THE MEASUREMENT OF ULTRA-VIOLET QUANTA BY FLUORESCENCE PHOTOMETRY

By Wm. T. Anderson, Jr., and Lester F. Bird

Abstract

The relative intensities of monochromatic ultra-violet light determined throughout the ultra-violet mercury spectrum by the use of a fluorescence photometer employing widely different chemical substances were shown to check the intensities of the light given by the thermopile. The agreement between the photometric and thermopile measurements indicates that both methods may be employed for measuring accurately the energy in the ultra-violet region.

Introduction

The vital importance of the ultra-violet portion of the spectrum and quanta to the physician, biologist and chemist has greatly stimulated interest in quanta measurements. At present, the thermopile and galvanometer are satisfactorily, and almost exclusively, used for such measurements. There exists a need for a method which can measure ultra-violet quanta directly, and which responds to fewer quanta than the average thermopile. It would also be very advantageous to be able to make quantitative ultra-violet measurements without the necessity of the precautions required in radiometry, e.g., freedom from stray magnetic fields, elimination of stray visible and infra-red radiations, etc.

The phenomenon of fluorescence has been selected as a suitable quantum reaction for measuring ultra-violet light intensity. All fluorescent reactions, however, do not fullfil the requirements. In order to be satisfactory, the emitted fluorescence light must be proportional to the intensity of the absorbed exciting radiation. The spectral energy distribution of the fluorescence light must be independent of the intensity and wave-length of the incident light. The fluorescent material must remain essentially unchanged throughout the investigation.

Three widely different fluorescent materials were employed: (1) an inorganic substance, uranium glass; (2) a dyestuff, fluorescein; (3) an alkaloid, esculin, all of which absorbed completely the ultra-violet under the experimental conditions. These three substances fluoresce brilliantly on exposure to all wave-lengths of the ultra-violet. No chemical change is known to take place in the uranium glass, the glass being apparently unchanged after many hours of exposure. The esculin and fluorescein are known to be affected by continuous irradiation with ultra-violet light, but within the time of the investigation and for the intensities of light employed the alteration in the chemical composition is negligible.

The ultra-violet light received by these materials was converted into visible light of the regions comprising the blue, green and yellow. Since the exciting radiation was completely absorbed by these materials, in each case, all the energy should be converted. The visible light emitted by the fluorescent materials was easily measured by photometric methods using a monochromatic green filter. Errors in the observation of the fluorescence light, however, existed when the ultra-violet radiations penetrated appreciably since in the case of the uranium glass and fluorescein only the light emitted by the irradiated surface was viewed. Light produced beneath the surface was not effective because of scattering and absorption. The method employed in viewing the esculin included almost all of the light produced. The penetrations for all three substances are negligible for wave-lengths shorter than 3340 Angstrom units.

Outline of Investigation

The photometer was arranged in the usual form employing the inverse square law of illumination. A frosted 100 watt nitrogen filled lamp was mounted on a car whose motion was guided by a track. The intensity of

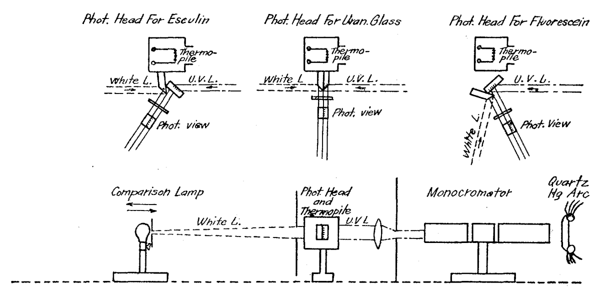

Fig. 1. Photometer and thermopile for ultra-violet light measurement.

the light could be adjusted by means of a diaphragm located immediately in front of the lamp when the maximum motion was not sufficient to cover the range of illumination required. A block of opal, or milk, glass was used as the illuminated comparison screen. The entire apparatus was arranged so that the illumination of the comparison screen varied inversely as the square of the distance to the diaphragm. The fluorescent material and the block of opal glass were arranged in each case as a photometer head so that the white light from the opal glass and the fluorescence light could be viewed side by side with an almost invisible edge between them. To the eye, the light from the illuminated screen and from the fluorescent material appeared as two elongated rectangles side by side and of equal size. The white light from the milk glass and the colored light from the fluorescent material were viewed through a monochromatic green light filter so that both sources of light appeared to the eye to be of the same color. Owing to the high sensitivity of the eye to green light, balances could be made with considerable accuracy.

A quartz monochromator was used to illuminate the fluorescent material. The light source for the monochromator was a Hanovia scientific quartz mercury lamp. The mercury spectrum is emitted by this lamp and has strong lines throughout the near and middle ultra-violet regions. The monochromator provided ample separation of the wave-lengths so that practically pure monochromatic light was secured. During the experiment the monochromatic ultra-violet light was arranged to illuminate the fluorescent material and a balance of the emitted green light was secured on the photometer.

Since the measurements of the response of the fluorescent materials with respect to the incident radiation were purely relative, and the differences in the degree of reflection, of the exciting radiation at the surfaces, were slight throughout the range of wave-length studied, reflection introduced negligible errors.

The uranium glass was prepared in a block about 1.5 inches square with one edge bevelled to 45° and left rough-ground. The milk glass block for the comparison screen was prepared in a similar manner. The ultra-violet light was arranged to illuminate the bevelled edge of the fluorescent glass. The glass blocks were separated with rough finish black paper. Covering either source of illumination caused the corresponding blocks to disappear from the photometer view completely.

Solutions of the esculin and fluorescein were employed in suitable quartz bottles. These bottles were rectangular in form with ground and polished faces. The solution of esculin being clear, was entirely transparent to its own fluorescence light so that this light could be viewed from the back side of the bottle. The fluorescein, of the concentration used, was not transparent to its own fluorescence light and so its light had to be viewed on the irradiated face. This procedure introduced some error since the wave-length 3660 Angstrom units penetrated into the solution slightly and because of absorption and scattering all the light produced was not available for measurement. The light of wave-length 3660 Angstrom units also penetrated uranium glass very readily but the use of a rough-ground surface seemed to limit the penetration in this experiment so that but little error was introduced.

The thermopile and photometer head were mounted side by side on a little car so arranged that the exciting ultra-violet could be readily directed on either the thermopile or the photometer head. The car was guided by a track and stops were adjusted so that the instruments were always returned to the same spot.

The intensity of the band of ultra-violet light was measured first on the thermopile, then by the fluorescence photometer, numerous checks were made and two observers alternated at reading the photometer, their average results being recorded.

Measurements of the fluorescence of these three substances demonstrated that they all responded equally for all wave-lengths, i.e., there was no selective action. When the intensity of the fluorescence light, measured photometrically, was plotted against wave-length, the curves for all three substances were exactly the same shape and could be made to coincide by employing the proper constants. The constants were necessary because the

TABLE I. *Epxerimentol data.*

Wave-length	Distance of screen from lamp	Distance²	$\frac{k}{(\text{Dist.})^2}$	Galvanometer deflection
	Uranium glass ($k=1.109\times10^4$)			
2537	18.8	353	31.4	27.0
2650	19.3	373	29.7	29.0
2800	31.3	980	11.3	14.0
2967	29.3	757	14.65	14.0
3130	11.55	133.3	83.2	75.0
3660	9.42	88.7	125.0	123.0
	Esculin solution ($k=2.34\times10^4$)			
2537	28.12	792.0	29.6	30.0
2650	30.25	917.0	25.6	29.0
2800	40.7	1653.0	14.16	10.0
2967	33.5	1124.0	20.8	21.1
3025	24.75	614.0	38.1	38.0
3130	17.5	306.0	76.5	80.0
3660	13.43	180.5	129.6	127.0
	Fluorescein solution ($k=2.34\times10^4$)			
2537	25.43	648.0	36.1	41.0
2650	27.25	744.0	31.4	29.0
2800	40.5	1640.0	14.27	16.0
2967	32.31	1045.0	22.4	24.0
3025	25.75	644.0	35.2	34.0
3130	18.0	324.0	72.3	78.0
3660	16.56	274.0	85.5*	125.0

* Radiation not totally absorbed on the surface.

photometer employed only the green component of the fluorescence spectra for the intensity measurements and the energy distribution in the fluorescence spectra of these three substances was not the same. The constants in any

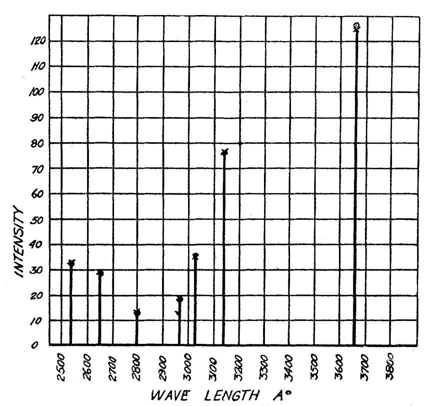

Fig. 2. Measurement of the ultra-violet lines of the mercury arc spectrum by two methods, showing the close agreement for all frequencies. Circles are measurements with the photometer; crosses are measurements with the thermopile.

case merely determine the reference light strength for the photometer and can be any value without affecting the proportionalities in the various regions. When these curves were compared with the curve obtained by plotting the galvanometer deflections against wave-length, they were found to have the same shape, and a proper constant made the galvanometer deflection coincide with the photometer readings indicating that the thermopile and the fluorescent material measure the same relative intensity of ultra-violet light.

Conclusions

The relative intensities of fluorescence excited at various wave-lengths in the ultra-violet are in remarkably close agreement, indicating that the efficiencies of conversion of ultra-violet into visible light are quite uniform. In view of the widely different chemical constitution of these substances and their agreement in responding to the ultra-violet wave-lengths it is evident that the fluorescence of these substances gives a true relative measure of the ultra-violet quanta received.

TABLE II. *Comparison of photometer readings and galvanometer deflections.*

	Values of $100 \times \frac{\text{photometer reading}}{\text{galvanometer deflection}}$			
Wave-length	Uranium glass	Esculin solution	Fluorescein solution	Average percent
2537	116.2	98.8	88.0	101.0
2650	97.6	88.4	108.2	98.1
2800	80.8	141.0	89.1	100.2
2967	104.5	98.8	93.3	98.9
3130	111.0	95.6	103.4	99.8
3660	101.5	102.0		101.7

Since the relative intensity of the monochromatic ultra-violet light at the various wave-lengths as determined by the thermopile agrees so satisfactorily with that obtained by the photometric measurements of the fluorescence light emitted by these three substances, it seems certain that both methods correctly measure the quanta received at ultra-violet wave-lengths. The fluorescence photometer and the thermopile may be satisfactorily employed for measuring quanta.

The authors wish to acknowledge the interest and many helpful suggestions of Dr. W. W. Coblentz of the Bureau of Standards, and Professors K. T. Compton and H. S. Taylor of Princeton University.

RESEARCH LABORATORY,
HANOVIA CHEMICAL AND MFG. COMPANY, NEWARK, N. J.
May 7, 1928.