

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

SELF-INTEGRATING CHEMICAL ACTINOMETRY FOR ULTRAVIOLET DOSAGE OR OTHER SPECIFIC PURPOSES

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A good chemical actinometer must accurately predict the photochemical reaction rate, x , in a second system as a definite function of, y , its own rate when exposed to the same light source. The implied condition is, of course, that absorption is complete and $x_{\lambda_1}/y_{\lambda_1} = x_{\lambda_2}/y_{\lambda_2} = x_{\lambda_3}/y_{\lambda_3}$ for all wave lengths involved. While all this has long been realized, actinometers in general have relied upon guess work or lucky compensations of effects to attain the desired end.

The Ives physical photometer^{1,2} automatically integrates, at any instant, in terms of thermopile deflection, the luminous equivalent of a polychromatic light source as seen by the average human eye. A filter, between source and thermopile, transmits for each wave length a fraction of incident radiation proportional to its luminous efficiency. Thus the total relative "brightness" of two sources differing widely in spectral energy distribution can properly be compared. The magnitude of any other photochemical effect could be similarly referred to the response of any non-selective radiometer if the sensitivity curve for the effect were given.

Radiometry by thermopile or bolometer requires cumbersome apparatus, favorable environment and considerable experience. A device for integrating, by chemical means, the total efficiency, for a given photochemical purpose, of any polychromatic light source ought to be widely useful. Because of the present interest in ultraviolet dosage we submit the following, with emphasis upon the general applicability of the method. Eidenow³ has discussed (with bibliography) six different devices, physical or chemical, for predicting relative efficiencies of various light sources in producing erythema (sunburn) on human skin. These include liberation of iodine from hydriodic acid, silver halide papers, selenium cell, Keller's modified iodide solution, time required to kill infusoria and Webster's methylene blue acetone. Other devices are the darkening of lithopone,^{4,5} the uranyl oxalate actinometer,⁶ cadmium photoelectric cell,⁷ and total energy transmitted by a silver film.⁸ Of these methylene blue, the cad-

¹ Ives, *Trans. Illum. Eng. Soc. N. Y.*, **10**, 101 (1915).

² Coblenz and Emerson, *Bur. Standards Bull.*, **14**, 231 (1918).

³ Eidenow, *Lancet*, **209**, number 5320 (1925).

⁴ Pfund, *Proc. Am. Soc. Testing Materials*, **23**, II, 369 (1923).

⁵ Janet Clark, *Am. J. Physiol.*, **69** (1924).

⁶ Moss and Knapp, *J. Soc. Chem. Ind.*, **44**, 453 (1925).

⁷ Griffith and Taylor, *J. Hyg.*, **44**, 453 (1925).

⁸ Miethe and Stenger, *Z. wiss. Phot.*, **19**, 57(1919).

mium cell and the silver film have sensitivity curves very roughly corresponding to that of the erythema reaction. But evidence is lacking that any of the above give reliable predictions when used with light sources of widely differing spectral energy distributions, and theory predicts that they could not do so, especially as they respond to light of wave lengths outside of the range productive of erythema.

Hausser and Vahle⁹ isolated seven monochromatic radiations, measured intensities by thermopile and times required to produce a standard erythema. Their plot of efficiency against wave length is unsymmetrical and extends from 313 $m\mu$ to 254 $m\mu$ and beyond with a peak at 297 $m\mu$.

We selected for the actinometer reaction the photolysis of *p*-benzoquinone in fifty per cent. alcohol. Dr. P. A. Leighton, instructor in chemistry in this Laboratory, has investigated this reaction, proving the quantum yield practically constant between 313 $m\mu$ and 254 $m\mu$. Analysis by iodimetry proved a further advantage. We are very grateful to Dr. Leighton for permission to use these and other facts in advance of the publication of his own paper.

As the curve of Hausser and Vahle is based on ergs, not quanta, we multiplied its ordinates by numbers inversely proportional to the corresponding wave lengths, and replotted. The ordinates thus corrected gave directly the proper relative transmissions of the ideal filter, since the amount of light transmitted at any wave length must photolyze a mass of quinone proportional to the erythema-producing power of the corresponding light component in the original source. The assumption that all the monochromatic effects can be integrated by summation appears reasonable in this case, as no induction period exists and only a few per cent. of the reaction mixture is decomposed. The rate of photolysis of quinone behind the filter is then proportional to the physiological effect of the naked source if the reciprocity law holds for both reactions.

Examination of data on light transmission suggested that the following, plus a suitable absorbent for the visible spectrum, might meet our requirements: quinine, α - and β -naphthylamine, triphenylmethane, auramine, Sudan G, tartrazine, α - and β -naphthol, stypticine (cotarnine) and carbostyryl. Using a spectro-radiometer kindly loaned by Dr. P. A. Leighton, we measured their transmissions and found that none would do even when the solvent was varied. Later we discovered a promising spectrogram of picric acid by Uhler and Wood¹⁰ and developed a filter having 1 cm. of 0.00025 *M* picric acid between a sheet of red-purple Corex glass 2.5 mm. thick and one of clear Corex. Fig. 1 superposes the transmission curve, B, of this combination upon the ideal transmission curve described above, A. The transmissions on the left are too great, but roughly com-

⁹ Hausser and Vahle, "Strahlentherapie," 13 (1923).

¹⁰ Uhler and Wood, *Carnegie Instit. Wash. Pub.*, 1907.

pensate for the complete extinction of the relatively inefficient region beyond 270 $m\mu$. We know of no practical light source whose emission in the last-mentioned region is large in comparison with that between 313 $m\mu$ and 270 $m\mu$. Red light, which is transmitted by this filter, has no effect on quinone. While this filter is not perfect, it sufficed for present purposes. The picric acid solution was changed after each experiment in spite of the fact that its transmission was not greatly altered by the exposure. To the back of the clear Corex plate was cemented a second glass ring, 5 cm. in diameter and 3 cm. long, also having a tubulure. To the rear edge of this ring was cemented a plate of ordinary glass completing a cell of 45cc. capacity.

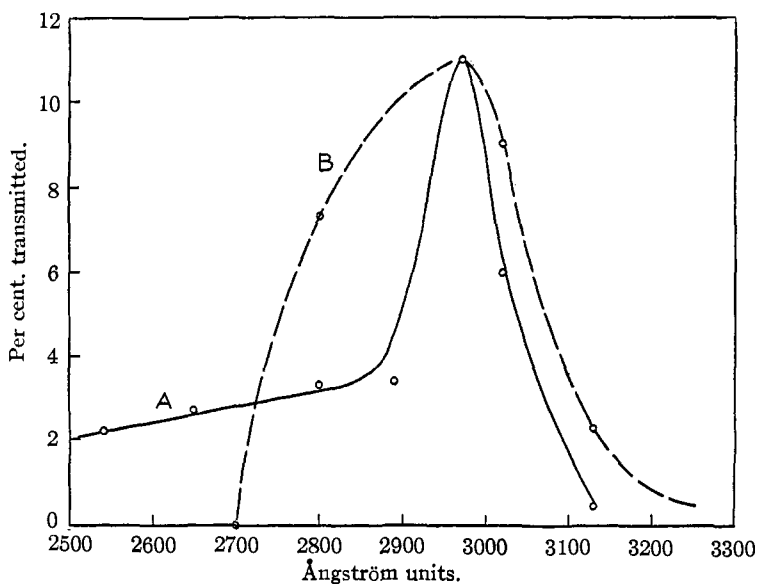


Fig. 1.

Quinone, three times sublimed at the lowest possible temperature, was dissolved in 50% ethyl alcohol to form 100 cc. of 0.002 M solution. The alcohol had been fractionated, preserving only the middle portions. This solution must be made up just before use, as its absorption spectrum varies somewhat with time. It absorbs the "erythema light" completely.

Figure 2 shows the arrangement of apparatus, unchanged during the measurements. The light source was an arc between 5 mm. carbon rods, cored or uncored,¹¹ set up in a feeding mechanism regulated constantly by hand, maintaining always an alternating current of 10 amperes with an

¹¹ Spectral energy distribution curves by Coblenz, Dorcas and Hughes, *Bur. Standards Sci. Paper*, 539, 548 (1926).

arc voltage of 50. To accelerate the photolysis we used two quartz condensers each 11 cm. in diameter and 17 cm. in focal length, such as are found in moving picture projectors. Next came a quartz cell 50 mm. square and 2 cm. thick, filled with circulating water to cut down the infra red. We believe that the spectral energy distribution of the source was not affected seriously, for our purposes, through absorption and reflection by condensers and water cell. The filter and reaction cell followed, kept cool by an air blast. The diverging cone of long ultraviolet just filled the cell.

Forty-five cc. of quinone was delivered into the cell by a special pipet and the same volume into a dark vessel beside it. After irradiating the

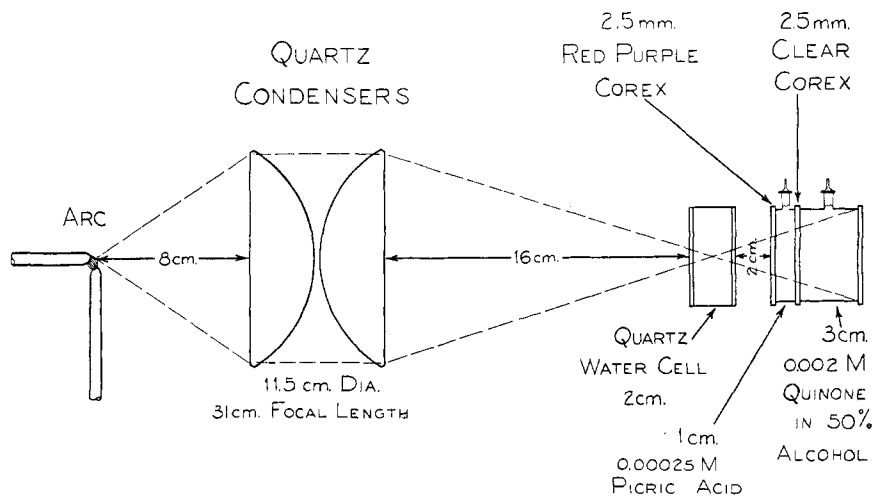


Fig. 2.

first for about two hours, both were cooled in ice and titrated simultaneously with 0.004 *N* thiosulfate, adding 10 cc. of 1 *N* iodide and of 1.5 *N* hydrochloric acid at the start, with starch at the end. The difference was taken as a measure of photolyzed quinone, with elimination of the small dark reaction, and of oxidation by air during titration.

The results appear in Fig. 3. Quinone photolyzed per hours, y , is plotted vertically against x , the reciprocal of the time necessary to produce a uniform erythema upon the skin of one of us, using the same carbons with 20 amperes instead of 10, a variation not likely to upset *relative* efficiencies. The point *K* was closely checked by a duplicate experiment; as the spectral energy distribution of the cobalt arc¹⁰ is not extraordinary its small divergence can safely be attributed to uncertainties in comparing skin colorations. Roughly, $y = ax$. For the more efficient sources, a line of the type $y = ax + b$, where b is relatively small, is a better approximation. The change in slope is not due to absorption by reaction products

but this might make trouble if quinone photolysis exceeded 15% of the whole. We hope to follow up the indication of a threshold intensity. Apparently the reciprocity law does not hold exactly for the erythema reaction and here our results are at variance with those of Hausser and Vahle. We believe that the actinometer described above is more sound in principle and reliable in performance than others proposed for the purpose in question. It will integrate variations in total intensity and in spectral energy distribution over the period of its use. Such actinometers could not be recommended for general photochemical research, because

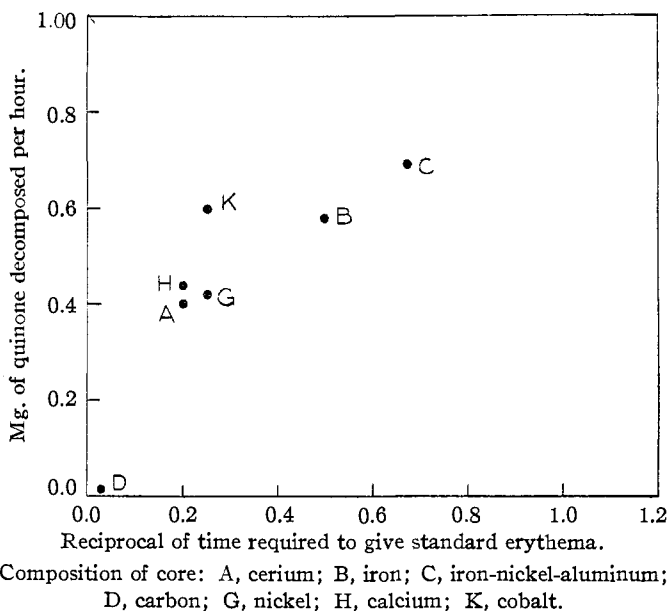


Fig. 3.

the radiometric work with monochromatic light needful to establish the two sensitivity curves and the proper filter would better be applied directly to the solution of the problem in hand. They should be useful, however, to study any single photochemical effect where many experiments must be made in various places. Among these are photography, where sensitivity curves are known; antirachitic therapy, whose curve should soon be available, and even chlorophyll assimilation, whose curve or curves, when known, might prove hard to reproduce in a filter.

Summary

Red-purple Corex glass, plus 1 cm. of 0.00025 *M* picric acid, transmits, at each frequency, light wattage proportional to efficiency in producing erythema (sunburn) in human skin. Quinone in 50% alcohol was photo-

lyzed behind this filter which was compensated, at each wave length, for the photochemical efficiency of this photolysis according to (unpublished) data by P. A. Leighton. Changes in total intensity and in spectral energy distribution are integrated by this device. The losses per hour in iodine value y were for seven carbon arcs, cored and uncored, plotted as ordinates against x , the reciprocals of times in which the same sources, without filters, produced a standard erythema. Roughly, $y = ax$. For the more efficient sources, $y = ax + b$ is preferable. The indicated threshold value will be further studied. Similar chemical actinometers for such purposes as photography, antirachitic therapy or even chlorophyll assimilation are possible.

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THE CHEMICAL EFFECTS OF HIGH FREQUENCY SOUND WAVES I. A PRELIMINARY SURVEY

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Introduction

Experiments on the production of sound waves for submarine signaling by a reversal of the Curie piezo-electric effect with quartz crystals in oscillating fields have been in progress for some time in several countries.¹ Since, however, the kinematic coefficient of viscosity increases as the square of the frequency, high frequencies would be absorbed rapidly in water, and these experiments have necessarily been conducted at relatively low frequencies. Recently one of us in conjunction with R. W. Wood² has shown that sound waves of great intensity may be similarly produced in high frequency fields, and that they are readily absorbed by liquids and solids. For this purpose a 2-kilowatt oscillator, capable of producing powerful oscillations with frequencies from 100,000 to 500,000 per second was employed; the quartz crystals, varying from 6 to 12 mm. in thickness and 50 to 80 mm. in diameter, were immersed in oil between two electrodes. The voltages used in submarine signaling are of the order of 1500, but the limiting voltage in our work is determined only by the sparking distance in oil between the two electrodes. In this way voltages of the order of 50,000 are possible and a corresponding increase in intensity of radiation is secured, since the amplitude of vibration

¹ A review of the literature on this subject is given in I. B. Krandall, "Theory of Vibrating Systems and Sound," McGraw-Hill Book Co., N. Y., 1926, p. 142.

² Wood and Loomis, *Phil. Mag.*, vii, 4, 417 (1927). This paper contains a comprehensive account of the physical and biological effects of supersonic waves, including detailed description of the apparatus for producing them.