

## A New Chemical Method for Measuring the Ultra-violet Ray.

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1. There have been several methods to measure the ultra-violet ray using the photochemical reaction of solution. Among them, the methylene blue-acetone method contrived by Webster, Hill and Eidinow<sup>(1)</sup> and the uranyl acetate-oxalic acid method by Moss and Knapp<sup>(2)</sup> are well known. When these mixed reagents are irradiated with the ultra-violet ray, photochemical reactions take place which are more or less proportional to light energy. Thus, relative intensity of light may be obtained by quantitative determinations of reaction products.

But, as these reactions are not so sensitive and since at least ten to thirty minutes are necessary for the time of exposure, they are not useful for following a rapid change or measuring weak ultra-violet ray. For these purposes, the photochemical reaction of the leuco-base of triphenyl-methane dyestuff seems to be the most promising.

In fact, I. G. Farbenindustrie in Germany offered Bioklimatische Ultra-violet Dosimeter using a colorless sulfite of fuchsin. However, it has not sufficient sensibility to measure quickly weaker radiation. The author's intention has been to make more sensitive ultra-violet radiation from the sun and the sky using the photochemical reaction of the leuco-base of crystal violet.

2. Lifschitz<sup>(3)</sup> found that when colorless cyanide or sulfite of triphenyl-methane dyestuff is irradiated with the ultra-violet ray, the color of the original dyestuff develops immediately which gradually disappears again in the dark.

E. Weyde and W. Frankenburger<sup>(4)</sup> studied the photochemical behavior of leuco-bases of crystal violet. According to them, the rate of coloration of the leuco-base by ultra-violet ray is proportional to the quantity of light energy. The quantum yield of this photochemical reaction is almost nearly 1 in the region from 3135 Å to 2537 Å, and the maximum sensibility lies at about 2700 Å. The temperature coefficient of the reac-

(1) L. Hill, *Proc. Roy. Soc.*, A 114 (1927), 265.

(2) Moss and Knapp, *J. Soc. Chem. Ind. Trans.*, 44 (1925), 453.

(3) Lifschitz, *Ber.*, 52 (1919), 1419; 61 (1928), 1463; Lifschitz and Joffe, *Z. physik. Chem.*, 97 (1921), 426; Lifschitz, *Z. wiss. Phot.*, 29 (1930), 91.

(4) E. Weyde and W. Frankenburger, *Trans. Faraday Soc.*, 27 (1931), 561 (The Photochemical Processes. A General Discussion.); E. Weyde, W. Frankenburger and W. Zimmermann, *Z. physik. Chem.*, B 17 (1932), 276; *Naturwissenschaften*, 18 (1930), 206.

tion is also practically 1 in the range from  $-6^{\circ}$  to  $+40^{\circ}\text{C}$ .

We have made an instrument for measuring the ultra-violet radiation using the cyanide of crystal violet as follows:

5 c.c. of the saturated solution of the leuco-base in absolute alcohol is sealed in a quartz glass ampule with an inner diameter of 13 mm. and length of 9 cm. Ten other hard glass ampules of the same size are each charged with 5 c.c. of the alcoholic solution of pure crystal violet. These are used as colorimetric standards. The concentration of the latter solution is  $1.72 \times 10^{-5} \times (2/3)^n$  mol/litre where  $n$  is a positive integer from 0 to 9 respectively. As the solubility of the leuco-base in absolute alcohol is  $5.8 \times 10^{-5}$  mol/litre at room temperature,  $1.72 \times 10^{-5}$  mol/litre is equal to its 8/27.

We define a color standard with the concentration  $n = 0$  as grade 10 and successively,  $n = 1$  as grade 9, and so on. Measurement of light intensity is done as follows.

When an ampule containing the leuco-base solution is exposed to light for five to sixty seconds, a violet color appears. The ampule is shaken during exposure so as to mix the solution well. The time of exposure is measured with a stop watch. Then it is quickly compared with color standards protecting against the ultra-violet ray completely. When a depth of color thus attained falls between those of two color standards, the grade is read to a fractional number.

The depth of color should be proportional to the quantity of light energy received in the solution which is the product of time of exposure ( $t$ ), light intensity and the surface area. Therefore, even for the same intensity of light, coloration of leuco-base solution would be different with a different time of exposure. We must reduce the coloration to that which would be obtained for a definite time exposure. Hence, we define the normal grade as a grade of color which develops when the leuco-base solution is exposed to the ultra-violet ray for just sixty seconds.

In actual cases, the time of exposure is not usually sixty seconds, so we reduce a grade of color directly observed to the normal grade to compare its light intensity with others. Let  $G$  be the normal grade,  $G_t$ , a grade obtained directly in an observation and  $t$ , time of exposure in seconds,  $G$  is calculated from the following equation.

$$G = G_t - (\log t - \log 60) / \log 3/2 \quad (1)$$

When  $G$  is thus calculated, relative intensity of light may be easily obtained as described in the next section.

3. There is a following relation between the normal grade  $G$  and the light intensity  $E(\text{erg/cm}^2 \cdot \text{min.})$

$$\log E = \log \kappa + (G - 1) \cdot \log 3/2 \quad (2)$$

where  $\kappa$  is a constant depending on the wave length of light etc.

In the case of monochromatic ray, the light energy  $E$  consumed for the photochemical decomposition of the leuco-base is expressed in the following formula;

$$E = m N h \nu / s t \quad (3)$$

where  $m$  is the number of mol of dyestuff formed;  $N$ , avogadro's number;  $h$ , Planck constant;  $\nu$ , the frequency of light wave;  $s$ , the area of irradiated surface of solution, 25 cm<sup>2</sup>.;  $t$ , time of exposure in minutes. This formula holds only in the ideal case where the quantum yield is 1 and the dark reaction is negligible. But for practical purposes, the leuco-base solution is made so as to finish the dark reaction in fifteen to thirty minutes, therefore, the rate of dark reaction can not be regarded as negligible. Moreover, the presence of impurities in reagents and the formation of a yellow decomposition product of unknown composition disturb the photochemical reaction. It is impossible to estimate these causes of error quantitatively,

The loss of light energy by reflexion and absorption may be estimated approximately as follows. According to L. Harris and J. Kaminsky<sup>(5)</sup>, the rate of reflexion between the interface of the air and the quartz glass is 0.094 % at 3130 Å and at the interface between alcohol and quartz glass it is about 0.0004 %. Thus, the total depletion by reflexion is not more than about 0.09 %.

Let intensity of normal incident light be  $I_0$ , then intensity of transmitted light  $I$  is,

$$I = I_0 \times 10^{-K \cdot c \cdot d} \quad (4)$$

where  $K$  is the absorption coefficient of the leuco-base solution,  $3.16 \times 10^{-4}$ ;  $c$ , its concentration,  $5.8 \times 10^{-5}$  mol per litre;  $d$ , depth of liquid. As the solution is contained in an ampule, the depth of liquid is.

$$d = 2\{r^2 - (\alpha r)^2\}^{\frac{1}{2}} \quad (5)$$

where  $r$  is the inner radius of an ampule, 6.5 mm.; and  $\alpha$  is a variable between 0 at the margin and 1 at the center of the ampule. From the above formulae, we obtain approximately 1.9 % as the mean value of absorption. Therefore, it may be said that about 2 % of light energy is lost by reflexion and absorption before the formation of dyestuff begins. After the dyestuff is formed, it will act as an absorber of light, the rate of which is proportional to its concentration.

Since radiation from ordinary light sources, for example, quartz mercury lamp, the solar radiation etc., is by no means monochromatic,

(5) L. Harris and J. Kaminsky and R. G. Simard, J. Am. Chem. Soc., 57 (1935), 1151.

the light energy can not be calculated simply by the formula (3). In short, the quantitative determination of the ultra-violet ray is impossible due to complicated sources of uncertainty as explained above.

However, it may be said that only an approximate relative value of light energy can be obtained by such simple colorimetric determination of dyestuff produced by light having the same distribution of wave length. And also, at least, the mere estimation of the order of energy may be given. For instance, in the case of measuring the solar ultra-violet light intensity, the following approximate treatment can be allowed.

4. When we combine the wave length distribution curve of the solar radiation with that of the sensitivity of the leuco-base solution, an almost triangular area is obtained whose base extends from 3450 Å to 2850 Å. The wave length which divides this triangle into two equal areas is 3105 Å. Therefore, we may consider that in measuring the intensity of the ultra-violet solar radiation with our method, it may be approximately assumed without committing a great error as the monochromatic ray having the wave length of 3150 Å. When we put in the formulae (2) and (3) the value of  $\nu$  corresponding to this wave length, the value of  $\kappa$  is obtained as follows:

$$\kappa = 0.03423 \times 10^4 \text{ erg/cm.}^2, \text{ min.}$$

With the above value of  $\kappa$ , we can calculate the intensity of the ultra-violet ray of the sun quite approximately by multiplying  $E$  by the reciprocal of the rate of absorption (0.019), assuming that the light energy is fully used for the photochemical decomposition of leuco-base molecules. As stated above, this is not the case, therefore the calculated value would be always smaller than the true intensity. But the relative intensity of the ultra-violet radiation of the sun can be fairly well measured by this method. It has been applied with good results to observe even the rapid change of radiation as in the case of the solar eclipse, or weaker radiation such as on a rainy day. The sensitivity and the convenience of this method are by far better than other chemical methods and comparable even to photo-electrical tubes. But it is a weak point of this method that the sensitivity decreases gradually in the course of time.

### Summary

The author has contrived a new instrument to measure the relative intensity of the ultra-violet radiation using the leuco-base of crystal violet. A quartz glass ampule containing the leuco-base solution is exposed to light and the dyestuff thus produced is determined colorimetrically with a series of a standard solution of crystal violet contained in ampules of the same size. The method of measurement is explained.

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