3480, or 3484 would then be suitable.

In the present titration procedure, no attempt is made to shield the vessel from the general scattered and extraneous radiation of the room. The filter that has proved to be most satisfactory under such conditions is a combination of Corning glass filter No. 3421 and a lens from a cheap pair of sun glasses. This lens appears to be slightly darkened, as by smoking, when viewed by reflected light and absorbs ultraviolet and blue light, transmitting yellow and red light. A transmission characteristic was obtained for this combination and is shown in figure 3. The total energy transmission for the visible wave lengths is much less than that for the yellow filter alone, and the general shape of the transmission curve for the combination also is different, in that the curve has been flattened materially in the yellow region.

CONCLUSIONS

1. A simple procedure for using a Baird grating spectrograph for the determination of transmission characteristics in the visible region has been described.
2. The transmission characteristics of quinalizarin and beryllium, quinalizarin complex in N/4 NaOH solution were determined. Curves for the complex are somewhat higher in the blue end of the spectral region and somewhat lower in the red end than those of, quinalizarin.
3. The transmission characteristics indicate that a yellow filter such as Corning Nos. 3421, 3480, or 3484 would be of aid during titration.
4. The transmission characteristic of a combination of Corning glass filter No. 3421 and a dark glass, which was found suitable for use during the titration, also was determined.