The Photo-chemical and Photo-electric Measurement of Submarine Illumination.

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Accounts have been given in previous papers (1925, 1926, 1928) of measurements of submarine illumination carried out near Plymouth by means of photo-electric cells. A further paper (1929, 3) recorded the results so obtained during 1928. An account is now given of photochemical measurements made in that year, simultaneously with the photoelectric measurements.

ADAPTATION OF THE URANYL OXALATE METHOD FOR SUBMARINE MEASUREMENTS.

We have elsewhere (1929, 5) described the use, in daylight photometry, of a 0·1 N solution of oxalic acid approximately 0·01 M with respect to uranyl sulphate $UO_2SO_4 \cdot 3H_2O$. The concentration of uranyl sulphate actually used was 4·27 g. per litre, following the practice of other workers, but the rate of decomposition of oxalic acid is independent of the concentration of uranyl sulphate within fairly wide limits.

After exposure of the solution in quartz, or glass, test tubes the oxalic acid remaining was titrated with potassium permanganate. As the amounts used in the deeper submarine measurements were very small, it was necessary to titrate with the greatest care, and an allowance was made colorimetrically for any excess of permanganate added in the final drop.

It was especially desired to obtain information concerning the penetration of the ultra-violet portion of the spectrum. Uranyl oxalate is sensitive to this region, and also to the violet and blue of the visible spectrum, but the sensitivity decreases as the wave-length increases. Quartz tubes were used so that the full effect of the shorter waves should be registered, but the decomposition in both air and water is mainly due to the visible rays and to the glass-passing portion of the ultra-violet. Using tubes of quartz and of Monax resistance glass suspended vertically in air, it was found that the rate of reaction was 1·14 times as great in the former as in the latter. In other words, only one-eighth part of the decomposition was due to the ultra-violet cut out by the glass. This is very nearly a measure of the portion which is physiologically active in producing erythema, and in activating ergosterol, as explained elsewhere (1929, 6).

Since the decomposition results in the liberation of gas, the rubber corks inserted in the tubes were, at first, provided with narrow glass tubes closed by rubber tubing with a small slit and terminating in a piece of glass rod. The arrangement permits of the escape of gas, while the pressure of the water effects a seal by causing the walls of the rubber tubing to collapse. It was found, however, that the valves often leaked, and, since the rate of decomposition is much reduced under water, the method adopted in all the measurements recorded here was to secure the stoppers with copper wire. The tubes were then attached by copper wire to a weighted line marked in metres. Care was taken to avoid exposing the tubes before they were lowered, and, on hauling up, the wires were snipped and the tubes placed in a light-tight box.

So far as we are aware there is no evidence that the small excess pressure due to the decomposition products in any way affects the rate of reaction; in other words, it is not a reversible reaction.

Marshall and Orr (1928) state, however, that "there are two objections to the use of the method in the sea. As decomposition goes on, gases are evolved, causing an increase in pressure which inhibits the reaction, and in addition there is superimposed the pressure of the column of sea-water overlying the tube. In the second place absorption of light of very short wave-length by sea-water is rapid, and the results obtained below the surface are low." No experimental evidence is adduced for the statement that the excess pressure (of carbon monoxide and carbon dioxide) inhibits the reaction, which implies that the exertion of pressure upon these gases results in the synthesis of oxalic acid in the presence of water and uranyl sulphate under the action of light. The pressure of the column of sea-water is immaterial, being entirely supported by the walls of the tube and stopper. It remains to be proved that light of short wave-length is rapidly absorbed.

A possible error due to the shading of the tubes by the ship was avoided by attaching the end of the line, to which the tubes had been tied, to the middle of a spar with cork floats at each end. This was then lowered into the sea, and the ship drifted away from it to the full length of the rope, about 20 metres. This method could not be used with the photo-electric photometers owing to their weight. Thus the latter readings are somewhat reduced by shading, though, owing to the precautions taken to lessen this as much as possible, the effect is not important.

AERIAL AND SUBMARINE RATES OF DECOMPOSITION.

For comparison with the tubes lowered into the water, similar tubes, each with 10 c.c. of the reaction mixture, were suspended from the topping lift running from the mizen-mast to the end of the boom. These were uncorked, and swung about a mean vertical position, so that they registered the effect of horizontal light. The tubes lowered into the water also took up a vertical position in a flat calm, when there was no drift. Their angle with the vertical became greater and greater the faster the drift, so that no real comparison could be made between the submarine and aerial rates of decomposition. Table I shows the rates in air and in water. The former may be seen to be from about two up to nearly four times as great as the rates at one metre depth, but no exact comparison is permissible owing to changes in the angular distribution of the light in passing through the water surface, and to the reduction in reflection losses at the surface of the tube when immersed.

TABLE I.

DECOMPOSITION OF URANYL OXALATE SOLUTIONS, 0·1 N WITH RESPECT TO OXALIC ACID, EXPOSED IN CLOSED QUARTZ TUBES 13 × 1·3 CM. (INTERNAL DIAMETER) AND LOWERED IN THE SEA TO THE DEPTHS SHOWN.

The angle with the horizontal varied according to rate of drift of the ship. Work at Station E1, bottom at 72 m.

RATES OF DECOMPOSITION IN C.C. OF 0·1 N OXALIC ACID PER HOUR.

m.	July 11	July 23	Aug. 9	Aug. 29	Sept. 18	Sept. 18	Oct. 2	Nov. 30
0 (air)	10·22	10·67	5·46	9·72	7·31	5·91*	8·07	0·98
1	4·03	4·83	1·51	3·57	1·94	1·87	2·17	0·42
5	2·26	3·38	0·67	2·11	1·43	1·44	1·12	0·21
10	1·29	2·05	0·24	1·09	0·80	0·875	0·54	0·12
15	0·69	1·07	0·103	0·39	0·45	0·53	0·25	0·055
20	—	0·34	0·027	—	0·28	0·365	—	—
25	—	—	0·020	—	0·15	—	—	—
40	—	—	0·000	—	0·095	—	—	—
Exposure, minutes	120	92	180	93	114	114	136	130

PERCENTAGE RATES OF DECOMPOSITION.

m.								
1	100·0	100·0	100·0	100·0	100·0	100*	100·0	100·0
5	56·1	70·0	44·4	59·1	73·8	77·1	51·7	50·0
10	32·4	42·5	15·9	30·5	41·2	46·8	24·9	28·6
15	17·1	22·2	6·8	10·9	23·2	28·4	11·5	13·0
20	—	7·0	1·8	—	14·4	19·5	—	—
25	—	—	1·3	—	7·7	—	—	—
40	—	—	—	—	4·9	—	—	—

* In Monax resistance glass tubes of approximately the same dimensions as the quartz tubes. In air on this date rate in quartz tube was 1·24 times that in glass tube at time of experiment. Asterisk refers to all depths.

At 1 m. the rate varies from 30·4 to 2·65 mg. of crystalline oxalic acid decomposed per hour. The values are, however, recorded in cubic centimetres rather than in milligrams, as this enables the degree of accuracy of the titration to be judged better. The second column for September 18 contains the results obtained using glass tubes instead of quartz. In air and at 1 m. the rates in quartz exceed those in glass, at 5 m. the two are equal, and beyond that the rate for glass is the greater. The values in quartz in air are naturally the greater, since the effect of the shorter waves is added on, but as the proportion of shorter waves becomes reduced, this effect diminishes. The fact that the glass tube rates become the greater below 5 m. can only be attributed to a difference in the angle at which the tubes were riding owing to the unequal weights in water of the closed tubes, the quartz being the greater.

TABLE II.

Under C and E are Tabulated the Absorption Coefficients, μ_v, Calculated on the Actual Mean Depths, as Determined Photo-chemically by Uranyl Oxalate and by Vacuum and Gas-filled Potassium Photo-electric Cells. Under C M are Shown Values of μ_v Obtained using Monax Resistance Glass Tubes Instead of Quartz.

	July 11		July 23		August 9		August 29	
m.	C	E	C	E	C	E	C	E
5	0·125	0·101*	0·095	0·075*	0·204	0·183*	0·132	0·123*
10	0·129	0·100	0·115	0·083	0·187	0·181	0·169	0·107
15	—	—	0·180	0·109	0·217	0·192	—	—
20	—	—	—	—	0·165	0·178	—	—
C/E	1·26	—	1·46†	—	1·05	—	1·31	—

	September 18			October 2		November 30	
m.	C	E	CM	C	E	C	E
5	0·098	0·086*	0·084	0·154	0·166*	0·139	0·156*
10	0·116	0·076	0·100	0·150	0·129	0·134	0·125
15	0·105	0·084	0·087	—	—	—	—
20	0·110	0·092	—	—	—	—	—
C/E	1·37	—	1·10‡	1·02	—	0·97	—

* Taking surface losses as 15 per cent.

† Or 1·33 excluding probably erroneous value for 15 m.

‡ CM/E.

Note.—Mean value of C/E = 1·21, and CM/E = 1·10.

In Table II are shown the values of the vertical absorption coefficient, μ_v, calculated as usual from $\mu_v = \frac{2\cdot3}{\delta}(\log_{10}p_1 - \log_{10}p_2)$ where δ is the difference in depth and p_1 and p_2 the percentages of the light at the two depths, as given in Table I; the depths shown are the mean depths for the values there recorded. Beside the photo-chemically determined (C) values of μ_v, those obtained photo-electrically (E) are tabulated; the values of the latter are the mean of two series, made with photometers L and K while the tubes were being exposed, for the first four dates, and are the values obtained with photometers L, K, and J, respectively, for the final three. As previously shown (1928), L has its maximum sensitivity at 4000 Å.U. and K at 4400 Å.U. J, being also a potassium gas-filled photometer, probably resembles K.

Taking the mean of the same number of values of μ_v, determined by each method, over approximately the same depth, it may be seen that the ratio C/E varies from 0·97–1·46, mean of seven series 1·21. Using glass tubes the ratio is 1·10. We may conclude that the photo-electric measurements and the photo-chemical in glass tubes cover approximately the same spectral region, viz. 4800 Å.U. to 3400 Å.U., so that they measure substantially the same degree of absorption and scattering by the water. The quartz tubes, however, permit of the passage of the shortest wavelengths found in sunlight reaching the earth, namely, down to about 3000 Å.U. The scattering of these shorter waves by the water must be considerably greater than that of the longer. In the air their relative activities are 14 : 100, as deduced from the quartz to glass ratio 1·14. In water, however, the shortest waves are cut out more rapidly than the longer ones, as shown by the higher value of the absorption coefficient, which may be regarded as compounded of the coefficients for the portion that passes glass and for the portion that is stopped by glass.

SUMMARY.

1. The uranyl oxalate method of daylight photometry has been used to determine the absorption coefficient of water at depths down to 40 metres at International Hydrographic Station E1, about 10 miles S.W. of the Eddystone in the English Channel off Plymouth. Using quartz tubes on seven days from July to November inclusive the absorption coefficient varied 0·095 for 5 m. on July 23rd to 0·217 for 15 m. on August 9th; no seasonal variation was shown. The interpretation of the coefficients has been discussed in the paper dealing with the photo-electric measurements.

2. The ratio of the photo-chemically determined coefficients (using quartz tubes) to the photo-electrically determined values (obtained with potassium vacuum and gas-filled glass cells) varied from 1·02 to 1·46 or to 1·37, omitting a probably erroneous value from a series. Using glass tubes the same ratio was 1·10. The ratios are based upon mean values for the various depth series.

3. The higher absorption coefficient determined photo-chemically may indicate a greater absorption of the shortest wave-lengths, in which case one would expect the ratio of the coefficients to decrease with depth ; of this there is, however, no evidence.

REFERENCES.

Atkins, W. R. G., and Poole, H. H. 1929, 5. The uranyl oxalate method of daylight photometry and its photo-electric standardization. Sci. Proc. Roy. Dublin Soc., **19**, 321–339.

—— 1929, 6. The photo-chemical and photo-electric measurement of the radiation from a mercury vapour lamp. *Loc. cit.*, **19**, 355–364.

Marshall, S. M., and Orr, A. P. 1928. The photosynthesis of diatom cultures in the sea. J. Marine Biol. Assoc., N.S., **15**, 321–360.

Poole, H. H., 1925. On the photo-electric measurement of submarine illumination. Sci. Proc. Roy. Dublin Soc., **18**, 99–115.

Poole, H. H., and Atkins, W. R. G. 1926. On the penetration of light into sea-water. J. Marine Biol. Assoc., N.S., **14**, 177–198.

—— 1928. Further photo-electric measurements of the penetration of light into sea-water. *Loc. cit.*, **15**, 455–483.

—— 1929, 3. Photo-electric measurements of submarine illumination throughout the year. *Loc. cit.*, **16**, 297–324.