

## Appendix

## A

## Actinometry

There are a variety of chemical actinometry that have been developed over the years. In this section, a few of the actinometers are described.

### A.1 POTASSIUM FERROXALATE ACTINOMETRY

The governing chemical reaction is represented as ferrous ions + oxalate gives rise to ferrous ions and carbon dioxide i.e.,  $2\text{Fe}^{+++} + \text{C}_2\text{O}_4^{2-} = 2\text{Fe}^{++} + 2\text{CO}_2$ . The ferrous ion thus formed is estimated spectrophotometrically as its phenanthraline complex at 510 nm. Ferric ions form only weak complex with Phenanthraline and is transparent at 510 nm. This actinometer has some advantages and also some disadvantages. The possible advantages are (1) The method is easy and can be adopted and used quickly (2) Does not depend on difference reading between large numbers to determine the amount of conversion (3) Quantum Yields are accurately known (4) Can be adopted to the blue region of the visible spectrum. The major disadvantages of this method are (1) Only short irradiation is enough (2) High absorption necessitates light filtering or corrections have to be applied.

### A.2 SOLUTIONS REQUIRED

(1) 10 Phenanthroline ( 0.2 percent by weight) in water (2) Buffer solution (82 grams of sodium acetate +10 ml of concentrated sulphuric acid diluted to 1000 ml with water. (3) Ferric sulphate solution (100 grams of ferric sulphate hydrated + 55 ml concentrated sulphuric acid diluted to 1000 with water. (4) Standardised 0.1 M EDTA 5.0.08 M  $\text{FeSO}_4$  in 0.1 M sulphuric acid (6) Standard 0.1N potassium chromate solution (7) One percent diphenylamine in concentrated sulphuric acid [Solutions 5-6 are required only to determine the extinction coefficient of ferrous phenanthroline complex. One can also use a reported value of  $1.11 \times 10^4$

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**A.3 EXTINCTION COEFFICIENT OF FERROUS PHENANTHRALINE COMPLEX**

The following sequence of steps may be followed for this determination.

1. Titrate of 0.08 M ferrous sulphate solution in 0.1 sulphuric acid with a standard 0.1 N potassium chromate using a few drops of diphenylamine solution as indicator.
2. Dilute 0.08 M ferrous sulphate solution 20 times with 0.1 N sulphuric acid to get  $4 \times 10^{-4}$  M solution of ferrous sulphate.
3. To a series of six 25 ml volumetric flasks add 0, 1, 3, 5, 7, 9 mls respectively the solution in 2
4. Add enough 0.1 N sulphuric acid to each of these solutions in 3 to bring the volume approximately 12.5 ml
5. To each of these solutions in 4 add 2 ml of the 0.2% phenanthroline solution.
6. Add six ml of buffer solution to each of the volumetric flasks and dilute to the mark.
7. Measure the absorption of each of these solutions at 510 nm in a 1 cm cell versus a solution prepared as above without ferrous sulphate.
8. Plot the absorption values obtained versus complex concentration and determine the extinction coefficient from the slope.

**A.4 PREPARATION OF ACTINOMETER SOLUTION**

1. Titrate 0.2 N ferric sulphate solution with standard EDTA using 0.2 g of salicylic acid in 100 ml solution as indicator and buffered with 0.3 g glycine/100 ml solution to a pH of 3 to 4.
2. prepare a standard solution of  $K_2C_2O_4$  such that its molarity is six times that of ferric sulphate solution.
3. When actinometer solution is required, pipete 5 ml of the ferric sulphate solution, add 5 mls of the oxalate into a 100 ml volumetric flask and dilute to the mark with water.

**A.5 MEASUREMENT OF THE INTENSITY**

1. Pipete out into the reaction vessel a volume of  $K_3Fe(C_2O_4)_3$  necessary to be irradiated.
2. Irradiate the solution a definite time period.
3. Mix the irradiated solution and then pipete one ml of the actinometer solution into a 10 ml volumetric flask.
4. Add 2 ml of 0.2 phenanthroline solution.

**Table A.1** *Quantum yields of ferrous production from potassium ferrioxalate [The data have been reproduced from C. G. Hatchard and C. A. Parker, Proc. Roy. Soc., (London) A235, 518 (1956)].*

$\lambda(\text{nm})$	Concentration(moles/litre)	Quantum yield
254	0.006	1.25
297	0.006	1.24
313	0.006	1.24
334	0.006	1.24
361	0.006	1.21
405	0.006	1.14
436	0.006	1.11

5. Add a volume of buffer equal to half of the aliquot of actinometer solution taken.
6. Make up to the mark.
7. Prepare a blank solution following steps 3-6 with a nonirradiated volume of actinometer taken.
8. Measure the absorption of the solutions 6 and 7 versus water at 510 nm and note the difference.

## A.6 CALCULATION OF LIGHT INTENSITY

From the values given in Table A.1 select the appropriate quantum yield for ferrous production Using the absorption obtained, calculate the light intensity from the following formula  $I(\text{in Einsteins/min}) = AV_2V_3/tV_1\varepsilon\phi_\lambda$  where A is absorption of irradiated actinometer solution corrected for absorption of the blank;  $V_1$  in mls of the irradiated actinometer solution;  $V_2$  is volume of the actinometer solution irradiated;  $V_3$  is the volume of volumetric flask used for dilution of irradiated aliquot solution;  $\varepsilon$  is the extinction coefficient of ferrous phenanthroline complex at 510 nm ( $1.11 \times 10^4$ );  $\phi_\lambda$  is quantum yield of ferrous production at the wavelength of light used and t is time of irradiation in minutes.

## A.7 B.URANYL OXALATE ACTINOMETRY

### A.7.1 Solutions

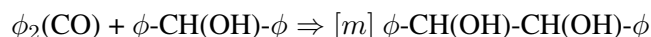
1. 0.01 M Uranyl sulphate in 0.05 M oxalic acid solution
2. Standardised 0.04 M  $\text{KMnO}_4$  solution.

**A.4 APPENDIX A****Table A.2** *Quantum yields of oxalate disappearance for uranyl oxalate [W. G. Leighton and G. S. Forbes, J. Am. Chem. Soc., 52, 313 (1930)].*

$\lambda(\text{nm})$	Quantum yield
254	0.602
265	0.582
302	0.570
313	0.561
366	0.492
405	0.563
436	0.584

**A.7.2 Procedure**

1. Titrate an approximate volume of the actinometer solution with the standardised permanganate solution. Titrate at 333 K in 1 n sulphuric acid solution of the oxalate.
2. Irradiate the desired volume of actinometer for appropriate time period.
3. Titrate the irradiated solution with permanganate.
4. Calculate the light intensity.

**A.8 C.BENZOPHENONE-BENZHYDROL ACTINOMETRY****A.8.1 Net Reaction****A.8.2 Discussion**

The rate expression for the system is  $(1/\phi_{Ph_2(CO)}) = 1 + k_1/k_2(BH_2)$ . If this is multiplied by the quantum yield of disappearance of benzophenone at a specific  $[BH_2]$  concentration, then the expression is  $\phi_a/\phi_{Ph_2CO} = \phi_a + \phi_a k_1/k_2(BH_2)$ . A Plot of the relative quantum yield ratio  $\phi_a/\phi_{2CO}$  versus reciprocal of the benzhydrol concentration gives an intercept of  $\phi_a$  and the light intensity can be calculated from this value.

**A.9 PROCEDURE**

1. Prepare 0.1 M  $\phi_2\text{CO}$  solution in benzene containing varying concentrations of benzhydrol (e.g. 0.3, 0.1, 0.07 and 0.05 M).
2. Degas with freeze thaw cycles and then irradiate.

**Table A.3** *Quantum yields for 2-hexanone Reactions in hydrocarbon solvent [D. R. Coulson and N. C. Yang, J. Am. Chem. Soc., 88, 4511 (1968)].*

$\phi$ -hexanone	0.327
$\phi_{acetone}$	0.252
$\phi_{propene}$	0.25
$\phi_{cyclobutanol}$	0.075

3. Dilute each tube 25 times and compare the absorption of each to diluted non irradiated samples.
4. Plot  $\phi_a/\phi_P h_2CO$  versus  $1/[BH_2]$  where  $[BH_2]$  is the average of the initial and final benzhydrol concentrations.
5. Determine  $\phi_a$  from the intercept.
6. Calculate the light intensity  $I = \Delta(\phi_2CO/\phi_a)$ .

## **A.10 2-HEXANONE ACTINOMETRY**

2-hexanone undergoes Norrish type II photochemical reaction to yield acetone (which can be determined by GC) or the disappearance of 2-hexanone or the formation of propene can also be determined.

### **A.10.1 Procedure**

1. Irradiate an approximate volume of a 1 M solution of 2-hexanone in pentane, hexane or cyclohexane.
2. Analyse in a carbowax or similar column and compare chromatographic peak areas to those obtained from a standard acetone solution.

For more details on this topic, the reader is requested to refer the book by Steven L. Murov "Handbook of Photochemistry", Marcel Dekker Inc, 1973.