prepared by heating ethylene chlorohydrin with sodium bicarbonate,[2] and was distilled twice in vacuum before use. It analyzed better than 99% pure.

Preparation of Glycidol.—In a 200-cc. flask attached to an 8″ long packed column arranged for vacuum distillation, a mixture of 92 g. of glycerol (1 mole) and 95 g. of ethylene carbonate (1.08 moles) was heated gradually during the course of 90 minutes to 145° under 75 mm. vacuum; then during 75 minutes at 135–155° under 34–36 mm. vacuum, and finally during 90 minutes at 155–240° under 10–15 mm. vacuum. In the early stages of the heating, ethylene glycol (60 g.) came over in the receiver until the vapor temperature at 11 mm. was 80°. The thick liquid residue during the final heating at 155–240° in vacuum (5–10 mm.) gradually decomposed to give a colorless liquid which distilled over below 60° at 5 mm. Yield of crude glycidol was 64 g. (86%). Upon redistillation, this boiled at 53–55° (10 mm.) and furnished 47 g. (63.5%) of pure product, n^{25}D 1.4346.

It was identified by means of its phenylurethan[3] derivative, m.p. 60–61° and by treatment with piperidine[3] to give 1-piperidinopropane-diol-2,3 melting at 83°.

In contrast to the above, a stirred mixture of 236 g. of diethyl carbonate (2 moles), 184 g. of glycerol (2 moles) and 1 g. of sodium methoxide when heated at 90–100° under a short column until no more ethyl alcohol distilled over, gave a sirupy residue, which upon distillation *in vacuo* yielded 16 g. of distillate, b. p. 70–80° (13–16 mm), from which 10 g. of glycidol (7% yield) could be recovered upon redistillation (b.p. 62–64° (10–11 mm.)).

Glyceryl Tricarbonate.[1]—A mixture of 100 g. of glycerol (1.087 moles) and 350 g. of diphenyl carbonate (1.63 moles) was heated *in vacuo* (6–8 mm.) at 135–45° under an 8″ column arranged for vacuum distillation. During a heating period of 9.5 hours, 267 g. of phenol (2.84 moles) distilled over into the receiver. The still-pot residue was a sirup which, in part, gradually solidified after standing for several days. It was mixed at room temperature with an equal volume of glacial acetic acid which dissolved most of the impurities, leaving behind 77 g. of crystalline product. After recrystallization from hot glacial acetic acid, it formed colorless crystals, m.p. 146–148°.

A 40-g. sample of this crystalline glyceryl tricarbonate was subjected to vacuum distillation as described above for the preparation of glycidol. After heating at 230–240° at 7 mm. for 1.5 hours, it showed no decomposition. At 300–320° decomposition set in. An acrid smelling liquid (1 g.) containing acrolein collected in the Dry Ice trap, and 7 g. of distillate in the vacuum receiver; neither of which contained glycidol.

Glycidol from Glyceryl Dicarbonate.—A mixture of 149 g. of diphenyl carbonate (0.697 mole) and 64.3 g. of glycerol (0.7 mole) was heated at 135–140° in vacuum at 5–7 mm. for five hours during which time 129 g. of phenol or 98.5% of the theoretical amount, distilled over into the receiver. The viscous still-pot residue was then heated at 185–190° for 3 hours at 5–7 mm. vacuum, yielding 35.5 g. of colorless liquid distillate. Upon redistillation this gave 31 g. (60% yield) of glycidol, b.p. 55–57° (10 mm.), identified by means of its piperidine derivative.[3]

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[2] G. Steimmig and M. Wittwer, U. S. Patent 1,907,891 (1933).

[3] T. H. Rider and A. J. Hill, THIS JOURNAL, **52**, 1527, 1530 (1930).

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Precision Actinometry at Low Light Intensities with Malachite Green Leucocyanide

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The quantitative measurement of low intensities of ultraviolet light, less than 10^{13} quanta/sec., offers many experimental difficulties. Calibrated thermopile or phototube systems of high sensitivity with which such measurements can be made are not available in many laboratories and recourse to chemical actinometry must be made. Uranyl oxalate solutions are used universally for the measurement of light intensities.[1] However, this actinometer is not ideally suited for the measurement of very low intensities since exposure times necessary to obtain the desired accuracy in these experiments are very great. The use of monochloroacetic acid photolysis[2] as an actinometer is restricted to experiments utilizing 2537 Å. radiation. It is generally unsatisfactory because of the large temperature coefficient of the quantum yield and the dark reaction for which correction must be made in the long experiments necessary at low intensities.

Harris, Kaminsky and Simard have made an important contribution to the problem of measurement of very small light intensities.[3] These authors reported that the photolysis of malachite green leucocyanide, *p,p′*-didimethylaminotriphenylacetonitrile, in ethyl alcohol solution resulted in the formation of an intensely colored dye with a quantum efficiency of 100%. The quantum yield of 1.00 was independent of the initial leucocyanide concentration, the intensity of the absorbed light, the temperature of the solution, and the wave length of absorbed light in the region 2480 to 3300 Å. The colored ion formed in the reaction, presumably $[(CH_3)_2NC_6H_4]_2C(C_6H_5)^+$, was found to be stable in acidified alcohol and identical to the colored ion of malachite green salts in the same solvent. The great sensitivity of this proposed actinometer makes it particularly suited for the measurement of very low light intensities. However, two important factors have prevented its general use. (1) No completely satisfactory method of preparation and purification of the leucocyanide has been available. (2) The reliability of the quantum yield determinations of Harris, *et al.*, has been questioned. These authors reported 1.07 ± 0.06 for the quantum yield of chloride ion formation in monochloroacetic acid photolysis[3]; this value was obtained by a comparison method using malachite green leucocyanide photolysis as a reference standard. A value of 1.05 for the quantum yield of monochloroacetic acid photolysis was reported earlier by Rudberg.[4] Recent redeterminations of this quantum yield indicate that the correct value is 0.32 at 25°.[2] These conflicting results make uncertain the accuracy of the quantum yields of malachite green leucocyanide photolysis reported by Harris, *et al.*[2,5] In the present report these two major limitations to the general use of the leucocyanide actinometer for measurement of low light intensities are eliminated. An improved method of preparation and purification of malachite green leucocyanide has been developed and is presented in this report. The quantum yield results of Harris and coworkers from photolysis of leucocyanide solutions have been confirmed by two independent methods.

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[1] W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

[2] R. N. Smith, P. A. Leighton and W. G. Leighton, *ibid.*, **61**, 2299 (1939); L. B. Thomas, *ibid.*, **62**, 1879 (1940).

[3] L. Harris, J. Kaminsky and R. G. Simard, *ibid.*, **57**, 1151, 1154 (1935).

[4] E. Rudberg, *Z. Physik*, **24**, 247 (1924).

[5] W. A. Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 83.

In the first method a calibrated thermopile–galvanometer system was used to measure light intensities with an experimental procedure similar to that used by Harris, *et al.* In the second method the quantum yields of the uranyl oxalate actinometer and malachite green leucocyanide solutions were compared in the same beam of 3130 Å. radiation. The results of both methods indicate that at low light intensities the quantum yield of dye formation is 1.00 at all wave lengths employed. At intensities above about 3 × 10^{13} quanta/sec., incident on an area of about 0.3 sq. cm., an apparent quantum yield less than unity is found. (See the data of runs 13 and 14 of Table I and runs 1, 2 and 3 of Table II.) This appears to be due to an appreciable absorption of light by the product dye which is removed inefficiently from the solution near the front of the cell when the rate of dye formation is very great and stirring is inadequate. (In agreement with this interpretation it was found that an increased stirring rate causes an increase in the apparent quantum yield at high intensities. Compare the data of runs 14 and 15 of Table I.) Because of the strong absorption of the product dye in the ultraviolet the leucocyanide actinometer is unsatisfactory for the direct measurement of high intensities of ultraviolet light.

The present work has confirmed the malachite green leucocyanide photolysis results of Harris, Kaminsky and Simard.[3] It appears to the present authors that the only error in the work of Harris, *et al.*, was introduced in the comparison of the yields of leucocyanide and chloroacetic acid photolyses. It is hoped that this confirmation of the accuracy of the original work of Harris together with the method of preparation of the malachite green leucocyanide presented in this report will make possible a much wider use of leucocyanide photolysis as a precision actinometer for the measurement of very low light intensities.

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Experimental

Preparation of Malachite Green Leucocyanide.[6]—The leucocyanide is prepared best using pure, anhydrous solvents and reagents. The method given will yield about 4 g. of the pure compound (56% of theoretical yield). (1) To a filtered 1% aqueous solution containing 9.3 g. of malachite green oxalate, add a cold, saturated aqueous solution containing 6 g. of potassium cyanide. Collect the precipitate, and wash with distilled water. (2) Dissolve the precipitate in cold 1% hydrochloric acid. Stir vigorously for one hour. Carefully neutralize the solution with cold 1% aqueous ammonia. Collect the precipitate, wash with distilled water and air dry. (3) Dissolve the crude product in 300 ml. of acetone, and filter the solution. Add 150 ml. of methanol acidified with several drops of glacial acetic acid. Remove rapidly 350 ml. of the mixture by distillation. Cool the remainder and, when crystallization is complete, filter and wash the crystals with 10 ml. of cold methanol. Save the filtrate. (4) Now employ reduced illumination (red safelight); dissolve about 2 g. of the crude product from (3) in 100 ml. of a 50% methanol–ethyl acetate solution. Add 30 ml. of methanol, 1 ml. of acetone, and several drops of glacial acetic acid. Remove about 105 ml. of the mixture rapidly by distillation. Cool the remaining solution and, when crystallization is complete, filter and wash the crystals with a small amount of methanol. Save the filtrates. (5) Repeat step (4) until a product sufficiently free from dye contamination is obtained. (The volume of the accumulated filtrates may be decreased by distillation, and more product may be recovered and reprocessed.) A product containing 0.001% dye and no trace of cyanide ion is obtained after five repetitions of step (4); m.p. 176–177°.

Anal. Calcd. for $C_{24}H_{25}N_3$: C, 81.09; H, 7.09; N, 11.82. Found[7]: C, 80.95, 81.10; H, 7.20, 6.99; N, 11.87, 11.69.

Quantum Yield Determinations. Method I.—The light source was a Hanovia type A burner (500 w.) operated with a current from a Nobitron (model E-200-3.3) d.c. regulated power supply. The desired wave length of the mercury arc spectrum was isolated with a Farrand (model 300 UV) quartz monochromator, and the light intensity was measured with an Eppley thermopile and galvanometer system calibrated with N. B. S. standard lamps. The procedures of photolysis and the calculation of quantum yields were carried out as described by Harris, *et al.*[3] Solutions of the leucocyanide were prepared in absolute ethanol rather than 95% ethanol used in most of the work of Harris. The absorption spectra of the leucocyanide and dye in the absolute ethanol solutions were essentially the same as those reported for the 95% ethanol solutions.[3] Photolyses were carried out in a Beckman quartz spectrophotometer cell (path length, 1.0 cm.). The photolyzed solution consisted of 3.80 ml. of leucocyanide in absolute ethanol to which was added 0.02 ml. of 0.3 *M* hydrochloric acid. This ratio of leucocyanide solution to acid solution was maintained in both Method I and II experiments. The cell containing the exposed solution following photolysis and a matched cell containing an initially identical but unexposed leucocyanide solution were placed in a Beckman (model DU) spectrophotometer; the optical density of the dye at 6200 Å. was determined using the unexposed solution as a blank. The 6200 Å. wave length chosen for concentration determinations was the maximum of a broad absorption band of the dye. The absorption coefficients of the dye formed on complete photolysis of dilute standard solutions of leucocyanide in ethanol (acidified as before) were the same in the visible as those of

TABLE I

QUANTUM YIELDS OF DYE FORMATION IN MALACHITE GREEN LEUCOCYANIDE PHOTOLYSIS IN ACIDIFIED ETHANOL AT ROOM TEMPERATURE

Number of run	Quanta per sec. × 10^{-13}	Concn. of leucocyanide, *M*	Quantum yield of dye
Wave length 2537 Å.			
1	0.44	3.9 × 10^{-4}	1.02
2	1.57	1.0 × 10^{-4}	1.00
3	1.53	1.0 × 10^{-3}	0.98
Wave length 2654 Å.			
4	0.98	1.0 × 10^{-4}	1.03
5	1.20	1.0 × 10^{-3}	0.99
Wave length 2804 Å.			
6	1.89	1.2 × 10^{-4}	0.99
Wave length 3130 Å.			
7	0.0317	1.0 × 10^{-3}	0.98
8	.101	1.0 × 10^{-3}	1.01
9	.83	1.0 × 10^{-3}	0.95
10	.79	7.5 × 10^{-4}	1.00
11	.86	3.9 × 10^{-4}	1.00
12	2.89	1.0 × 10^{-3}	1.03
13	7.54	1.0 × 10^{-3}	0.94
14	84.6	1.0 × 10^{-3}	0.70
15[a]	83.7	1.0 × 10^{-3}	0.81

[a] Rate of nitrogen bubbling was increased in this experiment.

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[6] Based on the work of A. Hantzsch and G. Osswald, *Ber.*, **33**, 307 (1900), and J. Lifschitz and Ch. L. Joffé, *Z. physik. Chem.*, **97**, 426 (1921).

[7] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

malachite green oxalate in the acidified ethanol. The absorption of the dye solutions at 6200 Å. followed Beer's law within the error of the determinations for solutions in which the dye concentration was in the range of 0.1 to 10 × 10^{-6} *M*. The molecular extinction coefficient, ϵ, at 6200 Å. for the dye in the acidified ethanol solutions (0.02 ml. of 0.3 *M* hydrochloric acid to 3.80 ml. of the leucocyanide in absolute ethanol solution) is 9.49 × 10^4 (an average value), where $\log_{10}(I_0/I) = \epsilon cl$. The time of the exposure was regulated so that the final dye concentration in most experiments was about 1 × 10^{-6} *M*. Exposure times of about 3 and 100 minutes were required for runs at light intensities providing 1 × 10^{13} and 3 × 10^{11} quanta/sec., respectively. Stirring was accomplished during photolysis by bubbling through the solution nitrogen gas saturated with ethanol. All of the experiments were carried out at room temperature (20–25°). The results are summarized in Table I.

Method II.—A ratio of quantum yields of uranyl oxalate and malachite green leucocyanide photolyses at 3130 Å. was determined at room temperature. An optical train providing pure, high intensity 3130 Å. radiation[8] followed the light source described in Method I. A collimated beam of light about 35 mm. in diameter and of constant intensity (±1%) was incident on the cell face. The photolysis of both solutions was effected in a quartz cell with 4.0-cm. path length. The cell contained 55 ml. of solution which was stirred magnetically during exposure. Concentrations of both solutions were such that essentially complete absorption of the light occurred. The uranyl oxalate solution (0.005 *M* in uranyl nitrate and 0.025 *M* in oxalic acid) was photolysed at full intensity. Filters with measured transmissions were placed in the light path to lower the intensity used in the leucocyanide photolyses, since the previous results indicated that absorption of light by product dye may be serious at high light intensities because of inadequate mixing. The concentration of leucocyanide solutions was 6.0 × 10^{-4} *M*. To 55.0 ml. of the alcoholic solution 0.29 ml. of 0.3 *M* hydrochloric acid was added before photolysis. Final dye concentration was about 1 × 10^{-6} *M* in each experiment. The data are presented in Table II.

TABLE II

COMPARISON OF QUANTUM YIELDS OF URANYL OXALATE AND MALACHITE GREEN LEUCOCYANIDE ACTINOMETERS AT 3130 Å. AND ROOM TEMPERATURE

	(1)	(2)	(3)	(4)
Number of run	Filter % *trans.*	Dye mol. formed/sec. × 10^{-15}	Calcd. dye mol. formed/sec. × 10^{-15} for full intensity	($H_2C_2O_4$ mol. decompd./sec.[a])/(dye mol. formed/sec.)
1	38.6	1.21	3.14	0.72
2	16.2	0.584	3.60	.63
3	8.81	.338	3.84	.59
4	3.32	.137	4.12	.55
5	1.99	.0820	4.12	.55

[a] Photolysis of uranyl oxalate solution at full intensity gave an average value of 2.27 × 10^{15} molecules of oxalic acid decomposed/sec.

The exposure times necessary in these experiments were about 10 hr. for the uranyl oxalate actinometer (10% oxalate decomposition) and from 19 to 371 sec. for the runs 1 and 5, respectively, in Table II. The data of column (2) of Table II are the measured rates of formation of dye in light decreased from full intensity by the filter of transmission given in column (1). The data of column (3) are calculated rates of dye formation for full intensity, (100) (rate in column (2))/(transmission in column (1)). Data of column (4) are the ratios of molecules of oxalic acid decomposed/sec. at full intensity, 2.27 × 10^{15}, to the calculated number of molecules of dye formed at full intensity, data of column (3). Absorption by dye product in the leucocyanide photolyses at low light intensities is unimportant with the stirring rate used; the data of these experiments, runs 4 and 5 of Table II, indicate a ratio of the quantum yield of the uranyl oxalate actinometer to that of the leucocyanide photolysis to be 0.55. The quantum yield of oxalate decomposition is 0.56 at 3130 Å.[1]; hence the quantum yield of malachite green leucocyanide photolysis at wave length 3130 Å. is estimated to be 1.02.

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Some Observations on Neptunium(V) Compounds[1]

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Although neptunium has a stable +5 oxidation state in solution,[3] the only Np(V) compounds which have hitherto been reported are Np(V) hydroxide[4] and mixtures of Np(V) oxychlorides of varying composition[5] obtained by rapid evaporation of HCl solutions.

The recent preparation of the oxide Np_3O_8[6] suggested a convenient starting material for the synthesis of Np(V) compounds, and it was of interest to attempt to determine the oxidation state of the neptunium in this compound. In one experiment 1 mg. of Np_3O_8 was dissolved in 5 cm.^{3} of 1 *M* $HClO_4$. Spectrophotometric examination of this solution with a Beckman Model D Spectrophotometer showed that the absorption was due only to Np(V) and Np(VI) ions. Approximately 1% of Np(IV) could have been detected by this means. This experiment does not rule out the existence of Np(IV) in Np_3O_8, however, since under the conditions of the dissolution Np(IV) would rapidly react with Np(VI) to form Np(V).[7] (Dissolution of U_3O_8 results in a mixture of U(IV) and U(VI) but here again the oxidation states in solution give no clue as to the situation in the solid since U(V) disproportionates into U(IV) and U(VI).)

Thermodynamic calculations for $NpCl_5$ give an estimated value of −246 ± 2 kg./mole for the heat of formation and a Cl_2 decomposition pressure of less than 10^{-3} atm. at 500°K.[8] Various attempts were made to prepare $NpCl_5$ from 2- to 4-mg. amounts of Np_3O_8: (a) Refluxing with 0.5 cm.^{3} of redistilled hexachloropropene at atmospheric pressure for 4 hours resulted in no reaction. (b) Bomb tube experiments with either hexachloropropene or carbon tetrachloride between 120–250° and 3–6 atm. also failed to yield a reaction. (c) Vapor phase chlorination with carbon tetrachloride carried out by passing CCl_4 vapors over the sample contained in a platinum boat in a hot tube furnace gave a reaction which resulted only in the formation of $NpCl_4$. A previous attempt to prepare $NpCl_5$ by reaction of $NpCl_4$ with Cl_2 at 500° was unsuccessful.[9] Np_3O_8 is thus quite different from U_3-

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[1] Reported in part at the Spring, 1950, Meeting of the American Chemical Society.

[2] On leave from Illinois Institute of Technology, Chicago, Ill.

[3] L. B. Magnusson, J. C. Hindman and T. J. La Chapelle, National Nuclear Energy Series, Vol. 14B, p. 1059, 1949.

[4] *Ibid.*, p. 1097.

[5] T. J. La Chapelle, UCRL-336, May, 1949.

[6] J. J. Katz and D. M. Gruen, THIS JOURNAL, **71**, 2106 (1949).

[7] R. Sjoblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).

[8] L. Brewer, L. Bromley, P. W. Gilles and N. L. Lofgren, MDDC-1417 (1947), corrected (1948).

[9] S. Fried and N. R. Davidson, National Nuclear Energy Series, Vol. 14B, p. 1072, 1949.