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Dye Dilution Method of Discharge Measurement

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ENGINEERING RESEARCH

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1. Introduction

The recent development of fluorescent dyes and a fluorometer, which can detect these dyes at very low concentrations, has made dye-dilution methods practical for measuring discharge. These methods are particularly useful for determining discharges under certain flow conditions which are unfavorable for making current meter measurements or volumetric calibration. Typical examples of such flow conditions are in closed conduits, ice-covered reaches and turbulent mountain streams. Other applications of such fluorescent techniques might be studies of seepage losses along streams or in-place orifices or Venturi meter calibrations.

The single-point, constant-rate-injection method is inexpensive and easy to perform provided a sufficiently long mixing distance is available. The accuracy of this method is related to the accuracy of determining the amount of dye injected, the final concentration, and to the dye loss in the measurement reach. With equipment presently available, the discharge of the injected dye is known within one percent and the concentration of the injected dye or the diluted dye can be determined to the nearest part per billion. Dye loss will vary with flow conditions, however, with the newest WT dye, the loss is so small as to be negligible under most flow conditions. The techniques and a measurement example are described in the following sections.

2. Theory

The basic advantage of dye dilution discharge measurement is that dye can be mixed completely with water. Two methods may be used for determining

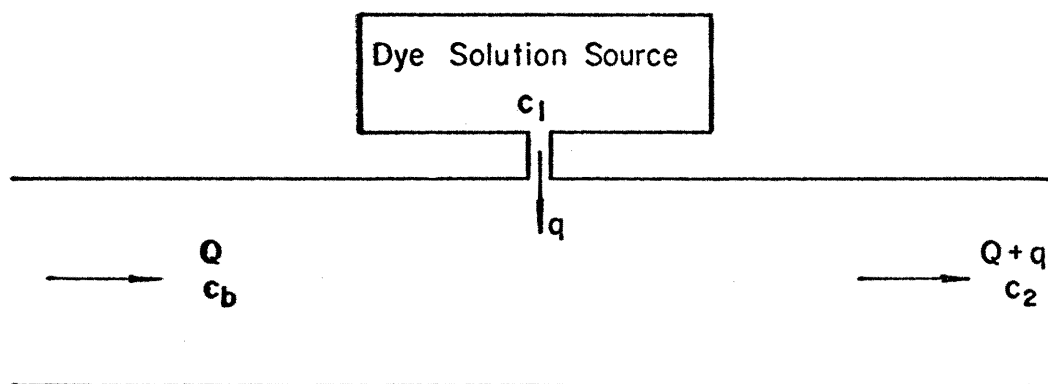


Fig. 1. Constant-rate-injection system

the discharge either in open channels or closed conduits. One method is the constant-rate-injection method and the other is the slug or total recovery method.

As shown in Figure 1, the constant-rate-injection method will, if the dye solution is injected constantly for a sufficient time period, give at a downstream point a plateau (Figure 2) on a concentration-time curve. The dye concentration at the cross section of the point downstream is constant. If there



is not any dye loss between the injection point and the sampling point, the

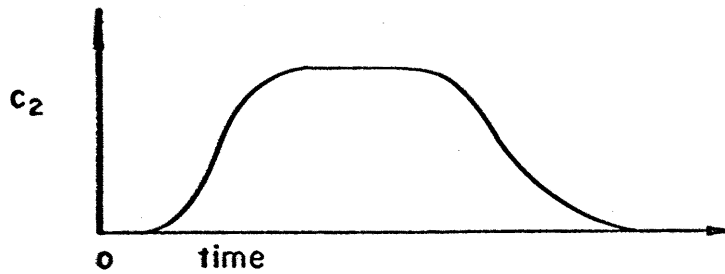


Fig. 2. Concentration-time curve for constant-rate-injection

quantity of dye measured at these two points should be the same. The concentration of dye solution is defined as:

$$c_1 = \frac{c_D V_D}{V_D + V_W} \quad (2-1)$$

where c_1 = concentration of dye solution
 c_D = concentration of dye
 V_D = volume or weight of dye
 V_W = volume or weight of distilled water;

thus $qc_1 + Qc_b = (Q + q)c_2$

$$Q = \left(\frac{c_1 - c_2}{c_2 - c_b} \right) q \quad (2-2)$$

where q = injection rate of dye solution
 Q = discharge to be measured
 c_1 = concentration of dye solution
 c_2 = dye concentration at sampling point
 c_b = background concentration which is equivalent to the dye concentration in water before the dye solution is injected.

The discharge can be calculated by measuring c_1 , c_2 , c_b and q .

The total-recovery method requires that the total volume of dye, which is suddenly dumped into a stream, be accounted for at the sampling site. At the

sampling site, the relation between time and the dye concentration is as shown in Figure 3.

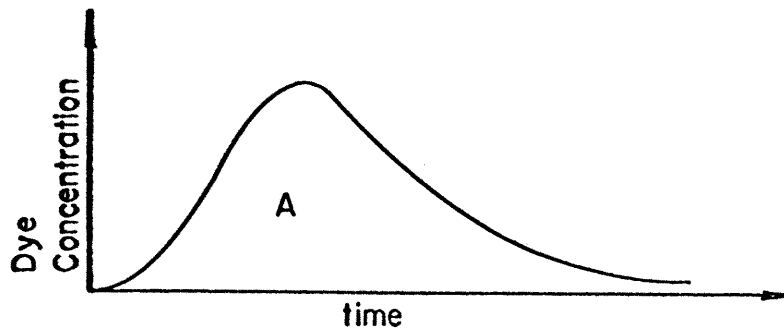


Fig. 3. Concentration-time curve for sudden dump

Figure 3, concentration-time curve for sudden dump, is plotted by measuring the concentration at different times. Based on the same reason that the quantity of dye, assuming there is no loss, is the same at the injection point and the sampling point.

then $V_1 c_1 = Q \int_0^{\infty} (c_2 - c_b) dt$

$$Q = \frac{V_1 c_1}{\int_0^{\infty} (c_2 - c_b) dt} , \quad (2-3)$$

where Q = discharge to be measured

V_1 = volume of dye solution introduced into the stream

c_1 = concentration of dye solution injected into the stream

c_2 = the measured dye concentration at a given time at the sampling point

c_b = the background concentration of the stream

t = time.

The term $\int_0^{\infty} (c_2 - c_b) dt$ is just the area under the concentration-time curve. In practice it can be approximated by

$$A = \sum_{i=1}^n (c_i - c_b) (t_{i+1} - t_{i-1})/2 , \quad (2-4)$$

where i = the sequence number of a sample
 n = the total number of samples
 t_i = time when a sample c_i is taken.

The constant-rate-injection (CRI) method is described in the following section. However, it should be noted that, if the concentration versus time curve is defined for CRI method, the discharge can be checked by using equation (2-3).

3. Equipment Required

The following equipment is needed for CRI method:

a. Dye solution injection equipment

There are several kinds of devices that can be used for constant-rate-injection. Two simple operation devices are recommended.

1. Mariotte vessel

The Mariotte vessel, as shown in Figure 4, is so designed that the dye solution discharges through an orifice under a constant head.

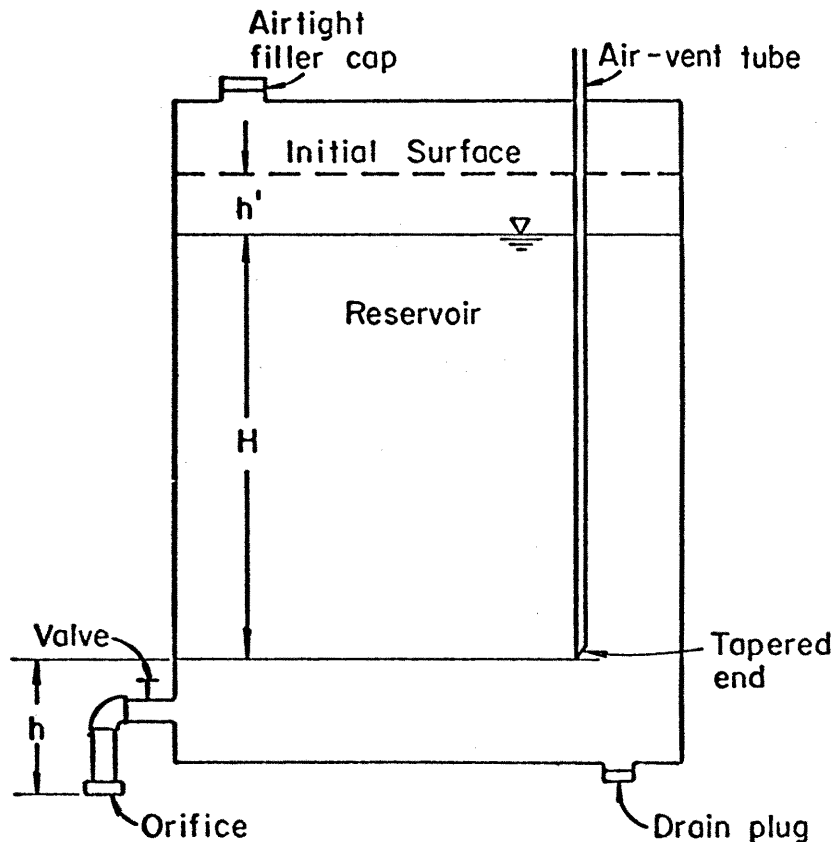


Fig. 4. Mariotte Vessel

The vessel must be airtight except for the air-vent tube. At the instant the valve is opened, the orifice has a head of $(h + H + h')$. The discharge of the solution causes a partial vacuum in the space above the dye. Finally, a pressure equilibrium is reached when the partial vacuum plus the solution head above the tapered end of the air-vent tube (H) equals atmospheric pressure. Then the discharge head on the orifice becomes h only. After this equilibrium condition is reached, air gets into the vessel from the tapered end of the air-vent tube. The discharge head on the orifice does not change until the solution surface is below the tapered end of the air-vent tube. The effective volume of the Mariotte vessel is the cross-sectional area times the height H . Different discharge rates can be obtained by using different sizes of orifices or changing h .

Discharge at more than one point may be obtained by installing the desired number of orifices in the tank. The Mariotte vessel cannot be used to inject dye solution into a pipe with pressure in it.

2. Aerofeed chemical dispenser

The TD series of Aerofeed chemical dispensers is designed to feed small quantities of liquid into pipe lines, tanks or open channels at manually adjustable constant rates without the need for electric power or water pressure. As shown in Figure 5, power to operate the dispenser is derived from a small quantity of compressed air. The compressed air forces the liquid through a filter, out through a tube, into the flow meter, through the flow regulator, and then via a flexible plastic tube to the point of application. The design of the control unit is such that a constant rate of flow is maintained at all times as long as the pressure in the tank is at least 4 to 5 psi higher than the pressure at the point of application. Detailed information may be found in the Aerofeed chemical dispenser instruction manual.

b. Measurement of dye concentration

The fluorometer utilizes an optical bridge analogous to a Wheatstone bridge, which measures the difference between light emitted by an excited sample of fluorescent material and a calibrated light path. Figure 6 shows a schematic diagram of the fluorometer. (G. K. Turner Associates, 1963, p. 13). The principle of operation of the fluorometer may be found in the operation manual. The concentration of dye

solution is obtained by this device. Ranges of concentration may be obtained by using different combinations of fluorometer scales and filters.

c. Samplers and containers

In pipe lines, tubes with valve controls can be mounted at desired positions to receive the samples. In open channels, hand samplers are used to take the samples at several verticals. As the dye concentration may change due to the exposition of dye under light, containers in dark colors are recommended.

d. Temperature control apparatus

Since the fluorescence of dye solution changes with temperature, a constant temperature apparatus is needed in order to keep the solutions at a constant temperature during analysis. This normally consists of a circulating pump, heater, and thermostat. The temperature-correction coefficients for Rhodamine WT, Rhodamine B, and Pontacyl pink dyes are given in Table 1. (Measurement of discharge by dye dilution method) (Hydraulic Measurement and Computation, Book 1, Chapter 14, 1965, U. S. Geological Survey, p. 13). If significant differences between the sample temperature and the standard solution temperature are noted during analysis, correction factors have to be applied to obtain the correct dial readings or concentrations. However, if analysis of all samples (injected dye solution c_1 and diluted sample c_2) are made at the same temperature, no corrections need to be made.

4. Procedure

a. Preparation of standard solution

In order to obtain calibration curves of fluorometer dial reading versus concentration, standard solutions containing known concentrations of dye must be prepared. At least three known concentrations of dye solutions for each fluorometer range used must be prepared. The range of concentrations needed depends on the fluorometer scale as well as the filters used.

The standard solutions can be obtained by a dilution procedure based on either a volumetric process or weighing process. As defined in equation (2-1),

$$c_1 = \frac{c_D V_D}{V_D + V_W}$$

the flow chart for dilution is shown in Figure 7. Sample computations are given on Table 2. The volumetric dilution processes are the same as the weighing processes providing that the volume of solution is used instead of weight. There is a certain relation between the concentrations by weight and by volume,

$$\begin{aligned} W_D &= \gamma_D V_D \\ W_W &= \gamma_W V_W \\ c_W &= \frac{c_D \gamma_D V_D}{\gamma_D V_D + \gamma_W V_W} , \end{aligned} \quad (4-1)$$

where W_D = weight of dye solution
 γ_D = specific gravity of dye solution
 V_D = volume of dye solution
 W_W = weight of distilled water
 γ_W = specific gravity of distilled water
 V_W = volume of distilled water
 c_W = concentration of dye solution by weight.

Since the volume of dye is much smaller than the volume of distilled water, the specific gravity of the diluted solution can be represented by γ_W , which is 1.0. Thus

$$c_W = \gamma_D \frac{c_D V_D}{V_D + V_W} = \gamma_D c_V , \quad (4-2)$$

where c_V = concentration of dye solution by volume.

In the computation of the discharge in streams, the term

$$\frac{c_1 - c_2}{c_2 - c_b}$$

in equation (2-2) is dimensionless, therefore, either c_V or c_W can be used to get the same discharge Q . Because of the

precision and easy operation, the weighing process is recommended.

After combining, the solution has to be shaken in order to get a uniform mixture. Once prepared, standard solutions can be stored in a dark place for a period of time.

b. Fluorometer calibration

Fluorometer readings are relative values of fluorescence intensity. To convert readings to concentrations of a fluorescent solute, the fluorometer has to be calibrated using standard solutions for each different scale. The concentrations are then just the readout on the fluorometer.

Fluorescence varies linearly with concentration below several hundred parts per billion. Instrument output is designed to be linear (within about one percent) with the amount of light reaching the photomultiplier. It follows that fluorometer dial readings vary linearly with concentration. Usually, a straight line can be fitted accurately by eye. If there is doubt, the method of least squares may be used to fit the line. Most of the calibration curves are straight lines passing through origin as shown in Figure 8. At very high

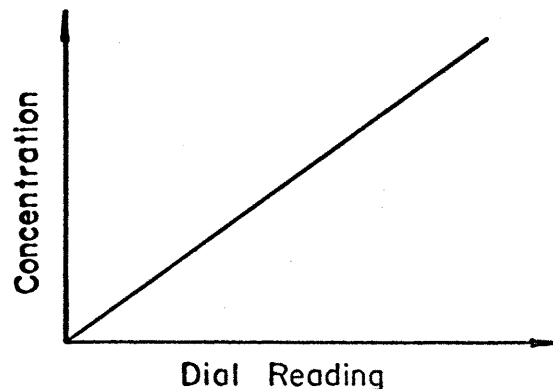


Fig. 8. Fluorometer calibration curve

concentrations, usually above several hundred ppb, a curved relation may be observed. It is recommended that the concentrations of samples be kept in the linear range by diluting the high concentration samples with known quantities of distilled water if necessary.

The fluorometer should be calibrated immediately before the sample analysis to have consistent dial readings. This is because the fluorometer may be moved and some of the electronic components may be touched.

An example showing the calibration of the fluorometer is given on the following pages, using the standard solution prepared as shown on page 17, Table 2. The calibration curves are shown on Figures 9 and 10 for scale 3x and 10x respectively.

c. Preparation of injection dye solution

Dye is never injected at full strength (20%) into a stream or pipe, but is diluted using the method described previously. However, because the injector has some residual dye after being used, the dye solution is not diluted to an exact concentration, but is only diluted to a concentration in the desired range in concentration after complete mixing in the fluid to be measured.

The concentration of the injection dye solution may be computed as

$$c_1 = \frac{(Q + q) c_2}{q} , \quad (4-3)$$

where c_1 = the concentration of the injection dye solution
 Q = the discharge to be measured (estimated)
 q = the desired injection rate
 c_2 = the desired concentration of the solution after mixed.

The quantity of solution needed depends on the injection rate and the injection time duration. The injection dye solution may be prepared approximately as follows:

$$W_o = \frac{c_1 \times W_w}{c_o} , \quad (4-4)$$

where W_o = the quantity of known concentration of dye solution needed (in weight)
 c_o = the known concentration of the dye solution to be diluted
 W_w = the quantity of distilled water needed (in weight)
 c_1 = the desired concentration of the injection dye solution (From equation (4-3)).

Once c_1 and W_w are determined by equation (4-3), and with the time duration of the injection, W_0 can be obtained by using a certain known concentration of dye solution. Usually, the original solution, WT dye for example, with the concentration of 2×10^8 ppb, is used.

d. Selection of injection rate q

The injection rate is dependent on the discharge to be measured and the concentration of the injected dye solution. Because low concentrations have more accurate dial readings, a concentration of 5 ppb (c_2) for the sample, after mixing, is recommended. Figure 11 shows a chart for selecting the injection rate for $c_2 = 5$ ppb. An example is illustrated on the figure.

e. Injection and sampling

The general procedure for the measurement is as follows: the injection rate is measured by a cylinder and a stopwatch before and after the test. Usually, the injector needs a couple of minutes to obtain a steady injection rate. For a single point constant-rate injection, the dye solution is usually injected at the center of a pipe or a channel.

In order to get complete mixing, the sampling point has to be a distance L (the mixing distance downstream) from the injection point. The mixing distance varies with the geometry and hydraulic characteristics of the reach or pipe. An equation developed by Nobuhiro Yotsukura, an engineer with the U. S. Geological Survey, (written communication, 1965) may be used as a guide to determine the mixing distance in a channel. The equation, which is based on flume studies using a tracer solution injected in the center of the channel, is given as

$$L = \frac{1.49}{2\alpha^2\beta} \frac{R^{1/6}}{n\sqrt{g}} \frac{W^2}{D_m} \quad (4-5)$$

where

L = the distance downstream from the dye solution injection point

α = a constant which is given as six for the point where the dye first comes in contact with the banks and as two for the point of complete mixing of the dye

β = an empirically determined coefficient for which values have been found ranging from 0.3 to 0.8 in natural streams, but which may have values over a greater range

R = the hydraulic radius of the channel

n = the Manning roughness coefficient

g = the gravitational constant

w = the mean width of the stream

D_m = the mean depth of the stream.

In a pipe line, the experiments done by R. W. Filmer and V. M. Yevjevich indicate that the concentration decreases rapidly with distance downstream from the injection point. The distances between the injection and sampling points depend on the accuracy of the measurement needed. For more than one injection point, the distance needed for complete mixing may be shorter.

Sampling in a pipe, a single tube or several distributed tubes are used. Samples taken at several verticals by hand in a channel are required. The accuracy of the measurement of the discharge in a stream is increased if a velocity weighted sample is taken using the ETR method and a DH 48 hand sampler.

Sampling time affects average dye concentration. It has been shown that a two minute sampling time decreased substantially the error in the time-average dye concentration. (R. W. Filmer and V. M. Yevjevich, Report, CSU, 1966)

f. Sample analysis and discharge computation

The concentration of samples is determined by the relative readings on the fluorometer. Standard solutions and samples in test tubes are put in a constant temperature bath. The temperature in the bath should be higher than the room temperature. Also, the fluorometer should be allowed to heat up. It takes one and half hours for the fluorometer to reach its steady temperature (approximately 96°F). Analyzing the samples under unsteady temperature will cause deviation on the relative readings.

The calibration curve is made for the fluorometer as described in equation (4-b). On testing the sample, its concentration can be obtained by relating the corresponding reading on the fluorometer to the calibration curve. If the temperatures of the

samples are not the same as that under which the calibration curve was made, temperature corrections for the concentrations, as shown in Table 1, are required. Since the temperature at the fluorometer is higher than that of the samples, care must be taken when the readings on the fluorometer are read. After putting the sample in the sample holder, the fluorometer reading will reach a certain value then decrease because the fluorescence intensity of dye solutions decrease with increasing temperature. The maximum steady reading for each sample is taken to determine the dye concentration of the sample.

The sample of the injection dye solution is taken before or after the injection. The dilution procedures of the solution are the same as described in the preparation of standard solution. The finally diluted solution can be measured on the fluorometer, and its concentration may be determined. An example is given herein.

The computation of discharges is based on equation (2-2) where the determination of c_1 , c_2 , c_b and q have been discussed previously. Following is an example for the discharge computation in a pipe line. Also, a standard form is attached.

a. Injection rate

Volume of cylinder $V = 90 \text{ ml}$
 Time $T_1 = 39.10 \text{ sec.}$
 $T_2 = 38.95 \text{ sec.}$
 Average Time $\bar{T} = 39.025 \text{ sec.}$

$$\text{Injection rate } q = \frac{90}{39.025} = 2.3062 \text{ ml/sec.}$$

$$1 \text{ cfs} = 28316.85 \text{ ml/sec.}$$

b. Sample analysis (primary filter 1-60, secondary filter 23A)

(1) Sample No.	(2) Dial Reading	(3) Average	(4) Fluoro. Scale	(5) Filter %	(6) Sampler Temp. °F	(7) Concent. C_2 ppb	(8) Sampling Time sec	(9) Temp. Correction	(10) C_2 After Correction ppb	(11) Discharge Q cfs	(12) Remarks
2-1	6.10 6.10	6.10	10x	10	80	1.98		1.00	1.98		Back- ground
2-3	35.50 35.40	35.45	3x	10	80	16.80	120	1.00	16.80	1.740	
2-4	7.30 7.10	7.20	10x	10	80	2.17		1.00	2.17		Back- ground
2-6	23.40 23.60	23.50	3x	10	80	11.94	120	1.00	11.94	2.640	
2-7	12.80 12.60	12.70	10x	10	80	3.01		1.00	3.01		Back- ground
2-9	20.40 20.40	20.40	3x	10	80	10.65	120	1.00	10.65	3.375	
2-10	16.00 16.00	16.00	10x	10	80	3.83		1.00	3.83		Back- ground
2-12	21.10 21.10	21.10	3x	10	80	10.93	120	1.00	10.93	3.632	

c. Discharge computation

Discharges are computed as follow and enter in column (11) of the table for sample analysis. The concentration of the injection dye solution c_1 was obtained as 3.16660×10^{-5} ppb from page 18. From equation (2-2)

$$Q = \left(\frac{c_1 - c_2}{c_2 - c_b} \right) q$$

Substituting all the figures into the equation

$$Q_{2-3} = \left(\frac{316660 - 16.80}{16.80 - 1.98} \right) \frac{2.3062}{28316.85} = 1.740 \text{ cfs}$$

$$Q_{2-6} = \left(\frac{316660 - 11.94}{11.94 - 2.17} \right) \frac{2.3062}{28316.85} = 2.640 \text{ cfs}$$

$$Q_{2-9} = \left(\frac{316660 - 10.65}{10.65 - 3.01} \right) \frac{2.3062}{28316.85} = 3.375 \text{ cfs}$$

$$Q_{2-12} = \left(\frac{316660 - 10.93}{10.93 - 3.83} \right) \frac{2.3062}{28316.85} = 3.632 \text{ cfs}$$

I. DYE INJECTION:

II. COLLECTION AND ANALYSIS OF MEASUREMENT SAMPLES

 $\Sigma =$ $\Sigma =$

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Table 1. Temperature-correction coefficients for Rhodamine WT, Rhodamine B and Pontacyl pink dyes			
Temperature Difference (T _s - T)* [F°]	Temperature-correction coefficient		
	Rhodamine WT	Rhodamine B	Pontacyl Pink
-20	1.36	1.35	1.38
-15	1.25	1.25	1.27
-10	1.16	1.16	1.17
- 8	1.13	1.13	1.14
- 6	1.09	1.09	1.10
- 5	1.08	1.08	1.08
- 4	1.06	1.06	1.07
- 3	1.05	1.05	1.05
- 2	1.03	1.03	1.03
- 1	1.02	1.02	1.02
0	1.00	1.00	1.00
+ 1	0.99	0.99	0.98
+ 2	0.97	0.97	0.97
+ 3	0.96	0.96	0.95
+ 4	0.94	0.94	0.94
+ 5	0.93	0.93	0.92
+ 6	0.91	0.91	0.91
+ 8	0.89	0.89	0.88
+10	0.86	0.86	0.85
+15	0.80	0.80	0.79
+20	0.74	0.74	0.73

*T_s = the standard curvette-sample temperature

T = the curvette-sample temperature at the time the sample was tested in the fluorometer

Table 2. Preparation of Standard Solution

(1) Flask No.	(2) Flask Wt. gm	(3) Water Gross Wt. gm	(4) Water Net Wt. gm	(5) Dye Sol. Gross Wt. gm	(6) Flask Wt. gm	(7) Dye Sol. Net Wt. gm	(8) Wt. of New Solution (4)+(7) gm	(9) Dilution Factor $\frac{(7)}{(8)}$	(10) C_1 ppb	(11) $C_2 = (9) \times C_1$ ppb
1	0*	990.000	990.000	49.260	38.550	10.710	1000.710	1.070×10^{-2}	2×10^8	2.140×10^6
2	0	990.000	990.000	49.158	38.385	10.773	1000.773	1.076×10^{-2}	2.140×10^6	2.303×10^4
4	0	1980.000	1980.000	59.067	38.381	20.686	2000.686	1.034×10^{-2}	2.303×10^4	238.097
5	0	800.000	800.000	88.280 91.670 87.159 88.129	38.452 38.494 38.501 38.604	49.828 53.176 49.658 49.525	1002.187	0.2017	238.097	48.035
						$\Sigma = 202.187$				
7	0	930.000	930.000	88.311 58.857	38.421 38.419	49.890 20.438	1000.328	0.0703	238.097	16.735
						$\Sigma = 70.328$				
8	0	800.000	800.000	89.174 87.286 87.512 88.858	38.054 38.020 38.005 38.026	51.120 49.266 49.507 50.832	1000.725	0.2006	48.035	9.635
						$\Sigma = 200.725$				
3	0	900.000	900.000	88.833 87.772	37.966 38.035	50.867 49.737	1000.604	0.1005	48.035	4.830
						$\Sigma = 100.604$				
11	0	750.000	750.000	88.128	38.059	50.069	800.069	0.0626	48.035	3.010

*Weighing scale was set on zero when the flasks were weighted.

Table 3. Calibration of Fluorometer (primary filter 1-60
secondary filter 23A)

(1) Flask No.	(2) Concentration ppb	(3) Temperature °F	(4) Scale	(5) Filter %	(6) Dial Reading	(7) Average
Dull tube		80	3x	10	0	0
7	16.735	80	3x	10	36.40 36.60	36.50
8	9.635	80	3x	10	16.50 16.90	16.70
3	4.830	80	3x	10	5.60 5.40	5.50
11	3.010	80	3x	10	1.80 2.40	2.10
Dull tube		80	10x	10	10.00	10.00
7	16.735	80	10x	10		
8	9.635	80	10x	10	53.00 53.20	53.10
3	4.830	80	10x	10	24.60 24.40	24.50
11	3.010	80	10x	10	12.80 12.40	12.60

Table 4. Dilution of the Injection Dye Solution

(1) Flask No.	(2) Flask Wt. gm	(3) Water Gross Wt. gm	(4) Water Net Wt. gm	(5) Dye Sol. Gross Wt. gm	(6) Flask Wt. gm	(7) Dye Sol. Net Wt. gm	(8) Wt. of New Solution (4)+(7) gm	(9) Dilution Factor $\frac{(7)}{(8)}$	(10) C_1 ppb	(11) $C_2 = (9) \times C_1$ ppb
13	0	780.000	780.000	77.126	55.334	21.792	801.792	2.178×10^{-2}	C_1	$2.178 \times 10^{-2} C_1$
14	0	780.000	780.000	68.749	38.411	30.338	810.338	3.744×10^{-2}	$2.178 \times 10^{-2} C_1$	$1.0176 \times 10^{-3} C_1$
15	0	780.000	780.000	44.535	20.042	24.493	804.493	3.045×10^{-2}	$1.0176 \times 10^{-3} C_1$	$3.098 \times 10^{-5} C_1$

C_1 = Concentration of the injection dye solution

The solution with a concentration of $3.098 \times 10^{-5} C_1$ has a reading of 18.20 on the fluorometer at scale of 3x with a 10% filter, the solution has a temperature of 80°F. From the calibration curve on page 23 the concentration $C_2 = 9.81$ ppb, then

$$3.098 \times 10^{-5} C_1 = 9.81$$

$$C_1 = \frac{9.81}{3.098 \times 10^{-5}} = 3.16660 \times 10^5 \text{ ppb}$$

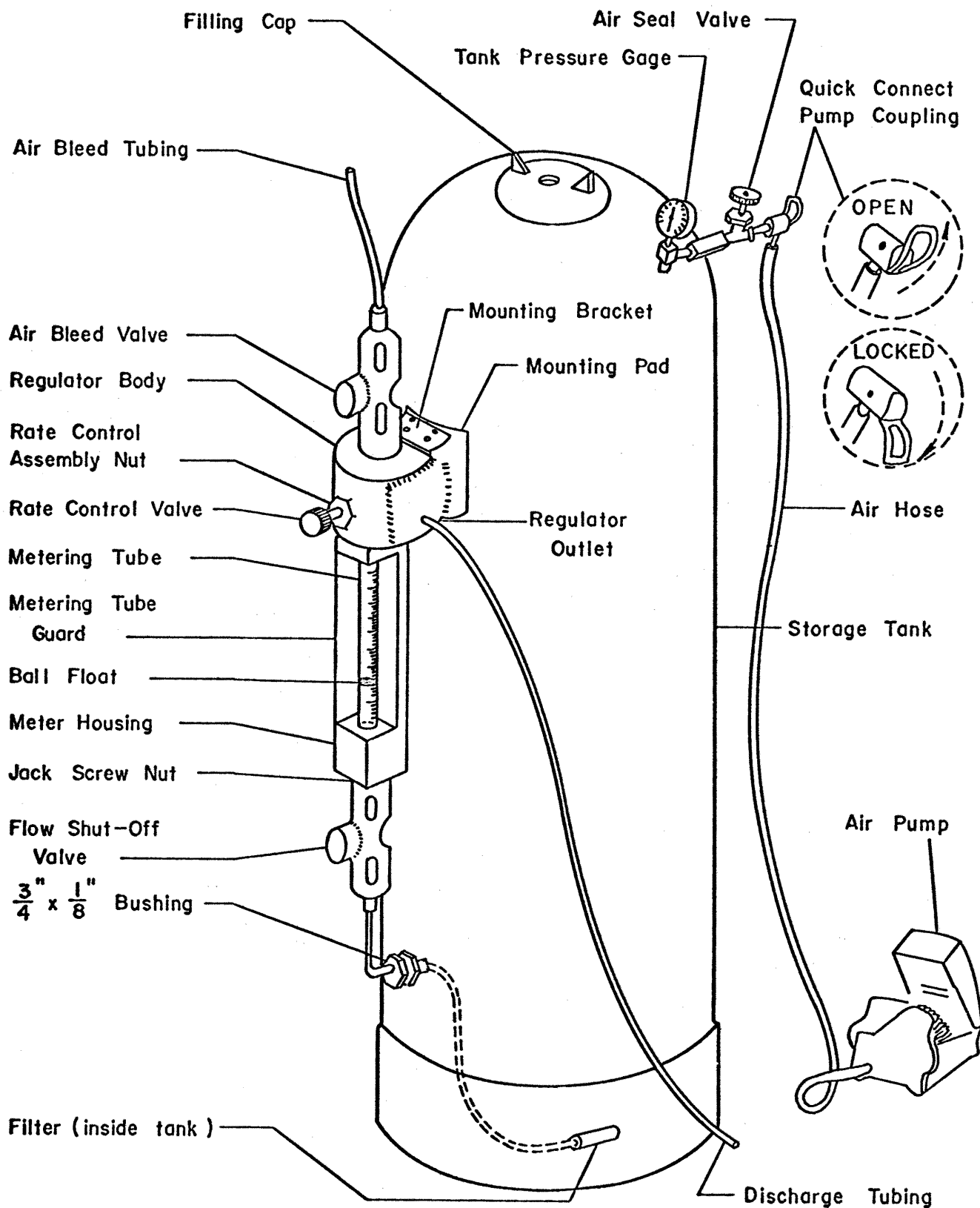


Fig. 5. Series TD Parts Identification

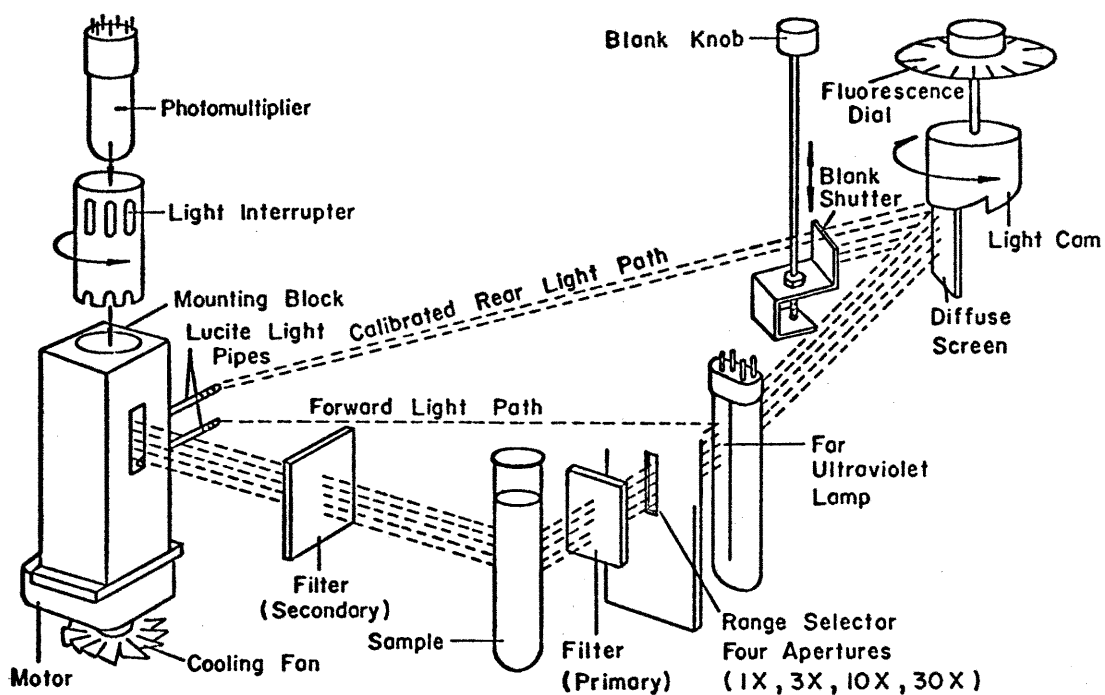


Figure 6. Schematic diagram of the fluorometer (from G. K. Turner Associates, 1963, p. 13).

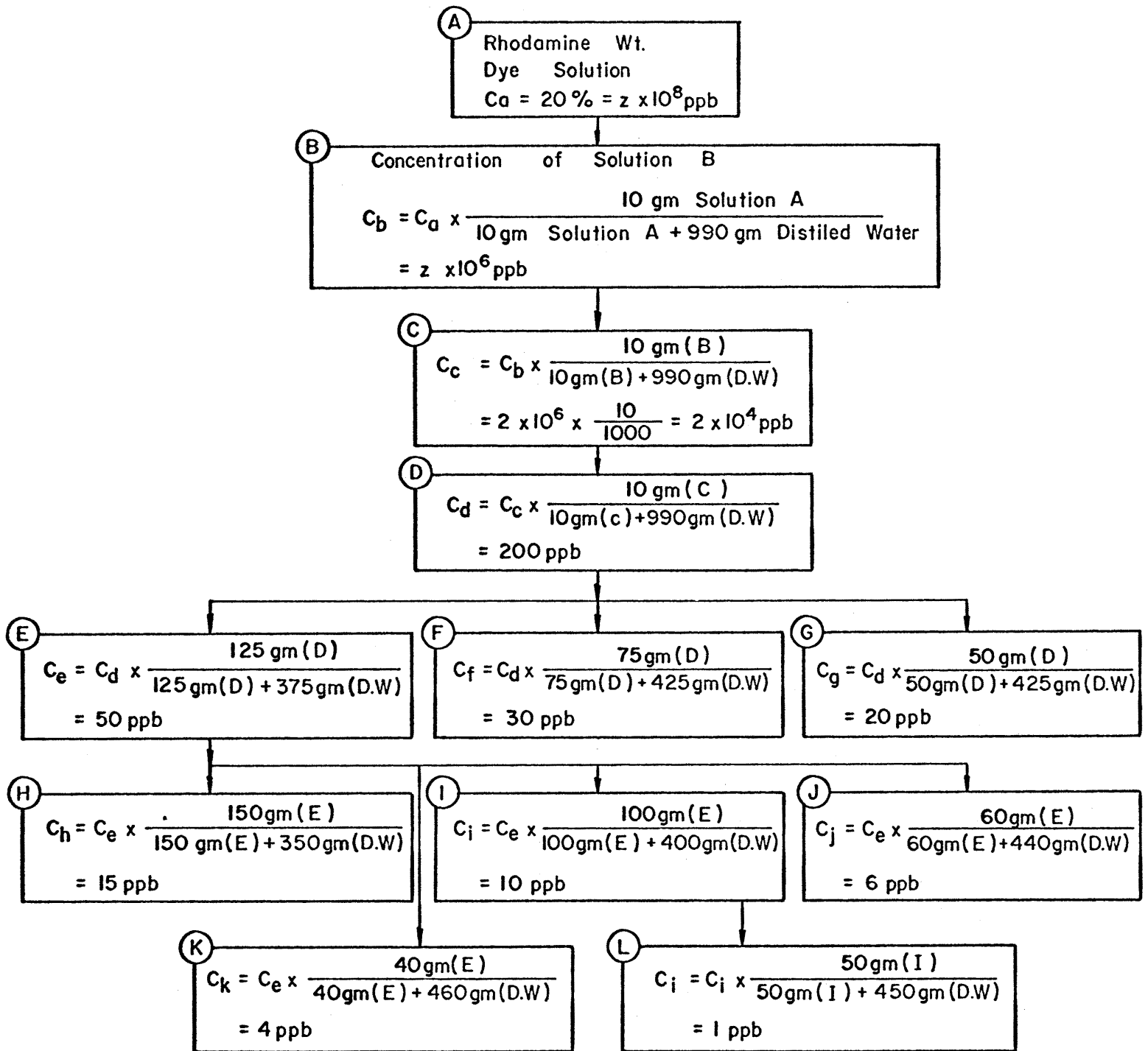


Fig. 7. Dilution flow chart for standard solution

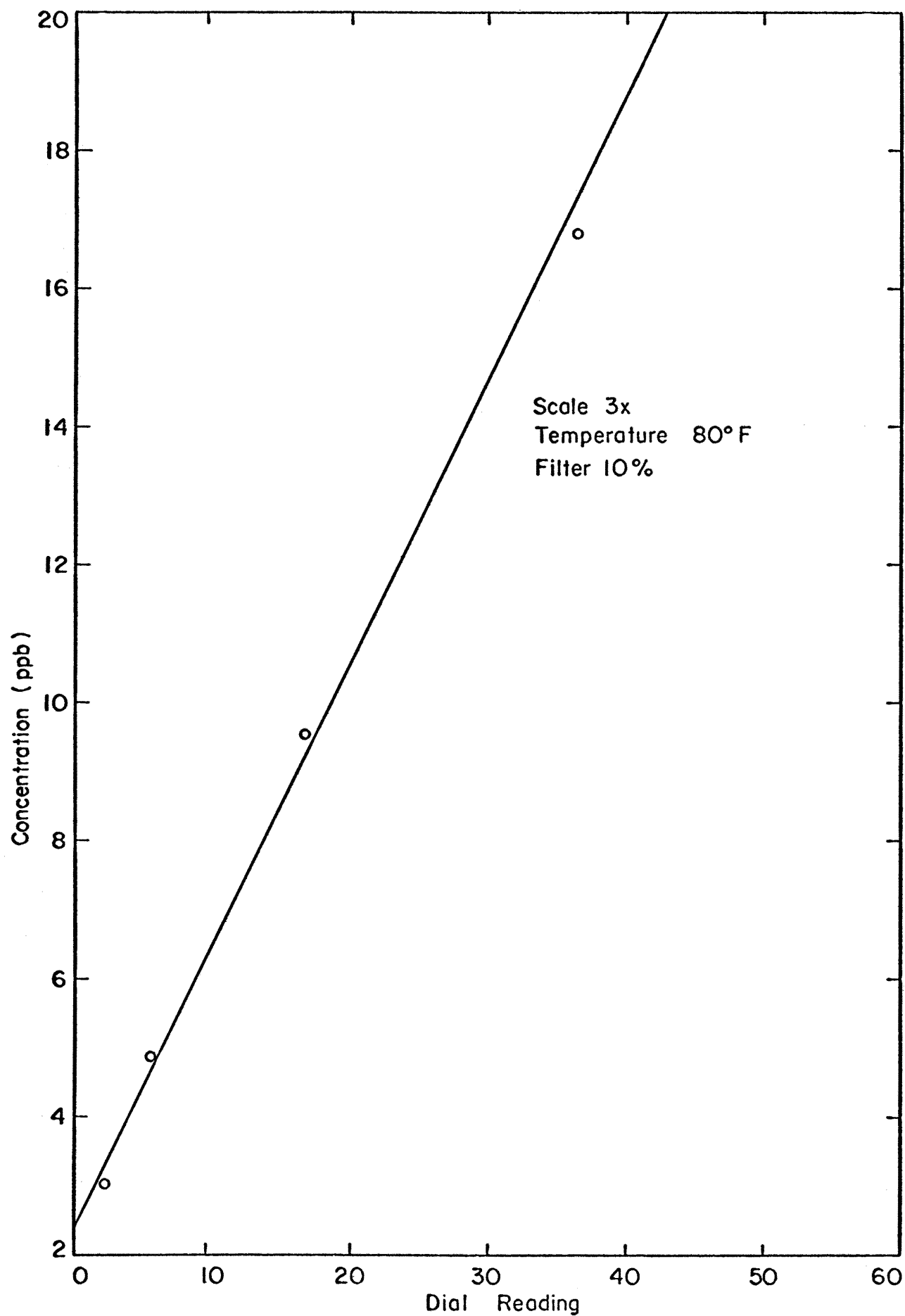


Fig. 9. Fluorometer Calibration Curve

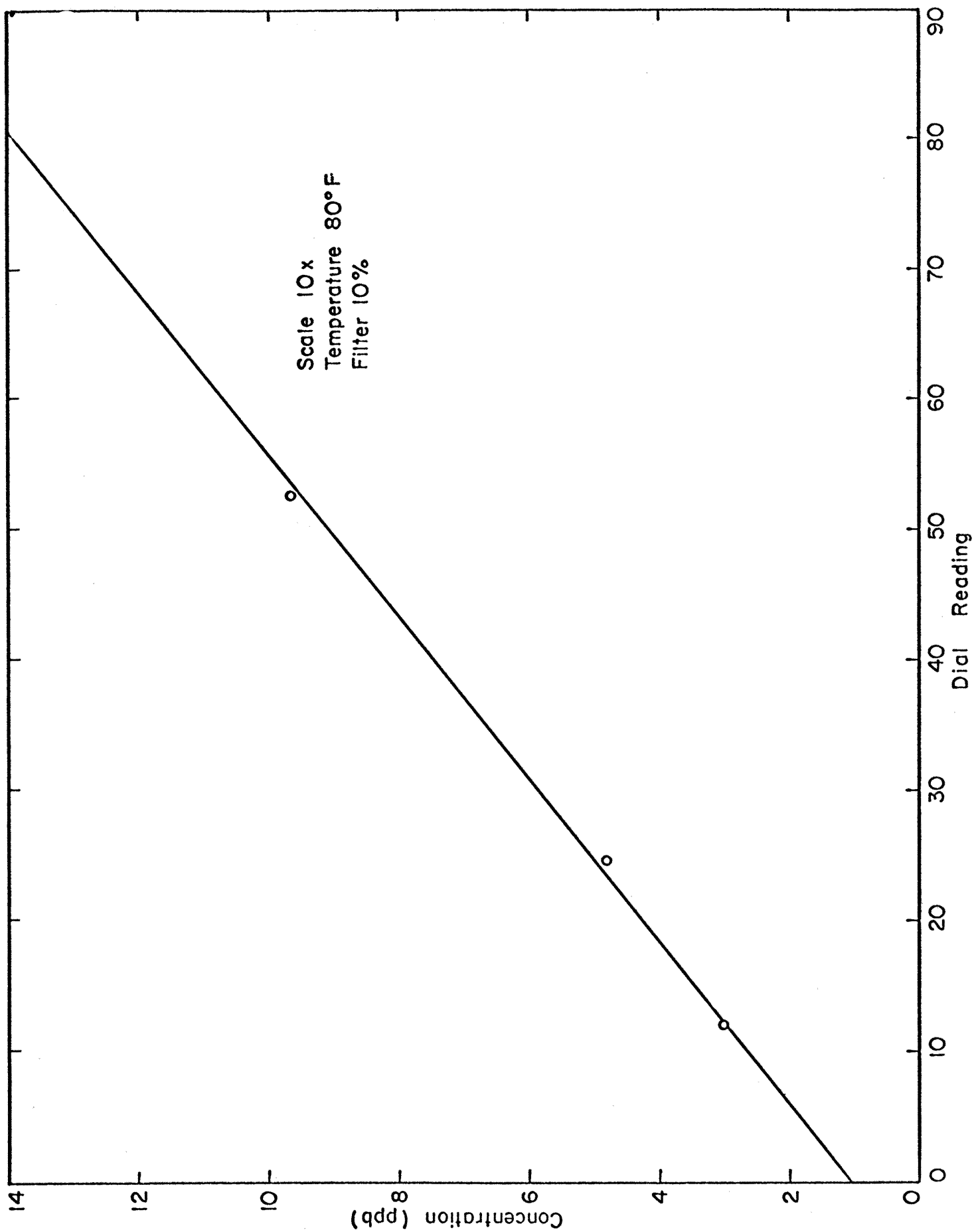
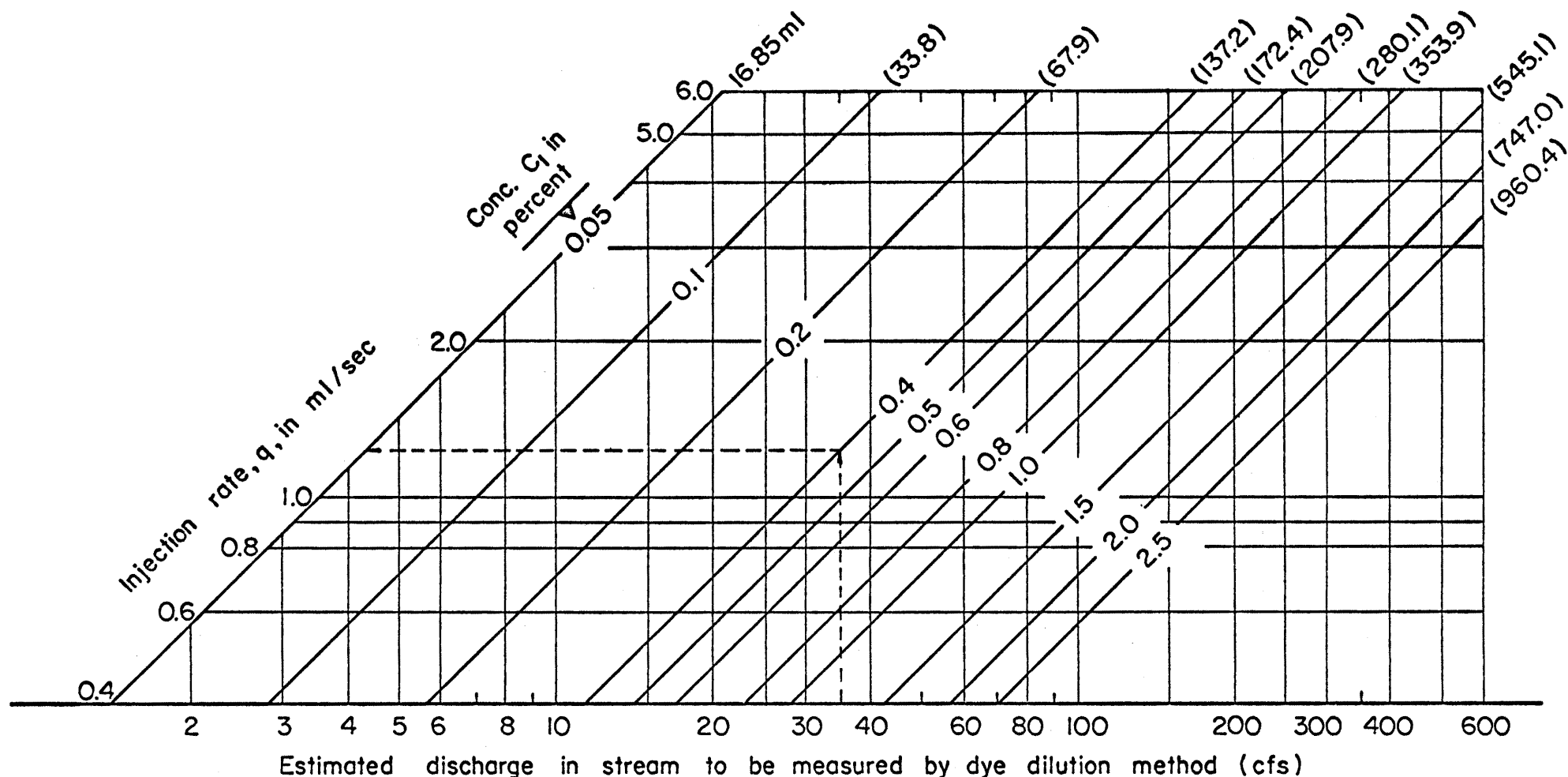


Fig. 10. Fluorometer Calibration Curve

(a) DYE QUANTITIES REQUIRED FOR DIFFERENT DISCHARGES ($C = 5$ ppb)



Example: Estimated stream discharge is 35 cfs; required injection ($C = 0.4\%$) rate is therefore about 1.24 ml/sec which requires that ball setting on rate meter on aero-feed tank needs to be about 25: at this rate, if the tank has 8 liters of dye, approximately 1.8 hours of continuous injection is available before the tank is empty.

Note: Different aero-feed tanks may have different calibrations and each should be determined.

Figure 11.

(b) AEROFEED CALIBRATION

