CHAPTER 7.—MEASUREMENT OF DISCHARGE BY TRACER DILUTION

GENERAL

The measurement of stream discharge by dilution methods depends on the determination of the degree to which an added tracer is diluted by the flowing water. Any substance can be used as a tracer if it meets the following criteria:

1. It dissolves readily in water at ordinary temperatures.
2. It is either absent in the water of the stream or present only in very low concentrations.
3. It is not decomposed in the water of the stream and is not retained or absorbed in significant quantity by sediments, plants, or other organisms.
4. It can be detected in extremely low concentrations by simple methods.

5. It is harmless to man and animals in the concentration it assumes in the stream.

Until recent years chemical salts, primarily common salt (NaCl), were usually used as the tracers injected into the streams. The use of salt tracers, on all but the smallest streams, was limited, however, to the sudden-injection method, because of the difficulty of handling the large quantities of salt solution required by the usually more accurate constant-rate-injection method. In recent years, and particularly in the U.S.A., the use of dye tracers in the constant-rate-injection method has become the most popular method of discharge measurement by tracer dilution. That has resulted from the development of fluorescent dyes and fluorometers that can detect those dyes at very low concentrations. The use of fluorescent dyes is not as popular in Europe as in the U.S.A. There, colorimetric analysis, using sodium dichromate as the tracer dye, is the most widely used means of measuring discharge by the constant-rate-injection method. However, where the sudden-injection method is to be used, the use of common salt as a tracer is still preferred, particularly on the smaller streams, because of the greater ease in handling salt and in determining concentrations. Radioactive elements, such as gold 198 and sodium 24, have also been used in recent years as the tracers in the sudden-injection method, but the use of such elements is still (1980) considered experimental.

The tracer-dilution methods of measuring discharge are more difficult to use than the conventional current-meter method, and under most conditions the results are less reliable. Dilution methods should therefore not be used when conditions are favorable for a current-meter measurement of discharge. Tracer-dilution methods of measuring discharge in open channels can be used advantageously in rough channels that carry highly turbulent flow.

THEORY OF TRACER-DILUTION METHODS

In the tracer-dilution methods of measuring discharge, a tracer solution is injected into the stream to be diluted by the discharge of the stream. From measurements of the rate of injection, the concentration of the tracer in the injected solution, and the concentrations of the tracer at a sampling cross section downstream from the injection site, the stream discharge can be computed.

Either of two methods may be used for determining the discharge of a stream by tracer dilution. The first method, the constant-rate-injection method, requires that the tracer solution be injected into the stream at a constant flow rate for a period sufficiently long to achieve a constant concentration of the tracer in the streamflow at the downstream sampling cross section. The second method, the sudden-

injection method, requires the instantaneous injection of a slug of tracer solution and an accounting of the total mass of tracer at the sampling cross section. Another use is often made of the sudden-injection method that is not concerned with degree of dilution. Where the cross-sectional area of the flow is constant, as in pressure conduit, the sudden-injection method may be used to determine the velocity of flow; discharge can then be computed by using that velocity and the known cross-sectional area. (See p. 533.)

THEORY OF THE CONSTANT-RATE-INJECTION METHOD

A constant-rate-injection system is shown schematically in figure 115. If the tracer is injected for a sufficiently long period, sampling of the stream at the downstream sampling cross section will produce a concentration-time curve similar to that shown in figure 116. The stream discharge is computed from the equation for the conservation of mass, which follows:

$$QC_b + qC_1 = (Q + q)C_2$$

or

$$Q = \left[\frac{C_1 - C_2}{C_2 - C_b} \right] q,$$

(24)

where

q is the rate of flow of the injected tracer solution,

Q is the discharge of the stream,

C_b is the background concentration of the stream,

C_1 is the concentration of the tracer solution injected into the stream, and

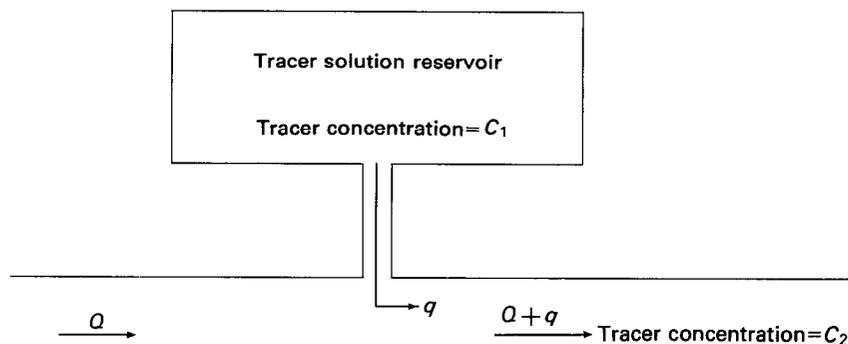C_2 is the measured concentration of the plateau of the concentration-time curve (fig. 116).

FIGURE 115.—Constant-rate-injection system.

THEORY OF THE SUDDEN-INJECTION METHOD

If a slug of tracer solution is instantaneously injected into a stream, sampling of the stream at the downstream sampling cross section will produce a concentration-time curve similar to that shown in figure 117. The equation for computing stream discharge, which is again based on the principle of the conservation of mass, is

$$Q = \frac{V_1 C_1}{\int_0^\infty (C - C_b)dt},$$ (25)

where

Q is the discharge of the stream,

V_1 is the volume of the tracer solution introduced into the stream,

C_1 is the concentration of the tracer solution injected into the stream,

C is the measured tracer concentration at a given time at the downstream sampling site,

C_b is the background concentration of the stream, and

t is time.

The term $\int_0^\infty (C - C_b)\, dt$ is the total area under the concentration-time curve. In practice the term $\int_0^\infty (C - C_b)dt$ can be approximated by the term
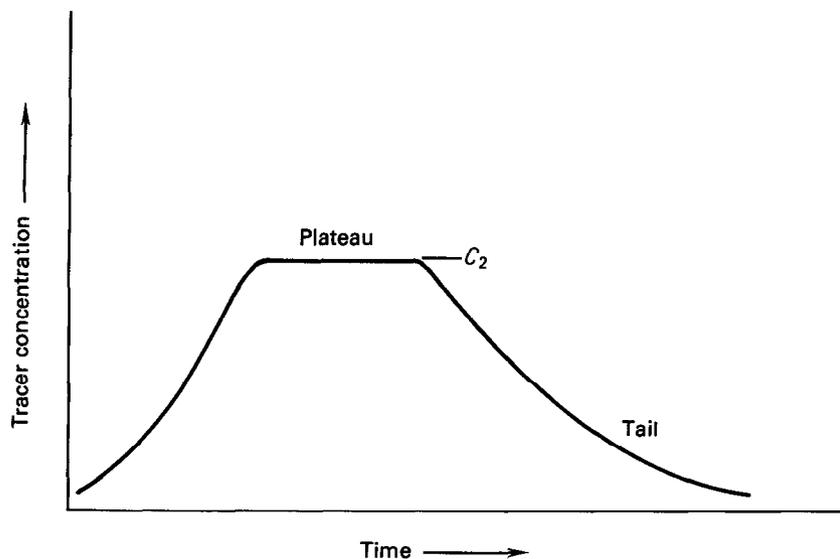

FIGURE 116.—Concentration-time curve at downstream sampling site for constant-rate injection.

$$\sum_{i=1}^{N} (C_i - C_b)(t_{i+1}-t_{i-1})/2,$$

where

i is the sequence number of a sample,

N is the total number of samples, and

t_i is time when a sample, C_i, is obtained.

FACTORS AFFECTING THE ACCURACY OF TRACER-DILUTION METHODS

Even if it is assumed that measurements of concentrations and of the injection rate are error free, there still remain three factors that affect the accuracy of tracer-dilution methods of measuring discharge. Those factors are stream turbidity, loss of tracer between the injection site and the downstream sampling site, and incomplete mixing throughout the stream cross section before the downstream sampling section is reached.

TURBIDITY

Turbidity may either increase or decrease the recorded tracer fluorescence depending upon the relative concentrations of tracer and turbidity (Feuerstein and Selleck, 1963). To minimize the effect of turbidity, samples should be permitted to stand long enough to allow
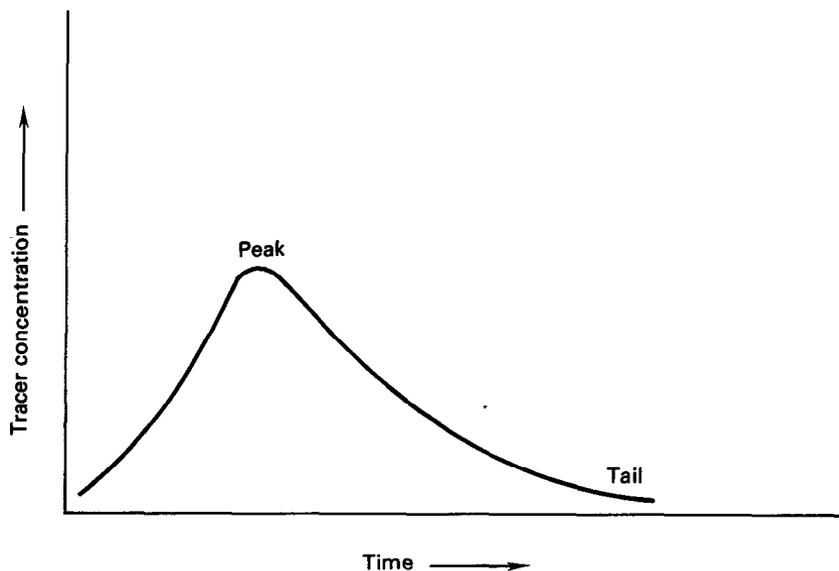
FIGURE 117.—Concentration-time curve at downstream sampling site for sudden injection.

suspended solids to settle prior to fluorometric analysis (p. 231, 240). Use of a centrifuge for the purpose of separating the suspended solids is even more effective, but a centrifuge is seldom used for that purpose in stream-gaging work.

LOSS OF TRACER

The computation of stream discharge, as mentioned earlier, is based on equations for the conservation of mass. Consequently, the accuracy of the computed discharge will be adversely affected if some of the tracer is lost in the reach of channel between the injection site and the downstream sampling site. Tracer losses are primarily due to sorption and chemical reaction between the tracer and one or more of the following: streambed material, suspended sediments, dissolved material in the river water, plants, and other organisms. For most of the tracers used, chemical reaction is a minor factor in comparison with sorption. The degree of tracer loss by sorption for a particular tracer varies primarily with the type and concentration of suspended and dissolved solids in the water. In routine stream gaging by the tracer-dilution method no attempt is made to quantify tracer loss by sorption; instead, the "best" tracer available from the standpoint of being least affected by sorption is used.

Photochemical decay is also a source of tracer loss which varies with the tracer material used and its residence time in direct sunlight. Loss from that source is usually negligible, even with fluorescent dyes, if the proper dye is used and if residence time in direct sunlight is limited to only a few hours, as it usually is in stream-gaging work.

Equations 24 and 25 show that loss of tracer will result in a computed discharge that exceeds the true stream discharge.

CRITERIA FOR SATISFACTORY MIXING

Tracer-dilution measurements require complete vertical and lateral mixing at the sampling site. Vertical mixing is usually accomplished very rapidly compared to lateral mixing; therefore, the distance required for lateral mixing is the primary consideration. Frequently, long reaches are needed for complete lateral mixing of the tracer. The mixing distance will vary with the hydraulic characteristics of the reach. Engmann and Kellerhals (1974) have demonstrated that ice cover significantly reduces the mixing capacity of a reach of river.

When the constant-rate-injection method is used, complete mixing is known to have occured when the concentration C_2, shown in figure 116, has the same value at all points in the downstream sampling cross section. When the sudden-injection method is used, complete

mixing is considered to have occurred when the area under the concentration-time curve, shown in figure 117, has the same value at all points in the downstream sampling section.

For a reach of channel of given geometry and stream discharge, the length of reach required for adequate mixing of the tracer is the same for either of the two methods of tracer injection. Several formulas are available for estimating the required mixing length for a particular set of conditions, but these formulas, while useful as guides, are too simplistic to give adequate consideration to the degree of mixing desired. Perfect mixing is seldom the optimum goal (see below) because perfect mixing usually requires an extremely long reach of channel, along with a correspondingly long period of injection in the constant-rate-injection (CRI) method and a correspondingly long period of sampling in the sudden-injection (SI) method.

Figures 116 and 117 are only rudimentary illustrations of the two methods. For either method to be successful an understanding is needed of the interrelations among mixing length and injection and sampling times. Figure 118 attempts to illustrate those interrelations for both types of injection. It is important to realize that unless adequate mixing is known to exist at a given sampling site, the tracer cloud in the SI method must be sampled for its entire time of passage at several locations laterally in the channel, such as at A, B, and C in figure 118. Similarly, in the CRI method the plateau concentration must be sampled at several locations laterally in the channel. Experience indicates that regardless of method or stream size, at least three lateral sampling points should be used at each sampling site.

Figure 118 indicates that there is an optimum mixing length for a given stream reach and discharge. Use of too short a distance will result in an inaccurate accounting of the tracer mass passing the sampling site. Use of too great a distance will yield excellent results, but only if it is feasible to inject the tracer for a long enough period (CRI method) or to sample for a long enough period (SI method). An optimum mixing length is one that produces mixing adequate for an accurate discharge measurement but does not require an excessively long duration of injection or sampling.

As mentioned earlier, figure 118 shows that the tracer cloud resulting from a sudden injection must be sampled at the sampling site from the time of its first appearance there until the time (T_t) of its disappearance at all points in the sampling cross section. For the same mixing reach and discharge, if the CRI method is used, a plateau will first be reached at all points in the sampling cross section at time T_t after injection starts at the injection site. Thus, it is seen that for the CRI method the duration of injection must at least be equal to T_c and injection should continue long enough thereafter to

Concentration

Definition sketch of sample points

• A
• B
• C

$\int B = \int C = \int A$

$\int B \approx \int C \approx \int A$

$\int B$ $\int A$ $\int C$

CRI   SI

T_c T_t Time

I. Short Sampling Reach

1 Areas under curves differ considerably in the SI method, lateral mixing incomplete

2 Rapid buildup to concentration plateaus of different levels in the CRI method

3 Discharge results will usually be poor, even by the use of such expedients as velocity-integrated sampling or discharge-weighting of the concentration data.

II. Optimum Sampling Reach

1 Areas under the curves nearly equal in the SI method, lateral mixing nearly complete

2 Fast buildup to plateaus of nearly equal concentration in the CRI method, lateral mixing adequate

3 Reliable discharge measurement can be made by the CRI method using a moderate injection time that exceeds T_c

III. Excessively Long Sampling Reach

1 Areas under the curves are identical in the SI method, perfect mixing

2 Slow buildup to plateaus of equal concentration in the CRI method but only after a long period of injection

3 Minimum duration of constant injection is equal to total time, T_c, that slug dye cloud is present

4 Reliable discharge measurement can be made by CRI method if injection period is long enough to exceed T_c

5 Results by CRI method will be poor if injection time is too short or sampling is discontinued too soon. Samples taken at time S would give impression that mixing is poor, as well as suggesting loss of dye
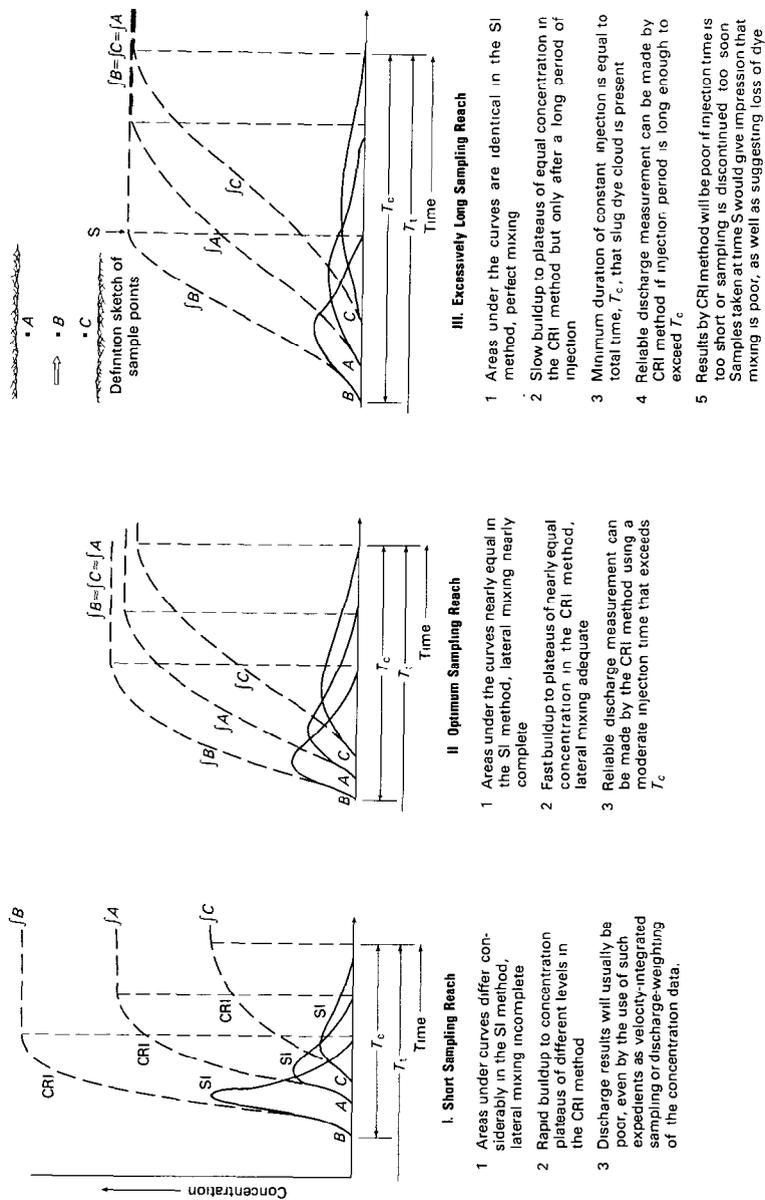
FIGURE 118.—Comparison of concentration-time curves obtained by SI and CRI methods, observed at three points in sampling cross section, for sampling reaches of three different lengths.

insure adequate sampling of the plateau. It should be noted that a stable condition of mixing is usually first attained in midchannel. Tracer lag along the streambanks will generally prolong the time required for complete lateral mixing.

The CRI method has become increasingly popular because reliable injection apparatus is available and the sampling process is relatively simple. If an injection period well in excess of T_c is used, the sampling can be done leisurely at several points in the sampling cross section. In the SI method the injection is simple, but the sampling process is much more demanding. More reliable results are usually obtained by the CRI method.

Figure 118 indicates that a satisfactory discharge measurement requires "nearly equal" areas under the concentration-time curves for the sampling points in the SI method and "nearly equal" concentration plateaus for the sampling points in the CRI method. A numerical criterion—P_m, the percentage of mixing—is often used as a quantitative index of the consistency of sampling results for the sampling cross section. A satisfactory discharge measurement can usually be obtained if the value of P_m is 95 percent or greater. The computation of P_m is discussed in the paragraphs that follow.

Percentage of mixing, P_m, is defined in this manual by the equation

$$P_m = 100 - \left\{ |X_A - X_m|Q_A + |X_B - X_m|Q_B + \right.$$

$$\left. |X_C - X_m|Q_C + \ldots \right\} \frac{50}{X_m Q}, \tag{26}$$

where

$X_A, X_B, X_C, \ldots$ are the areas under the concentration-time curves or, for constant-rate injection, the C_2 concentrations at the points A, B, C, ... across the sampling section;

X_m is the mean area under the concentration-time curves or, for constant-rate injection, the mean C_2 concentration for points A, B, C, ... across the sampling section;

$Q_A, Q_B, Q_C, \ldots$ are the subsection discharges applicable to the points, A, B, C, ...;

Q is the total stream discharge.

If the distribution of discharge is unknown at the sampling section, the cross-sectional subareas applicable to each point should be used in place of Q_A, Q_B, Q_C; total cross-sectional area should be used in place of Q. If both discharge and area distribution are unknown, as will often be the case, the appropriate widths may be used. Terms $|X_A - X_m|$, $|X_B - X_m|$, $|X_C - X_m|$, ... are absolute values.

The percentage of mixing can also be determined graphically, as shown in figure 119. Values of C_2 or $\int_0^\infty (C - C_b)dt$, depending on the

injection method used, are plotted for each sampling point against the distance from an initial point at water's edge. The mean value C_2 or $\int_0^x (C - C_b)dt$ is determined by dividing the area under the distribution curve for C_2 or $\int_0^x (C - C_b)dt$ by the total width of the section. The percentage of mixing, P_m, is then given as

$$P_m = \left(\frac{A}{A + B}\right) 100 \tag{27}$$

where

A is the area under the C_2 distribution and mean C_2 curves, or the area under the $\int_0^x (C - C_b)dt$ distribution and mean $\int_0^x (C - C_b)dt$ curves;

B is the area above the C_2 distribution and under the mean C_2 curves or the area above the $\int_0^x (C - C_b)dt$ distribution and under the mean $\int_0^x (C - C_b)dt$ curves.

The graphical technique illustrated in figure 119 can also be used if the distribution of discharge or area is known. The only change in the procedure that is required is a change in the abscissa of figure 119. In place of "distance from edge of water" either cumulative discharge or cumulative area from edge of water is substituted.

CALIBRATION OF MEASUREMENT REACH

Several theoretical studies have been made by the U.S. Geological Survey (for example, Yotsukura and Cobb, 1972) in which equations have been derived for determining the length of measurement reach required for satisfactory or complete mixing. However, the derived equations cannot be applied in the field without detailed information
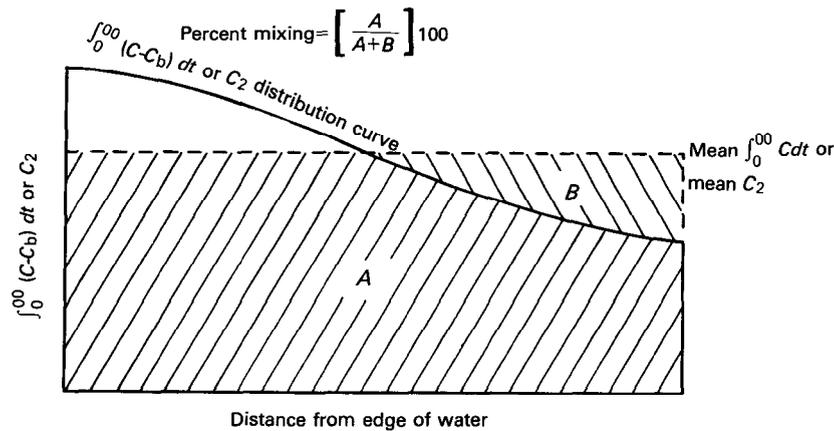

FIGURE 119.—Concentration-distribution curve illustrating the graphical method of determining the percentage of mixing.

on channel geometry and velocity distribution for the reach of channel. Consequently several gross formulas have been developed from the theoretical equations strictly for use as guides in determining a satisfactory length of measurement reach. Some of the simplified formulas follow:

a. Point injection at midchannel (English units)—

1.
$$L = 0.25 \frac{V}{(gDS)^{1/2}} \frac{W^2}{D},$$
(28)

where

L is distance downstream from the injection point,
V is mean velocity,
g is acceleration of gravity,
D is mean depth,
S is gradient of water surface or streambed, and
W is stream width.

2.
$$L = 0.6 \frac{R^{1/6}}{n g^{1/2}} \frac{W^2}{D},$$
(29)

where R is the hydraulic radius and n is the Manning roughness coefficient.

3.
$$L = 2V \frac{(W^2)}{D}.$$
(30)

b. Point injection at bankside (English units)—

$$L = 8V \frac{W^2}{D}.$$
(31)

Studies indicate that if more than one injection point is used, the mixing distance will vary inversely with the square of the number of injection points, provided that the injection points are located so that the dye will disperse equal distances both to the left and right of the injection points. This statement may seldom hold true for natural stream conditions, but it does indicate that the mixing length may be shortened considerably by using additional injection points.

In Europe the formula commonly used as a guide for determining the required length, L, between the injection site and sampling section is

$$L = 0.13C \frac{(0.7C + 6)}{g} \frac{b^2}{h} \text{(metric units)},$$
(32)

where

b is the average width of the wetted cross section,
h is the average depth of flow,
C is the Chezy coefficient for the reach $(15 < C < 50)$, and
g is acceleration of gravity.

Equation 32 is intended for use where injection is made at a single point in midstream.

Before making a discharge measurement by the tracer-dilution method, the proposed measurement reach should be calibrated to determine the length required for adequate mixing and the possibility of significant tracer loss. If repeated tracer-dilution measurements of the stream are to be made, it will be especially advantageous to make the calibration study comprehensive. One of the equations, 28 to 32, may be used as a guide in selecting a length of reach for the calibration tests; the quantity of tracer to be used for any given discharge is discussed later on pages 235–237. Instructions for calibration testing follow.

Select an injection site on the stream, and on the basis of one of the equations, 28 to 32, select several downstream sampling sites. Inject the tracer and then sample the water at three or more points in the cross section at each of the selected sampling sites. Take adequate samples at each point to define the plateau of the concentration-time curve if the constant-rate-injection method is used, or to define the entire concentration-time curve if the sudden-injection method is used. Analyze the samples and determine the percentage of mixing by use of equation 26. As mentioned earlier, for a satisfactory measurement of discharge the percentage of mixing should be at least 95. Mixing distances and losses may vary with discharge, and the reach may therefore have to be calibrated at more than one discharge. The quantity of tracer lost, if any, between successive sampling sites can be determined by a comparison of the values of C_2 (constant-rate-injection method) or of $\int_o^\infty (C - C_b)dt$ (sudden-injection method) obtained at each site. That determination provides a basis for the final selection of a sampling site from the several sites tested.

EFFECT OF INFLOW OR OUTFLOW BETWEEN INJECTION AND SAMPLING SITES

A satisfactory tracer-dilution measurement of discharge made in a reach that has no inflow or outflow between the injection and sampling sites will give the discharge occurring at all cross sections in the reach.

If tributary inflow enters the reach and if the tributary inflow is well mixed with the water in the main stream, the discharge measured will be that at the sampling site. If the tributary inflow is not well mixed, that fact may be evident from the difference in concentrations at the various sampling points in the sampling cross section; a low percentage of mixing would indicate that the particular sampling site could not be used for a satisfactory measurement of discharge.

If outflow occurs between the injection and sampling sites and if the tracer becomes completely mixed anywhere upstream from the outflow channel, the discharge measured at the sampling site will be that for the reach upstream from the outflow channel. If the tracer does not become completely mixed upstream from the outflow channel, the discharge measured at the sampling site will be indeterminate; the magnitude of the "measured" discharge will be dependent on the quantities of both tracer and water that are carried off in the outflow.

MEASUREMENT OF DISCHARGE BY FLUORESCENT DYE DILUTION

As mentioned earlier, the most popular type of tracer for the measurement of streamflow in the U.S.A. is fluorescent dye. The cost of the dye is relatively small because the quantity of dye needed for a discharge measurement is small; modern fluorometers are capable of accurately measuring dye concentrations of less than 1 μg/L (microgram per liter) and can detect concentrations as low as 0.02 μg/L.

FLUORESCENT DYES

Fluorescence occurs when a substance absorbs light at one wavelength and emits it at another, and usually longer, wavelength. The dyes commonly used as tracers are strongly fluorescent. They are organic dyes of the rhodamine family and are commercially available.

Dyes selected for use as tracers should (1) have a high detectability range, (2) have little effect on flora or fauna, (3) have a low sorption tendency, (4) have a low photochemical decay rate, (5) be soluble and disperse readily in water, (6) be chemically stable, (7) be inexpensive, (8) be easily separated from common background fluorescence, and (9) be easy to handle.

On the basis of recent studies in the U.S.A. on the adsorption potential and detectability of dyes, Rhodamine WT dye is recommended as the best dye available for use in dye-dilution measurements of discharge. Formerly used at times, but no longer recommended are Rhodamine B, BA, and Fluorescein.

FLUOROMETER

The fluorometer is an instrument that gives a measure of the strength of the light emitted by a fluorescent substance. Figure 120 is a schematic diagram of a fluorometer. The flurometer briefly described in this manual is the Turner model 111 fluorometer, and it is discussed because it is the instrument that is in general use by the U.S. Geological Survey. However, there are many satisfactory fluorometers that are commercially available, and for detailed in-

structions concerning any particular fluorometer it is necessary that the hydrographer consult the service manual prepared by the manufacturer of that instrument. The fluorometry techniques described in this manual are oriented toward use of the Turner fluorometer, but those techniques are applicable to most types of fluorometer. (Note.—The use of brand names in this manual is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.)

DESCRIPTION OF FLUOROMETER

The principle of the operation of the Turner model 111 fluorometer is described in the operating manual (1963, p. 12) as follows:

This fluorometer is basically an optical bridge which is analogous to the accurate Wheatstone Bridge used in measuring electrical resistance. The optical bridge measures the difference between light emitted by the sample and that from a calibrated rear light path. A single photomultiplier surrounded by a mechanical light interrupter sees light alternately from the sample and the rear light path. Photomultiplier output is alternating current, permitting a drift-free A–C amplifier to be used for the first electronic stages. The second stage is a phase-sensitive detector whose output is either positive or negative, depending on whether there is an excess of light in the forward (sample) or rear light path, respectively. Output of the phase detector drives a servo amplifier which is in turn connected to a servo motor. The servo motor drives the light cam (and the "fluorescence" dial) until equal amounts of light reach the photomultiplier from the sample and from the rear light path. The quantity of light required in the rear path to balance that from the sample is indicated by the "fluorescence" dial. Each of this dial's 100 divisions add equal increments of light to the rear path by means of a light cam.
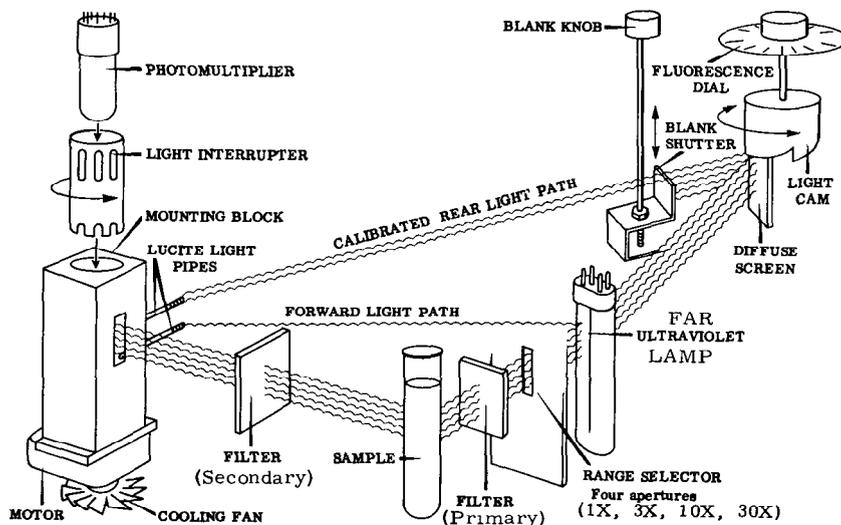

FIGURE 120.—Schematic diagram of the fluorometer (from G. K. Turner Associates, 1963, p.13).

Lamps.—At least three different lamps can be used as a light source for the fluorometer when the fluorescence of rhodamine dyes is tested. They are the general purpose ultraviolet lamp, the far ultraviolet lamp, and the green T–5 lamp. Although all three lamps work well, the far ultraviolet and green T–5 lamps are recommended as a light source because their outputs are compatible with the fluorescent properties of the dyes. Sensitivity of the fluorometer is increased approximately twofold to tenfold when the far ultraviolet and green T–5 lamps, respectively, are substituted for the general purpose ultraviolet lamp.

Filters.—The sensitivity of the fluorometer is directly related to the filter system employed. Light having undesirable wavelengths may be screened out by placing filters at two points in the fluorometer: (1) between the source light and the water sample and (2) between the water sample and the photomultiplier.

The filter (primary) recommended for use with rhodamine dyes for the absorbed light has a peak color specification of 546 mμ (millimicrons); that is, the greatest amount of light passed through the filter is at a wavelength of 546 mμ. Light at other wavelengths is subdued or eliminated. The recommended filter (secondary) for the emitted light has a peak color specification of 590 mμ. The peak color specifications for these filters are near the peak excitation and emittance wavelengths of the rhodamine dyes and will eliminate most natural background fluorescence. The filters may be used regardless of the type of lamp that is installed.

Doors.—Three main types of doors available for use with the fluorometer are the standard-cuvette (test tube) door, the temperature-stabilizing door, and flow-through door. All three doors are easily interchanged.

The standard-cuvette door is the easiest to use in the field for intermittent sampling and should be used with the green T–5 lamp. If the far ultraviolet lamp is used, a high-sensitivity kit should be installed on this door because it will increase the overall sensitivity of the fluorometer about tenfold. It is important to note that excessive sensitivity will be obtained if the high-sensitivity kit and green T–5 lamp are used together.

The temperature-stabilizing door is recommended for the final testing of samples. This door is similar to the standard-cuvette door with the high sensitivity kit but has, in addition, a water-cooled, copper block that surrounds the cuvette. Cooling water may be pumped or tap water of constant, or near-constant, temperature may be run through the door to stablize the sample temperature. Only round 12×75-mm cuvettes can be used with this door.

The flow through door permits continuous sampling which can be

recorded. A pump is used to circulate water from the stream through the cuvette in the door. The results may be recorded on any recorder with a 0 to 1 milliamp or 0 to 10 millivolt readout. The intake hose used with the flow-through door should be made of plastic or other nonabsorptive material. Different fittings and cuvette sizes are available for this door. The sensitivity of the flow-through door is about the same as that of the standard-cuvette door with the high sensitivity kit. That is so because of the larger cuvette used in the flow-through door.

Normally dye concentrations are not determined in the field because it is difficult to attain sufficient accuracy under such conditions. The flow-through door arrangement may be used for preliminary calibration of a reach, however. As a rule, bottle samples are collected and transferred to the laboratory for accurate fluorometric analysis.

EFFECT OF TEMPERATURE ON FLUOROMETRY

Accurate dilution discharge measurements require accurate fluorometry, and accurate fluorometry can only be attained in the laboratory where operating conditions are favorable. Temperature has a significant effect upon the fluorescence intensity of dyes. Fluorescence decreases with increasing temperature. This characteristic of the dyes has been investigated by several researchers, among them Feuerstein and Selleck (1963). For best results, all samples, including background and standard solutions, should be placed in a laboratory temperature bath and kept at constant temperature prior to fluorometric analysis. If the same temperature is used for all samples, no temperature corrections will be needed. If temperatures cannot be held constant, temperature corrections, as given in table 13 for Rhodamine WT dye, should be applied to dial readings or to concentrations.

Dunn and Vaupel (1965) point out the need for corrections to fluorometer dial readings as a result of changing compartment temperatures. However, tests by the U.S. Geological Survey showed that these corrections were needed only during the warmup period. A 1½-to 2-hr warmup will usually eliminate the need for this type of correction, although minor changes may still be observed thereafter. The warmup characteristics of each fluorometer should be determined. If possible, the fluorometer should not be operated where large temperature changes can occur rapidly.

CALIBRATION CHARACTERISTICS OF THE FLUOROMETER

Most fluorometers have a linear calibration ratio, meaning that dye concentration is directly proportional to the dial reading on the fluorometer and is related by the equation

TABLE 13.—*Temperature-correction coefficients for Rhodamine WT dye*

Temperature difference $(T_s - T)$[1]		Temperature-correction coefficient
F°	C°	
−20	−11.1	1.36
−15	−8.3	1.25
−10	−5.6	1.16
−8	−4.4	1.13
−6	−3.3	1.09
−5	−2.8	1.08
−4	−2.2	1.06
−3	−1.7	1.05
−2	−1.1	1.03
−1	−.6	1.02
0	0	1.00
+1	+.6	.99
2	1.1	.97
3	1.7	.96
4	2.2	.94
5	2.8	.93
6	3.3	.91
8	4.4	.89
10	5.6	.86
15	8.3	.80
20	11.1	.74

[1] T_s is the standard cuvette-sample temperature and T is the cuvette-sample temperature at the time the sample was tested in the fluorometer.

$$C = aD,　\quad (33)$$

where

   C is the dye concentration of the sample tested,

   a is a coefficient, and

   D is the fluorometer dial reading for the sample tested.

Solutions of known concentration are tested with the fluorometer, and the relation between concentration and dial reading is determined from equation 33.

Some fluorometers, however, do not have linear calibration ratios, and it is therefore necessary to determine the nature of the relation between concentration and dial reading by testing with standard solutions over a wide range of concentrations. A plot of concentration versus fluorometer-dial reading will give the shape of the calibration relation for the particular fluorometer. Experience to date indicates that nonlinear response occurs more frequently and to a greater degree at the low end of the curve; special effort should be made, therefore, to define that part of the curve.

If a fluorometer is found to have a nonlinear calibration relation, the instrument should be returned to the manufacturer for replace-

ment of parts or adjustment. Before an instrument is returned, one should be certain that the relation is truly nonlinear and not the result of an error in calibration. Inadequate instrument warmup is frequently the cause of a nonlinear calibration. If the instrument has to be used and the calibration is nonlinear, the derived nonlinear calibration curve should be used.

It is recommended that, if possible, dial readings of less than 10 be avoided, because the normal instrument error inherent in fluorometer operation can result in relatively large percentage errors for low dial readings. Low dial readings can be avoided by use of the proper fluorometer aperture. For example, the Turner fluorometer has four apertures, each designed to allow the passage of a different amount of light (fig. 120). The amount of light passed at each scale is approximately proportional to scale number; that is, the 30× scale will pass about 30 times as much light as the 1× scale. The relation between scales, for any fluorometer used, should be determined by testing each of several samples of different dye concentrations on more than one scale. A plot of dial readings for one scale against corresponding dial readings on another scale will give the desired relation. It should be mentioned here that low dial readings are unavoidable when testing the background (natural) fluorescence of river water. (See p. 231.)

PREPARATION OF STANDARD DYE SOLUTIONS FOR FLUOROMETER CALIBRATION

In calibrating the fluorometer it is necessary to first prepare samples of dye solution of known relative concentration, then test the samples in the fluorometer, and finally relate the readings on the fluorometer dial to the known relative concentrations. This matter of relative concentrations should be explained at this point. The accurate determination of stream discharge depends on the measurement of concentrations relative to each other; the absolute values of the concentrations are of no importance as long as the values of the concentrations are all determined in the same manner and all bear the same ratio to the absolute or true concentrations. Where the term "concentration" is used in this manual, it refers to "relative concentration"; the two terms are used here interchangeably. The calibration characteristics of the fluorometer were discussed in the preceding section of this manual. This section explains the preparation of standard dye solutions of various concentrations for use in the calibration process.

Standard dye solutions are prepared by diluting, with known amounts of water, the dye solution furnished by the manufacturer of the dye. The relative concentration of the furnished solution is the value given by the manufacturer. For example, if the manufacturer's

20-percent dye solution is used, its relative concentration is 200,000,000 $\mu g/l$. If the relative concentration of that solution differs from the true or absolute concentration by some small percentage, all diluted samples that are prepared from that batch of dye solution will have relative concentrations that differ from their absolute values by that same small percentage. Chlorinated tapwater should not be used in the dilution, because the chlorine present in the water quenches the fluorescence of rhodamine dyes.

The equipment and materials needed to make the dilutions are listed below. Where glass is specified for the equipment, other nonabsorptive materials may also be used.

1. Volumetric flasks (glass) of 100, 250, 500, 1,000, and 2,000 mL capacity.
2. Volumetric pipettes (glass) in an assortment of sizes.
3. Beakers (glass), or 1-gal (3.75 mL) glass jars.
4. Wash bottles (polyethylene).
5. Sample bottles (glass).
6. Masking tape and pen.
7. Distilled water. River or chlorinated tap water should not be used; however, tap water exposed to the air for 24 hr will lose its chlorine.

The dilution process is performed in steps, as illustrated in the example shown below. The relative concentration at each step is computed from the equation

$$C_n = \frac{C_i V_i}{V_a + V_i} , \tag{34}$$

where
      C_n is the new concentration,
      C_i is the initial concentration,
      V_i is the volume of initial concentration, and
      V_a is the added volume of water.

A flow chart similar to that shown in the example below is recommended when making the dilute solutions.

Example.—The original dye solution, as obtained from the manufacturer, is a 20-percent solution of Rhodamine WT. In making the solutions of known relative concentration, the process will be checked by duplicating the procedure for each of two samples. In other words, two samples of equal size of the original solution, are diluted in precisely the same manner. The resulting two dilute solutions are each diluted further in the same manner, and so on. As a result we will have two independent sets of standard solutions for use in calibrating the fluorometer.

To get back to the dilution process, 20 mL of the original 20-percent

solution is diluted to 2,000 mL with pure water. The concentration of the resulting solution is computed by use of equation 34. The process is repeated twice, each time using the solution last obtained, as indicated in the following flow chart:

$$C_n = \frac{20 \text{ mL of } (200 \times 10^6) \text{ } \mu g/L \text{ dye solution}}{2,000 \text{ mL total solution}} = \frac{1}{100} (200 \times 10^6) = 2 \times 10^6 \mu g/L$$

$$\downarrow$$

$$\frac{20 \text{ mL of } (2 \times 10^6) \text{ } \mu g/L \text{ solution}}{2,000 \text{ mL total solution}} = \frac{1}{100} (2 \times 10^6) = 20,000 \text{ } \mu g/L$$

$$\downarrow$$

$$\frac{20 \text{ mL of } 20,000 \text{ } \mu g/L \text{ solution}}{2,000 \text{ mL total solution}} = \frac{1}{100} (20,000) = 200 \text{ } \mu g/L$$

The solution obtained, with concentration equal to 200 $\mu g/L$, is referred to in this manual as a working standard solution because any lesser concentration that may be desired can be prepared from it by one additional serial dilution. For example, a dilution ratio of 1/200 will provide a solution with a concentration as low as 1 $\mu g/L$. No dilution ratios of less than 1/200 should ever be used. The working standard solution should be stored for future use. Experience has indicated that standard solutions of 200 or more $\mu g/L$ when properly stored in hard glass dark bottles out of direct light will keep for periods of at least 6 months. There is evidence, though not conclusive, to indicate that very weak standard solutions tend to deteriorate or to adhere slightly to the bottles in which they are stored.

The stored working standard solution may be used for periodically checking the fluorometer calibration to determine if changes in the calibration have occurred, and enough of the standard solution should be retained for future use if the same dye lot from the manufacturer is to be used for discharge measurements. New sets of standard solutions should be prepared after 6 months to avoid the risk of decay of fluorescence in the stored standard solutions. In addition, new sets should also be prepared when new batches of dye are to be used for discharge measurements because the dyes received from the manufacturer may vary from batch to batch.

If the fluorometer calibration is known to be linear, from previous tests using standard solutions made with distilled or unchlorinated tap water, only a limited few concentrations need be prepared and tested for the discharge-measurement calibration of the fluorometer. The concentrations prepared should approximate the plateau concentration expected in stream samples that will be taken during the discharge measurement.

OPERATION OF THE FLUOROMETER

The U.S. Geological Survey uses the Turner model 111 fluorometer. The fluorometer is operated in accordance with the following instructions.

Allow a warmup period of 1½ to 2 hr before any tests are made. This warmup period will permit the instrument temperature to stabilize. If possible, have all samples, including standard and background solutions, at the same temperature. Establish the zero point on the fluorometer by inserting the dummy cuvette in the cuvette holder, after which the dial is adjusted to zero with the blank knob. To test a standard solution, fill the cuvette with that solution, but before putting the cuvette into the fluorometer, wipe the outside of the cuvette dry with laboratory-grade paper tissue. That prevents distortion from droplets on the glass or contamination of the fluorometer, and possible erroneous readings when testing other samples. After wiping, insert the cuvette in the holder and close the fluorometer door. After the fluorometer dial reaches a stable reading, record the reading. As mentioned earlier, test each pair of several standard solutions of different concentrations on more than one fluorometer scale for calibration of the instrument. An alternate, and perhaps more desirable, course of action is to first test all field samples on one fluorometer scale. If that scale accommodates all field samples, calibrate only that one scale in the range found pertinent.

If a water sample from a discharge measurement is being tested, first rinse the cuvette with tap water and then, after shaking out excess droplets, rinse the cuvette with the sample being tested. The cuvette may then be filled. It is important that any sediment in the sample be allowed to settle and that any oxygen bubbles be removed. (Cold samples taken from streams with a high dissolved-oxygen content will often have bubbles form on the sides of the cuvette.) If the samples have been allowed to sit in a temperature bath overnight, the sediment will have settled and the oxygen bubbles will usually have been released. If the oxygen bubbles have not been eliminated by allowing the samples to warm up before testing, they can usually be removed by tapping the cuvette before testing.

The blank and background samples should be tested at intervals during the fluorometer operation as a check against possible instrument malfunction or change in instrument calibration. Background samples are water samples used to define the natural fluorescence of the stream. Natural fluorescence should be determined for any dye-dilution measurement. Always correct water-sample concentrations for this background effect.

The frequency of testing known relative concentrations will depend primarily on the number of stream samples. Known relative concentrations are ordinarily tested before and after the stream samples, but more frequent testing is desirable where numerous samples are involved

Sample bottles made of polyethylene, glass, or similar nonabsorptive material can be used repeatedly for sampling. After each measurement all sample bottles should be thoroughly rinsed and drained. The bottles, if stored, should be well separated from any dye-contaminated equipment.

Whatever the equipment used, care should be taken at every step in the discharge determination to prevent contamination of stream samples, standard solutions, and the equipment used for measurement and analysis. A sample can be contaminated, from the standpoint of concentration, by the addition of pure water as well as by the addition of minute quantities of dye from the analyst's hands or other source.

DYE-INJECTION APPARATUS

Apparatus for the injection of dye solution at a constant rate is of three types: mariotte vessel, floating siphon, and pressure tank.

MARIOTTE VESSEL

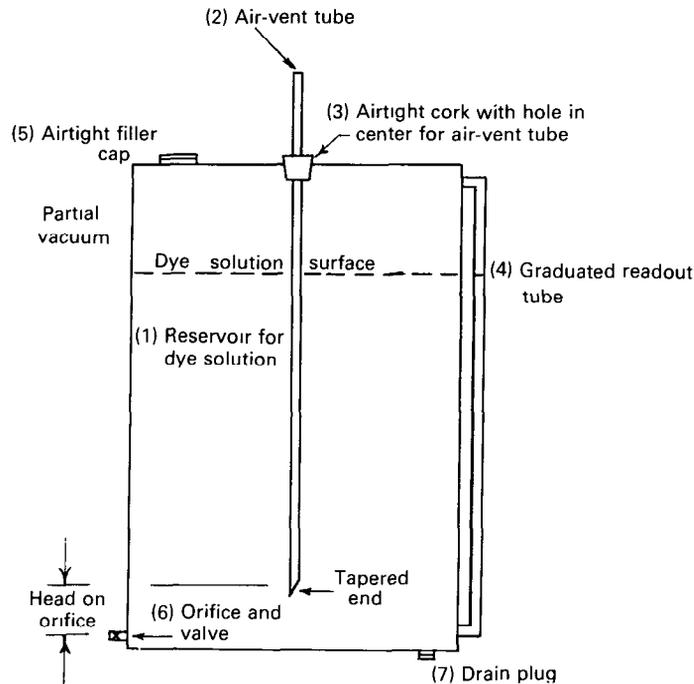The features of the mariotte vessel, shown in figure 121 are (1) an

FIGURE 121.—Mariotte vessel (constant-head device).

airtight tank that holds the dye solution, (2) an air-vent pipe inserted into the tank through (3) a rubber stopper that will form an airtight seal both on the tank and the vent pipe, (4) a plastic or glass readout tube for determining the level of the liquid in the tank, (5) a filling plug that must be airtight, (6) a discharge orifice and valve, and (7) a flushing orifice and valve.

The lower tip of the air-vent pipe should be tapered to prevent the tip from being placed directly on the bottom of the tank and thereby obstructing the air flow. Discharge at more than one point may be obtained by installing the desired number of orifices in the tank.

The operation of the vessel is as follows. When the discharge valve (6) is opened, the level of the dye solution in the tank (1) will drop, creating a partial vacuum above the liquid (the top of the tank must be airtight). As the level of the liquid continues to drop, the vacuum increases causing the level of liquid in the air vent (2), which is open to the atmosphere, to drop until it reaches the bottom of the vent. As the solution continues to be discharged, air will enter the tank through the vent causing an equilibrium between the partial vacuum formed above the liquid surface and the weight of the liquid above the bottom of the air vent. When this equilibrium has been reached, a constant discharge will have been attained and will continue until the liquid in the tank drops to the bottom of the air vent. The acting head is the different in elevation between the bottom of the air vent and the orifice.

FLOATING SIPHON

Constant injection of a dye solution is possible through the use of the floating siphon device shown in figure 122. The device is designed to discharge at a constant rate by maintaining a fixed head on the orifice. The features of the floating siphon are (1) a tank that holds the solution, (2) a float with siphon tube and guide assembly, and (3) priming valves that can be used in activating the siphon. The discharge tube with orifice is permanently attached to the float in the position shown. Note that regardless of the position of the float within the reservoir, the operating head on the orifice remains the same. Stable, uniform movement of the float and siphon assembly is possible through the use of guides and a balance counterweight. When the siphon is effective, the float and assembly will drop with the water surface but at the same time maintain a constant discharge because of the steady head operating on the orifice.

The mariotte vessel and the floating siphon can both be equipped with readout gages that are used to calibrate the reservoirs volumetrically. These gages can be read at selected time intervals during the injection period to determine the constant-flow rate. The flow rate can

also be determined by volumetrically measuring the discharge from the orifice for a given period of time.

PRESSURE TANK

A constant-rate injection of dye solution may be obtained by use of a pressure tank in combination with a flow regulator (fig. 123). The flow regulator maintains a constant pressure differential across a valve in the regulator, thus giving a constant flow rate at any setting of the regulator. A pressure differential of a few pounds per square inch must be maintained for the flow regulator to function properly.

The solution to be injected is poured into the pressure tank, and the tank is sealed. Air is then pumped into the tank, providing the necessary pressure for the regulator. The solution is forced from the tank, by the pressure, through the regulator and to the injection lines.

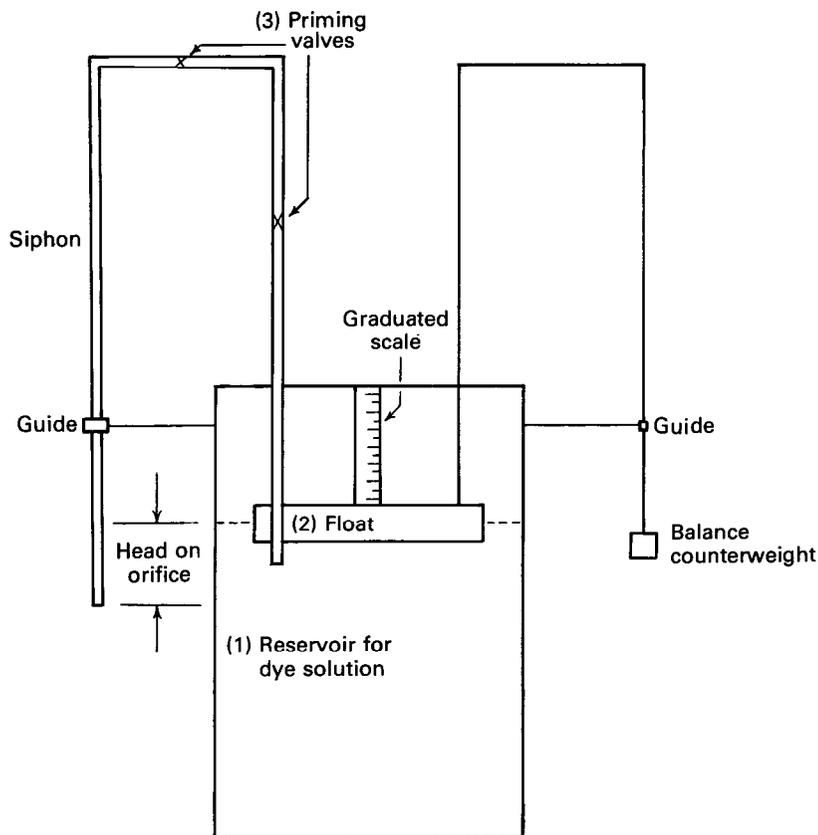Most commercially available flow regulators have a purge meter

FIGURE 122.—Floating siphon (constant-head device).

attached to them. These meters may be used to obtain the approximate desired flow rate. The flow rate used in the computations should be determined from a volumetric measurement of the tank discharge.

Pressure tank and flow regulator systems are commercially available. These systems are as light as 8 lb (3.6 kg), when empty, for an operating-pressure tank capacity of about 2 gal (7.5 L). Flow regulators may be obtained for flow rates between 0.012 and 4 gal/hr or more. Flow rates once established will be maintained within ±2 percent.

DETERMINATION OF QUANTITIES OF FLUORESCENT DYE FOR MEASURING DISCHARGE

QUANTITY OF DYE NEEDED FOR MEASUREMENT BY THE CONSTANT-RATE-INJECTION METHOD

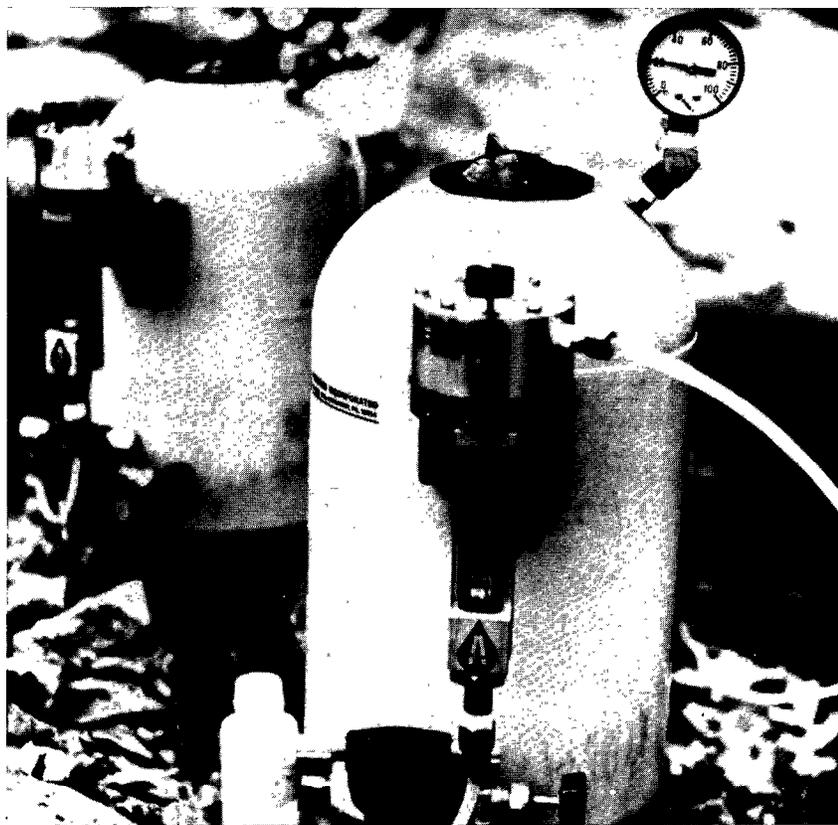The volume of dye required to make a discharge measurement

FIGURE 123.—Pressurized constant-rate injection tanks for injection of dye into streams.

using the constant-rate-injection method will depend on the discharge of the stream and on the total injection time. That volume can be estimated using the equation

$$V_d = 1.02 \times 10^8 \left(\frac{C_2}{C_d}\right) Q \, t_t,$$ (35)

where

V_d is the volume, in milliliters, of dye solution to be added to the water in the injection tank,

C_d is the concentration, in micrograms per liter, of the dye solution added to the water in the injection tank. If a 20 percent dye solution is added, the concentration of C_d is considered to be 200,000,000 μg/L. (See p. 228–229 for a discussion of relative and absolute concentration values.)

C_2 is the plateau concentration, in micrograms per liter, desired at the sampling site,

Q is the estimated stream discharge, in cubic feet per second, and

t_t is the total injection time, in hours.

The value of 1.02×10^8 is a combination of conversion factors. A concentration value for C_2 of 5 μg/L is recommended for Rhodamine WT.

The volume of tracer solution injected, which consists of the volume dye solution (V_d) plus added water, and the rate of injection are mutually dependent. Their limiting values are based on the size and characteristics of the dye-injection apparatus that is used. The capacity or volume of the apparatus divided by t_t gives the upper limiting value of the rate of injection, q. Any paired values of q and volume (qt_t) that are within the capability of the apparatus are satisfactory. However, it is recommended that no value of q less than 2×10^{-5} ft³/s (0.57 mL/s) be used, because low injection rates are difficult to measure accurately. It is further recommended that V_d be diluted sufficiently to give the injection solution a concentration of no more than 25×10^6 μg/L, because more highly concentrated solutions tend to clog the injection apparatus.

QUANTITY OF DYE NEEDED FOR MEASUREMENT BY THE SUDDEN-INJECTION METHOD

If discharge is to be measured by the sudden-injection method, it is recommended that common salt be used as the tracer, rather than dye. (See p. 250–256.) However, as a matter of general interest, an equation is given here for computing the quantity of dye required for a discharge measurement of that type.

The volume of dye required to make a discharge measurement by the sudden-injection method can be estimated using the following

empirical equation:

$$V_d' = 3 \times 10^7 \left(\frac{C_p}{C_d'}\right) Q t_p, \qquad (36)$$

where

V_d' is the volume, in milliliters, of dye solution of concentration C_d' to be introduced into the stream,

C_p is the peak dye concentration, in micrograms per liter desired at the sampling site,

Q is the estimated stream discharge, in cubic feet per second, and

t_p is the estimated time, in hours, for the dye peak to travel from the injection site to the sampling site.

The value of 3×10^7 is a combination of empirical equation constants and conversion factors. A concentration value for C_p of 10 μg/L is recommended for Rhodamine WT.

PROCEDURES FOR MEASURING DISCHARGE BY THE DYE-DILUTION METHOD

The only dye-dilution method that will be discussed here is the constant-rate-injection method. The sudden-injection method is not considered here because not only is it usually a less accurate method, but it is extremely laborious when dye is used and it can be applied with less effort by using common salt as a tracer. As mentioned earlier, the sudden-injection method requires that the entire concentration-time curve be defined, and for that purpose it is desirable to sample the stream concentration at intervals of less than a minute during periods of rapidly changing concentration. If the dye-dilution technique is used, it means that within a minute or so, grab samples must be obtained at all three sampling points in the sampling cross section. Furthermore, because it is recommended that at least 20 samples be taken at each sampling point to define the concentration-time curve, it means that a minimum of 60 stream samples must be analyzed by fluorometer, along with calibration and background samples. In short, it is not practical to use dye as a tracer in the sudden-injection method. Although recording fluorometers with flow-through doors are available, they seldom provide the precision required for a discharge measurement. When salt is used as the tracer, conductivity readings can be obtained at a point in a matter of a few seconds, by using a temperature-compensated probe and portable meter. (See p. 252–255.)

FIELD PROCEDURES

The following field procedures are recommended for determining

stream discharge by the dye-dilution method:

1. Select and calibrate the measurement reach (p. 220–222).

2. Select exact locations for the injection and sampling sites. Data obtained from the calibration tests are used in making the site selections, and consideration should be given to accessibility and convenience for conducting field operations. Bridges are often excellent for the purpose. The injection site for either single- or multiple-point injection should be one where the injection system can be readily observed and, if necessary, serviced. Select sampling sites where sampling is possible anywhere in the cross section. Locate a minimum of three sampling points in the cross section so that the section can be checked for lateral mixing.

The best location for a single-point injection is normally at the center of the cross section. A center injection generally produces the minimum possible mixing length if the dye is to be introduced at only one point. Space the injection points for a multiple-point injection so that each dye injection diffuses equal lateral distances.

3. Prepare the sample bottles. Show the following information on each bottle:

a. The sampling site (may be abbreviated).

b. Location of the sampling point in the cross section.

c. Sample number (if desired).

d. Sample time (use military time, that is, 24-hr clock system).

e. Date.

Make these notes with a ballpoint pen using masking tape for labels on the bottles. Note the time (sample time) when the sample is obtained.

4. Determine the amount of dye needed for injection from equation 35. The total injection time used in equation 35 includes the time required for the concentration plateau to have been reached at the sampling section and sufficient time to permit at least 15 min of sampling of the plateau.

5. Prepare the dye solution and injection equipment. Make certain that the solution is thoroughly mixed. Exercise caution in transporting the dye and do not carry excessive quantities of it on field trips. Dye in solution can be easily removed from containers by the use of pipettes. Adverse weather conditions, particularly high wind or rain, create serious problems in handling the dyes. Prepackaging of specific quantities of dye will facilitate operations in the field. River water taken at the site may be used in preparing the injection solution, but do not obtain river water immediately below a sewage outfall or at sites where chlorine is injected into the river system.

6. Obtain several background samples upstream from the injec-

tion site. Do this before handling the dye.

7. Obtain three samples of injection solution. These samples, each of about 2 oz (60 mL), may be taken immediately before or after the solution is injected into the stream.

8. Inject the diluted dye solution. Determine the actual rate of dye injection by timed observations of volume depletion in the injection tank. If a mariotte vessel is used for injection, check the fittings for air leakage before and during injection. Discharge will become constant within a few seconds after the orifice is opened if the tank is airtight. The sound of air bubbling from the air vent through the solution can be heard when the vessel is operating properly.

9. Do not inject the highly concentrated dye solution near the streambed; otherwise, the bed may be stained by the dye and excessive dye loss will result.

10. The time of arrival of the concentration plateau can be estimated from data obtained when the reach was calibrated. It is usually desirable to start sampling a little before the estimated time of arrival of the concentration plateau. Define the plateau with at least five samples at each of the three sampling points in the sampling cross section. If a fluorometer is available, the arrival and passage of the dye can be determined by using the flow-through door and recorder accessory, or by periodically testing individual samples using the standard door. Do not mistake a possible temporary leveling of the concentration-time curve as being the actual plateau. A short time should elapse between the taking of samples to minimize the effect of nonrepresentative surges of high or low concentration.

11. In obtaining stream samples at the sampling site, take samples just below the water surface and far enough from the banks to avoid areas of slack water. If possible, the sampling site should be at a contracted section of the stream or at one where velocities are fairly uniform across the entire section. The following equipment is needed for grab sampling:

a. Sampling device and line (for sampling from a structure).

b. Boots or waders (for sampling by wading).

c. Boat, motor, paddle, gasoline can, life jacket (for sampling by boat).

d. Bottles (glass or plastic, 4-oz, wide-mouth bottles are recommended).

e. Masking tape (for labeling samples).

f. Ballpoint pens (for making identifying notations on sample labels).

g. Watch.

12. Contamination of stream samples is always a possibility. When handling any dye, keep hands and clothes clean as a safeguard

against accidental contamination. Rinse bottles at least three times in stream water immediately before sampling. This precaution is necessary because bottles are used repeatedly and some may have had high concentrations of dye in them previously. Dye from stained hands can contaminate samples, resulting in erroneous concentration determinations; therefore, keep hands away from the uncapped mouths of bottles and out of the sample water.

13. Clean the injection and mixing equipment.

14. Store and carry sample bottles in an upright position to prevent leakage and to allow sediment to settle.

ANALYSIS AND COMPUTATIONS

Fluorometer analysis should not begin until the standard concentration solutions have been prepared. Place all samples, including background samples and standard concentration solutions, in a constant-temperature bath. By keeping the samples in the bath overnight, any sediment present will have an opportunity to settle, and any oxygen bubbles present will usually be released. After fluorometer warmup, all samples may be analyzed. Use of a constant-temperature bath will eliminate the need for temperature corrections. However, if for any reason a temperature bath was not used, the first step in the analysis procedure that follows is to make temperature corrections.

1. Correct each fluorometer reading for the effect of temperature by the following method. A standard cuvette-sample temperature is selected. This may be the mean, median, mode, or any other convenient cuvette-sample temperature recorded while testing the samples. The difference between each recorded cuvette-sample temperature and the standard temperature is used to select the appropriate coefficient from table 13. Temperature-correction coefficients are usually prorated with respect to time between temperature observations. Multiply the fluorometer dial-readings by the coefficients to obtain adjusted dial readings.

2. Next correct the dial readings, or temperature-adjusted dial readings if such adjustment had been necessary, for the effect of background fluorescence, as determined from the background samples. This background correction is applied to each water sample and to each sample of standard concentration.

Usually all fluorometer testing will be done using a single fluorometer aperture. If more than one aperature is used, obtain a background reading for each aperature and use a mean background value for correcting the dial readings. Do not use a mean background value if a definite change in background has been noted. A change in background fluorescence may result from a variety of causes such as

unstable fluorometer operation, increased suspended-sediment load, and the presence of sewage or industrial wastes. Enter the background readings in the notes. Subtract the background readings from the adjusted dial readings from step 1 above to obtain the final corrected dial readings.

3. Use the final corrected dial readings for the standard solution of known relative concentration to compute the fluorometer coefficient, a, in equation 33 (p. 227). When this standard solution is tested several times during a period of sample testing, the value of the coefficient is normally prorated, with respect to time, between testings.

4. Determine the relative concentrations of samples by multiplying the corrected dial readings, from step 2 above, by the coefficient, a.

5. Compute the stream discharge by use of equation 24. Because the background concentrations have already been subtracted from the stream sample concentrations, equation 24 becomes

$$Q = \left[\frac{C_1}{C_2} - 1 \right] q,$$

which can be simplified, without significant loss of precision, to

$$Q = \left(\frac{C_1}{C_2} \right) q. \tag{37}$$

An average value of C_2 is used in the computations. If the individual C_2 values show little variation among them, use the arithmetic mean. If the variation is significant, obtain the mean value of C_2 by weighting the mean plateau concentrations for each sampling point by the percentage of discharge associated with the sampling point. If the discharge distribution is unknown, but the area distribution is known, obtain the mean value of C_2 by weighting the plateau concentrations for each sampling point by the percentage of area associated with each sampling point. If both the discharge and area distributions are unknown, as will usually be the case, compute the mean value of C_2 by using percentage of width as the weighting factor.

6. Determine the percentage of mixing by using equation 26, or by use of the graphical procedure described on page 219–220. Reliable results are generally obtained when the percentage of mixing is 95 or more. Reliable results are also possible for flow conditions where the percentage of mixing is less than 95 if the discharge distribution at the sampling section is uniform or known.

SAMPLE COMPUTATION—CONSTANT-RATE-INJECTION METHOD

A sample computation of the constant-rate-injection method is

presented here based on data obtained on March 25, 1965, at Little Seneca Creek near Boyds, Md., in the course of a detailed investigation of dye-dilution methods of measuring discharge. The average width of Little Seneca Creek at the time of the measurement was 30–35 ft (9–10 m). Depths averaged between 1 and 2 ft (0.3 and 0.6 m). The streambed was composed mostly of gravel, with some rock outcrops. Flow in the measuring reach passed through several bends.

Calibration of the measurement reach at about the stage to be measured had indicated that a measuring reach of 1,800 ft (550 m) was satisfactory for adequate mixing when the dye was injected at three points across the stream. The calibration further indicated that the time required for the concentration plateau to arrive at the sampling site was about 45 min. Three sampling points, designated A, B, and C, respectively, were to be used at the sampling site. Grab-samples were taken immediately before and during the passage of the concentration plateau.

1. The required volume of dye (V_d), to be supplied from a mariotte vessel, was computed from equation 35,

$$V_d = (1.02 \times 10^8) \frac{C_2}{C_d} Q t_i .$$

The approximate value of the plateau concentration (C_2) desired at the sampling site was 5 μg/L. The estimated value of stream discharge (Q) was 50 ft³/s. The total injection time (t_i) was estimated to be 80 min (1.33 hr)—45 min for traveltime and 35 min to insure a concentration plateau of adequate duration. The dye to be used was Rhodamine WT, 20-percent solution, and C_d was therefore equal to 2×10^8 μg/L. Consequently,

$$V_d = (1.02 \times 10^8) \left(\frac{5}{2 \times 10^8} \right) (50) (1.33) = 170 \text{ mL.}$$

2. The discharge rate of diluted dye solution (q) from the injection vessel that was selected was 1.50×10^{-4} ft³/s. The volume of solution needed in the injection tank was equal to $q t_i$, where t_i was 1.33 hr, or 4,800 s. That volume was therefore

$(1.50 \times 10^{-4}) (4800) = 0.72$ ft³, or approximately 20,000 mL.

The 170 mL of dye solution was mixed with sufficient stream water to give an injection solution of 20,000 mL.

3. The concentration of the solution in the injection tank (C_n) was computed from equation 34,

$$C_n = \frac{C_i V_i}{V_a + V_i}$$

$$= \frac{(200,000,000) \ (170)}{20,000}$$

$$= 1,700,000 \ \mu\text{g/L}.$$

4. Timed observations of the change in the level of the dye solution in the injection tank showed the actual rate of outflow to be 1.51×10^{-4} ft³/s.

The steps that follow were taken in the office to complete the measurement.

1. A working standard solution of concentration 200 μg/L had previously been prepared (p. 229–230). A dilution ratio of 1/40 was applied to that solution to obtain two standard sample solutions whose concentration was 5.00 μg/L.

Standard solutions of 5.00 μg/L were used for calibration of the fluorometer because that was the expected value of the plateau concentration of the stream. (The concentration of the standard solutions should approximate the concentrations of the stream samples that will be used to compute stream discharge.)

2. A form for keeping notes was prepared as shown in figure 124. Column 1 of figure 124 shows the time when the sample was obtained in the field, and column 2 shows the time when the sample was tested in the fluorometer.

3. The samples had not been placed in a constant-temperature bath, and consequently temperature corrections were necessary. The samples, including those for background testing (stream water untouched by dye) and for fluorometer calibration (5.00 μg/L), were tested in the fluorometer. Columns 3 and 4 of figure 124 show dial readings on the fluorometer aperture that was used. Column 5 shows two temperature readings. The upper reading is the temperature of the water being circulated through the fluorometer door. The lower reading is the temperature of the fluorometer compartment. Obtain that temperature from a thermometer that can be taped to the compartment side at the left of the secondary filter. Column 6 shows the temperature of the cuvette sample. That temperature is taken immediately after the fluorometer dial is read by removing part of the water from the cuvette, inserting the thermometer in the cuvette, and replacing the cuvette in the door. Allow the thermometer to stabilize before reading. Compute temperature-correction coefficients from the observed cuvette-sample temperatures.

4. A standard cuvette sample temperature of 82°F (27.8°C) was selected for use. Temperature coefficients from table 13, correspond-

ing to the differences between 82°F and the observed cuvette-sample temperatures in column 6 of figure 124, were then obtained and recorded in column 7.

Little Seneca Creek near Boyds, Maryland,   March 25, 1965

(1) Sample	(2) Fluor. test	(3) 30X	(4) 10X	(5) circ./Comp	(6) cu-vette	(7) Temp coef.	(8) Adj. dial reading	(9) Back-ground reading	(10) correct-ed dial reading	(11) Q=c/b	(12) Concen-tration (ppm)	(13) Remarks
					Sample Point A							
Blank	1459	0										
1a	1500	65.8				1.02	67.1	1.2	65.9	.0759	5.00	*
1b	1501	67.7		79.5/93.5	83	1.02	69.1	1.2	67.9	.0736	5.00	*
										.0748		Mean
1250	1503	1.2				1.02	1.2	1.2	—	—	—	**
1313	1505	64.4				1.02	65.7	1.2	64.5	.0748	4.82	
1320	05	72.0				1.02	73.4	1.2	72.2	.0748	5.40	
1327	06	74.5				1.02	76.0	1.2	74.8	.0748	5.60	***
1335	07	75.8				1.02	77.3	1.2	76.1	.0748	5.69	***
1343	08	75.2				1.02	76.7	1.2	75.5	.0748	5.65	***
1350	08	75.2				1.01	76.0	1.2	74.8	.0748	5.60	***
1356	1509	74.6				1.01	75.3	1.2	74.1	.0748	5.54	***
											5.62	Mean
					Sample Point B							
Blank	1523	0										
1251	24	.3				1.00	.3	1.2	—	—	—	**
1322	27	71.0		80.9/93.5	81.5	1.00	71.0	1.2	69.8	.0747	5.21	
1328	27	74.6				1.00	74.6	1.2	73.4	.0747	5.48	***
1336	29	75.8				1.00	75.8	1.2	74.6	.0747	5.57	***
1344	30	76.2				1.00	76.2	1.2	75.0	.0747	5.60	***
1351	30	75.1				1.00	75.1	1.2	73.9	.0747	5.52	***
1357	1531	72.8				1.00	72.8	1.2	71.6	.0747	5.35	***
											5.50	Mean
					Sample Point C							
Blank	1546	0										
1252	1546	1.2				1.00	1.2	1.2	—	—	—	**
1315	48	65.8		80.0/94.0	82	1.00	65.8	1.2	64.6	.0746	4.82	
1321	50	73.3				1.00	73.3	1.2	72.1	.0746	5.38	***
1329	51	72.9				1.00	72.9	1.2	71.7	.0746	5.35	***
1337	52	72.0				1.00	72.0	1.2	70.8	.0746	5.28	***
1345	52	72.9				1.00	72.9	1.2	71.7	.0746	5.35	***
1352	53	72.0				1.00	72.0	1.2	70.8	.0746	5.28	***
											5.33	Mean
1a	1608	67.7				1.00	67.7	1.2	66.5	.0752	5.00	*
1b	1609	68.9				1.00	68.9	1.2	67.7	.0738	5.00	*
										.0745		Mean

Turner III Fluorometer Filters (546 mμ, 590 mμ), Far ultraviolet lamp. Temperature-stabilized door. Standard cuvette-sample temperature, 82°F. Tested 3-29-65
* Standard solution of known relative concentration. ** Background sample.
*** Sample used to compute C_2.

FIGURE 124.—Sample analysis sheet used for computing discharge by the constant-rate-injection method of dye dilution.

5. The adjusted dial readings in column 8 were obtained by multiplying the values in either column 3 or column 4 by the temperature coefficients in column 7.

6. The average temperature-adjusted fluorometer reading for background fluorescence, obtained by testing the unaffected stream water, was recorded in column 9. Its value, 1.2 in this test, was then subtracted from all temperature-adjusted readings in column 8, and the corrected dial readings were recorded in column 10.

7. The fluorometer coefficient, a, in column 11, was obtained as the average of the ratios of the known concentration of the two background samples (5.00 μg/L) to their corrected dial readings. The background samples were tested at the beginning and end of the fluorometer analysis, and the fluorometer coefficients obtained were prorated with time for use in the analysis.

8. The concentrations of the samples listed in column 12 were obtained by multiplying the fluorometer coefficients in column 11 by the corrected dial readings in column 10.

9. The concentrations obtained for each sampling point are normally plotted against sampling time to determine the average concentration of the plateau C_2 at each of the three sampling points, A, B, and C. In this example, no plots were made; instead, C_2 for each sampling point was computed, in column 12 of figure 124, as the mean of the last five values obtained, it being evident that those values were plateau values.

10. Because the three sampling points, A, B, and C, were evenly spaced across the stream, each of the three values of C_2 from step 9 were given equal weight in computing the mean value of C_2 for the entire sampling section:

$$\text{mean } C_2 = \frac{5.62 + 5.50 + 5.33}{3} = 5.48 \ \mu\text{g/L}.$$

11. The discharge was computed from the simplified form of equation 24 that is shown as equation 37 on page 241.

$$Q = \frac{C_1}{C_2} q$$

$$= \left(\frac{170 \times 10^4}{5.48} \right) (1.51 \times 10^{-4}) = 46.8 \text{ ft}^3\text{/s}.$$

12. Mixing percentage (P_m) was computed, using appropriate widths in equation 26:

$$P_m = 100 - \frac{[|X_A - X_m| W_A + |X_B - X_m| W_B + |X_C - X_m| W_C] \times 50}{(W_{total})(X_m)}$$

Because the sampling points were evenly spaced, W_A, W_B, and W_C may each be replaced by 1, and W_{total} may be replaced by 3. Then

$$P_m = 100 - \frac{\left[\,|5.62-5.48| \,+\, |5.50-5.48| + |5.33-5.48|\,\right] \times 50}{3(5.48)}$$

$$= 100 - \frac{(0.31)\times 50}{16.44}$$

$$= 99 \text{ percent (satisfactory)}$$

In the original study of Little Seneca Creek, the discharge had been measured by current meter for a comparison with the discharge obtained by the dye-dilution method. The current-meter discharge was 47.3 ft³/s, whereas the dye-dilution discharge was 46.8 ft³/s. The two values differ by 1 percent.

SIMPLIFIED PROCEDURES FOR MAKING NUMEROUS DYE-DILUTION MEASUREMENTS OF DISCHARGE

The preceding description of the method of measuring discharge by the constant-rate-injection method was highly detailed to give complete understanding of the procedure. It should be apparent that there are many details to be considered in collecting and analyzing the samples. If only an occasional dye-dilution measurement is to be made, the procedures described above should be followed. If numerous dye-dilution measurements are to be made on a routine basis, "mass production" methods may be instituted to simplify and speed the procedure.

The first simplifying step is the laboratory production of two batches of solution, each of which represents a working standard concentration. Bulk production of the two concentrations will considerably reduce the amount of time that would otherwise be required later for serial dilutions and for calibrating the fluorometer. The standard concentration that is needed for fluorometer calibration is one that closely approximates the C_2 (plateau) concentrations that will be obtained in the discharge measurements. The value of C_2 will usually approximate 5 μg/L. Consequently one working standard solution of 200μg/L should be produced in adequate quantity from the stock of 20-percent Rhodamine WT dye. The concentration of 200 μg/L is high enough to permit storage of the solution for at least 6 months with little danger of deterioration and is still low enough to produce, with a single dilution, concentrations that approximate any C_2 values that may be obtained in a discharge measurement.

The other solution of working standard concentration that should be produced in bulk is one that can be used as the injection solution in a discharge measurement without further dilution. By way of background explanation we examine figure 125, the basis of which is equation 37. Figure 125 shows the relation among Q, q, and C_1 for a constant value of C_2. The constant value of C_2 that is used is 5 μg/L, which is the optimum value of the plateau concentration in the constant-rate-injection method. Concentration values of C_1 ranging from 0.05 percent (0.5×10^6 μg/L) to 2.5 percent (25×10^6 μg/L) are shown in the diagonal lines of figure 125. To produce a C_1 solution of, say 0.4 percent, 8 L of water is added to the parenthetical quantity of 137.2 mL of 20-percent Rhodamine WT dye. Examination of figure 125 shows that with a given injection concentration (C_1) a wide range of discharges may be measured by merely changing the injection rate (q). For example, a C_1 concentration of 0.4 percent (4×10^6 μg/L) permits the measurement of stream discharges from 15 ft³/s to almost 300 ft³/s, while still creating a plateau concentration (C_2) of 5 μg/L. Even those discharge limits may be exceeded by allowing C_2 to vary from its value of 5 μg/L. By using figure 125 with a knowledge of the range of discharges to be measured, a suitable value of C_1 can be selected for use as a working standard concentration.

To recapitulate what has been said up to this point, two working standard concentrations should be used for laboratory production of bulk solutions.

1. A concentration (C_1) of 4×10^6 μg/L, or one more suitable for the range of discharges to be measured, should be used for one solution. That solution will be used, without further dilution, as the injection solution for discharge measurements.

2. A concentration of 200 μg/L should be used for the second solution. A single dilution of that solution will provide standard solutions for calibrating the fluorometer at concentration C_2 (usually about 5 μg/L). Both solutions must be made from the same batch of 20-percent Rhodamine WT dye that is received from the manufacturer.

The discharge measurements will be made in the manner described in the earlier sections of this chapter, but before analysis by fluorometer, all samples and standard solutions should be allowed to sit overnight in a laboratory temperature bath. That will eliminate the need for temperature corrections to fluorometer dial readings.

As the hydrographer gains experience with the dye-dilution method, he will find that he can dispense with the computation of percentage of mixing (P_m) at the conclusion of his fluorometer analysis. By visual inspection of the computed individual plateau concentrations, he will be able to judge whether or not satisfactory mixing had been attained at the site of his sampling
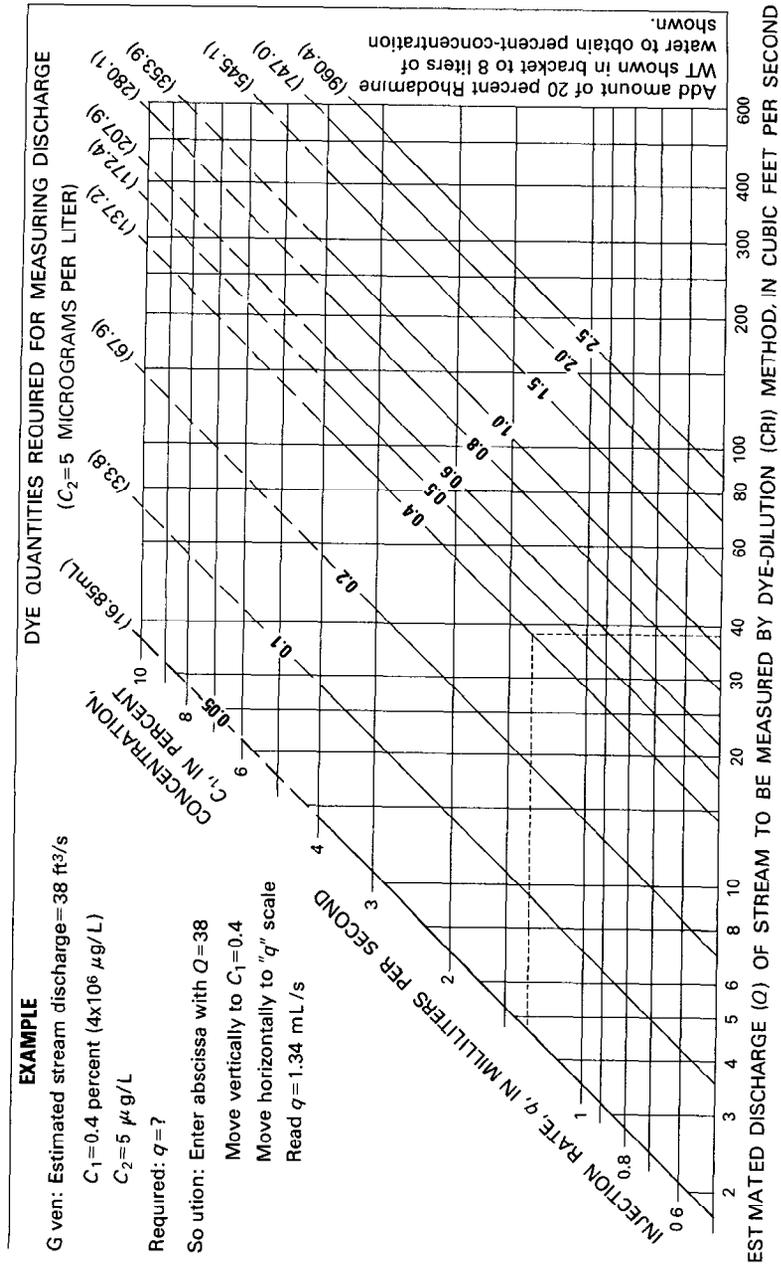
FIGURE 125.—Dye-injection rate of various stock dye concentrations related to estimated stream discharge.

MEASUREMENT OF DISCHARGE BY SODIUM DICHROMATE DILUTION

GENERAL

In Europe colorimetric analysis, using sodium dichromate $(Na_2 Cr_2O_7 \cdot 2H_2O)$ as the tracer, is the most widely used means of measuring discharge by the constant-rate-injection method. Because colorimetric analysis is rarely used in the U.S.A., the method will be described here only in brief; detailed descriptions are available in a report by the International Standards Organization (1973) and in a paper by Hosegood, Sanderson, and Bridle (1969).

The solubility of sodium dichromate is relatively high—the stock solution commonly used has a concentration of 600 g/L—and the salt satisfies most of the requirements for a tracer that are listed on page 211. Complications resulting from the presence of chromium ions in the water being gaged seldom occur, because natural waters generally contain few such ions. However, the nature and quantity of suspended sediment in the natural water can seriously affect the accuracy of analysis because of the possibility of sorption of sodium dichromate by the sediment. Another consideration in the use of sodium dichromate as a tracer is its potential toxicity to aquatic life, particularly in localized areas of high concentration; drinking-water standards in the U.S.A., for example, recommend a limiting concentration of 0.05 mg/L for chromium ions (Environmental Protection Agency, Environmental Studies Board, 1972, p. 62).

The factors that enter into the selection of a reach of channel for a measurement of discharge by sodium dichromate dilution are identical with those discussed earlier on pages 215–223. The types of apparatus for constant-rate-injection—mariotte vessel, floating siphon, and pressure tank—were described on pages 232–235.

The method of sampling for a discharge measurement by the constant-rate-injection method is similar to that described for fluorescent dyes (p. 237–240).

PRINCIPLE OF COLORIMETRIC ANALYSIS

Colorimetric analysis permits the measurement of extremely low concentrations of sodium dichromate. In that type of analysis a colorimeter is used to compare (1) the natural dilution of stream samples after tracer injection with (2) the known dilution of a stock solution of the salt. The comparison is based on differences in the absorption of light by the solutions after a reagent has been added to each of them.

The colorimeter is calibrated by the use of standard solutions, and it is recommended that the colorimeter used be one that gives a linear

relation between color intensity (concentration) and meter reading. The colorimeter coefficient is then equal to the known concentration of the standard solutions divided by the average of the colorimeter readings.

METHOD OF ANALYSIS BY COLORIMETER

As mentioned earlier, the stock solution commonly used for discharge measurements contains 600 g of sodium dichromate in each liter of solution. The injection rate of this stock solution depends on the estimated river discharge and the desired increase or rise in concentration of chromium ions (Cr^6) corresponding to the plateau concentration. That rise in concentration, $(C_2 - C_b)$ in the equation that follows, is generally in the range of 0.04 to 0.08 mg/L.

Discharge is computed by use of the equation

$$Q = \left[\frac{C_1}{C_2 - C_b} \right] q, \tag{38}$$

where
Q is stream discharge (m³/s),
q is rate of flow of injected solution (m³/s or mL/s $\times$ 10⁻⁶),
C_1 is concentration of the injected solution (mg/L),
C_2 is concentration of the plateau of the concentration-time curve shown in fig. 116 (mg/L), and
C_b is background concentration of the stream (mg/L).

MEASUREMENT OF DISCHARGE BY SALT DILUTION

GENERAL

As mentioned earlier, when salt is the tracer used in measuring discharge by the tracer-dilution technique, the sudden-injection method is generally used. Although the sudden-injection method is usually less accurate than the constant-rate-injection method, the difficulty of handling the large quantities of salt solution required by the constant-rate-injection method make the method impractical. Common salt (NaCl) is the salt tracer generally used because it is relatively cheap and it meets all the criteria for a tracer that are listed on page 211.

The basic principles behind the salt-dilution method are as follows. The ion concentration of a dilute salt solution, such as natural river water, increases as the salt content increases. Consequently, the easily measured electrical conductivity (conductance) of the solution is an index of the salt concentration. Furthermore, over a wide range of concentrations the conductance is directly proportional to salt concentration. Therefore, after injection of a concentrated salt solution

into a stream, the discharge can be computed by use of the ratios of the conductances of the injected and sampled salt solutions, instead of the ratios of the salt concentrations themselves. The procedure followed in the salt-dilution method is analogous to that used in the dye-dilution method in that relative conductance values are used rather than absolute values.

The factors that enter into the selection of the reach of channel for a salt-dilution measurement of discharge are identical with those discussed earlier on pages 215–223. Although loss of salt in the measurement reach by sorption is a negligible concern, reaches that have areas of slack water should be avoided, if possible, because the storage and slow release of tracer from those areas greatly prolongs the time required for the entire salt cloud to pass the sampling site. The sampling site should be free of excessive turbulence because the operation of the electrode cell that is placed in the stream to measure relative conductance is adversely affected by the presence of air bubbles.

The salt-dilution method of measuring discharge in open channels is littled used in the U.S.A. but is popular elsewhere, as in the U.S.S.R. The description of the salt-dilution technique that follows, and the sample computation that concludes the discussion, have been taken from a description of salt-dilution technique that follows, and the sample computation that concludes the discussion, have been taken from a description of salt-dilution stream gaging in the U.S.S.R. (World Meteorological Organization, 1962, p. 47–49). The subject is discussed under the following three headings:
1. Preparation and injection of the concentrated salt solution.
2. Measurement of relative conductance at the sampling site.
3. Computation of discharge.

PREPARATION AND INJECTION OF THE CONCENTRATED SALT SOLUTION

The following equipment is needed for the preparation and injection of the concentrated salt solution at the injection site:
1. Two tanks, each having a capacity of 60–70 L; one tank is used for preparation of the solution and the other for injection of the solution.
2. A measuring vessel of 10-L capacity, having a mark showing the exact level for 10 L of liquid.
3. A wooden or aluminum paddle for mixing the solution.
4. A vessel having a capacity of 0.3–0.5 L for adding small volumes of solution to the 10-L measuring tank.
5. A glass flask with a ground glass stopper, having a capacity of 20–30 mL, in which a sample of the solution is retained.
The quantity of salt (NaCl) required for injection depends on the

discharge to be measured; 1–2 kg of salt is needed for each cubic meter per second of stream discharge. The smaller unit quantity of salt is used for streams having a low natural concentration of dissolved material. In estimating the quantity of salt to be brought to the injection site, consideration should also be given to the possibility that the discharge measurement will have to be repeated.

The preparation and measurement of the injection solution takes place at the injection site, but at a distance from the river to avoid any accidental spill of salt or salt solution into the river. An accident of that kind could affect the results of the discharge measurement. To prepare the injection solution, the quantity of salt needed is first determined from an estimate of the discharge and the natural concentration of dissolved materials in the stream. The computed quantity of salt is then placed in one of the large tanks, and river water is added to the tank at the rate of 10 L to each 3 kg of salt. The mixture is then stirred to obtain a saturated salt solution. After the larger undissolved crystals have settled to the bottom of the tank, the solution is transferred to the second large tank, and its volume is carefully measured in the process, the transfer being made by means of the 10-L measuring vessel. An additional amount of river water sufficient to fill the small glass flask (20–30 mL) to its brim is then added to the measured solution in the second large tank. The flask and stopper are carefully rinsed in that tank, after which the contents of the tank are thoroughly stirred once more. The small glass flask is then filled with the solution, tightly stoppered, and is delivered to the sampling site downstream for later use there. The large tank now holds the volume of salt solution that was originally measured into it. The large tank is then moved to the river, and at a signal from the sampling site that all is in readiness there, the tank is overturned to spill its contents almost instantaneously into midstream. That act completes the work to be done at the injection site.

MEASUREMENT OF RELATIVE CONDUCTANCE AT THE SAMPLING SITE

A conductance meter (fig. 126) that is a modification of a Wheatstone bridge is set up at the sampling site. The principal elements of the meter are a rheochord, a 10,000-ohm resistance chamber, and an electrode cell immersed in the stream, well away from the bank. The resistance chamber is used to compensate for the natural conductance of the water in the stream so that the needle of the galvanometer reads zero. The indicator on the rheochord is also set at zero. When this has been done, the signal to inject the salt solution is sent to the injection site.

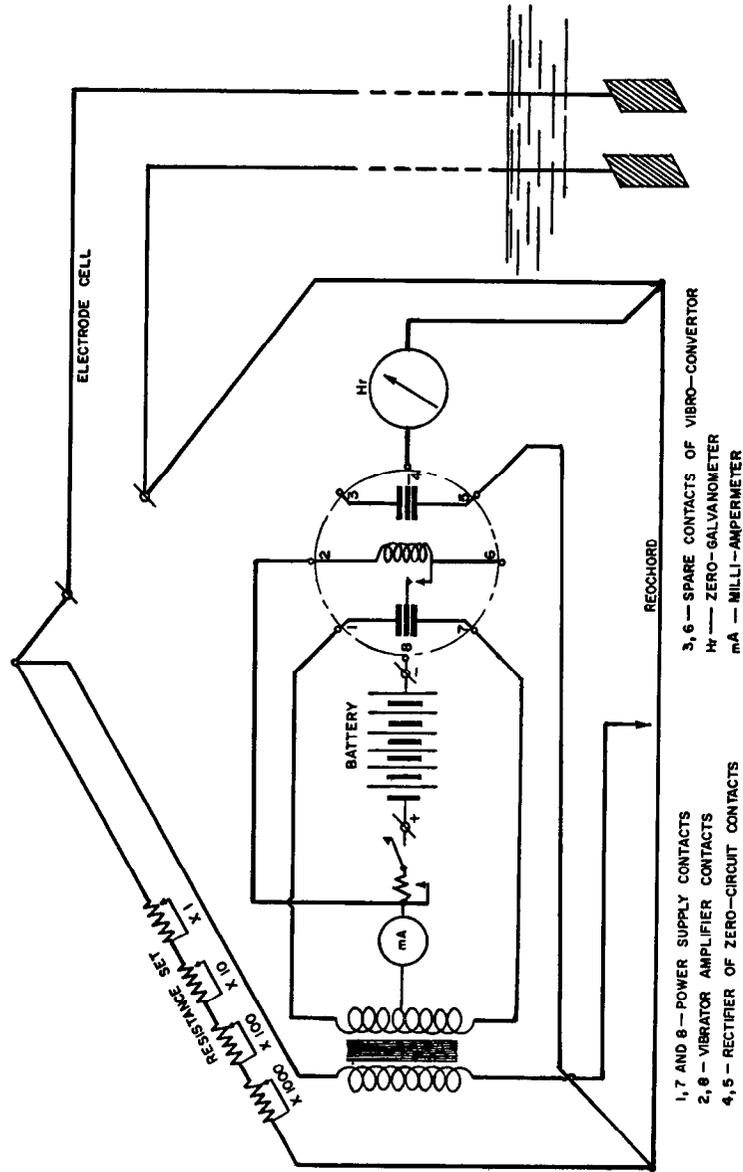After the solution has been poured into the stream at the injection

FIGURE 126.—Schematic diagram of conductance meter used in salt-dilution method of measuring discharge. (From World Meteorological Organization, 1962, p. 47.)

1, 7 AND 8—POWER SUPPLY CONTACTS
2, 8 — VIBRATOR AMPLIFIER CONTACTS
4, 5 — RECTIFIER OF ZERO—CIRCUIT CONTACTS

3, 6 — SPARE CONTACTS OF VIBRO—CONVERTOR
Hr —— ZERO— GALVANOMETER
mA — MILLI—AMPERMETER

site, the current is switched on in the conductance meter, and the stability of the compensation for natural conductance is checked. If the galvanometer needle has deviated from zero, it is returned to zero by changing the resistance. Constant observation of the needle then begins. When the needle begins a perceptible movement to the right, it is a sign that the solution, or ionic wave, is approaching, and the stopwatch is started. From that time on, the galvanometer needle is maintained in a position approximating the zero reading by turning the rheochord handle. Every 15 s the needle is returned exactly to zero and the indicator position on the rheochord scale is read. That reading represents relative conductance (P) expressed in tenths of a percent $(0/00)$:

$$P_W = 1,000 \left[\frac{(EC)_W - (EC)_o}{(EC)_o} \right] , \tag{39}$$

where EC is conductance (electrical conductivity), subscript W refers to the ionic wave, and subscript o refers to the natural water in the stream. (Note.—Conductance is the reciprocal of resistance.)

As the ionic wave passes the sampling site, relative conductance increases rapidly at first, reaches a peak, and then recedes slowly to zero or to a constant value slightly above or below zero. When the rheochord readings remain constant for 5 or 6 readings (1½ min) near the zero value, the measurement is terminated. Immediately thereafter the determination of the relative conductance of the injection solution begins, using the sample in the small flask obtained at the injection site just before the measurement began. For this determination the following equipment is needed:
1. A 10-L measuring vessel.
2. A jug for adding water to the measuring vessel.
3. A wooden or aluminum paddle for mixing the solution.
4. A 1-mL glass pipette.

The measuring vessel is rinsed three or four times with river water. It is then filled with river water to the 10-L mark, and the electrode cell of the conductance meter is immersed in it. The rheochord needle is set to zero, the current is switched on, and the resistance is adjusted to set the galvanometer needle to zero. The pipette is next rinsed in the injection solution that had been delivered in the small flask, and the pipette is used to add 1 mL of that solution to the 10 L of river water in the measuring vessel. The pipette is then rinsed three times in the vessel to insure that all of the extremely small volume of salt in the 1 mL of solution is introduced into the vessel. The contents of the vessel are then thoroughly mixed, and the relative conductance of the greatly diluted injection solution is measured with the meter, using the technique described for measuring relative conductance in the

ionic wave. The ratio of dilution for the sample of injection solution is 1:10,000, because 1 mL of injection solution was mixed with 10 L of river water.

COMPUTATION OF DISCHARGE

The simplest way to describe the computation of discharge from salt-dilution data is by means of an example. Assume that in the preceding discussion of methodology, the stream discharge had been estimated to be about 4.5 m³/s. The unit quantity of salt to be used was 2 kg/m³/s of discharge; consequently about 9 kg of salt was prepared. Water was added to the salt at the rate of 10 L per 3 kg of salt. As a result, 30 L (0.03 m³) of injection solution was prepared. This value is shown on line 1 on the left-hand side of the computation sheet in figure 127. At the sampling site, 10 L of river water (line 2) was mixed with 1 mL of injection solution (line 3), giving a dilution ratio of 10,000 (line 4). The resistance of the river water was found to be 969 ohms (lines 5 and 6), and the resistance of the sample of diluted (1:10,000) injection solution was found to be 691 ohms (line 7). The relative conductance of that sample, as read on the rheochord in tenths of a percent, was 402 (line 8). On line 9, the rheochord reading for the dilute sample of injection solution is checked mathematically by use of the measured resistances. The equation used on line 9 is identical with equation 39. On line 10 the relative conductance of the injected solution is computed by multiplying the relative conductance of the diluted injection sample by the dilution ratio.

On the right-hand side of figure 127 are shown the relative conductance values read on the rheochord scale at 15-s intervals during the 15-min passage of the ionic wave. Subtotals are shown for the three columns of relative conductance values; the grand total is 1,933. The data are presented graphically in figure 128, where relative conductance is plotted against time.

Discharge is computed from equation 40, the denominator of which is the area under the curve of relative conductance versus time:

$$Q = \frac{V_1 P_p}{F \pm \Delta F}, \tag{40}$$

where

Q is discharge, in cubic meters per second,

V_I is volume of the injected solution, in cubic meters,

P_P is relative conductance of the injected solution, in tenths of a percent,

F is the product of the sampling interval, in seconds, multiplied by the sum of the observed values of relative conductance, and

ΔF is a correction factor for any change in reading of the rela-

tive conductance of the natural river water between the start and end of the measurement:

$$\Delta F = \frac{P_{start} - P_{end}}{2}(t_n - t_1), \text{ where } t_n - t_1 \text{ is the time, in sec-}$$

onds, that elapsed during the measurement.

The discharge is computed in lines 11–16 on the left-hand side of figure 127. Line 11 shows the sampling interval—15 s; line 12 shows the sum of the observed relative conductances of the ionic wave—1,933; line 13 shows the computation of F—28,995; line 14 shows the computation of ΔF—there was no change in natural relative conductance during the 900 s that elapsed during the measurement. The value of the denominator of equation 40 is shown on line 15. The discharge, computed in accordance with equation 40, is shown on line 16.

MEASUREMENT OF DISCHARGE BY DILUTION OF RADIOACTIVE TRACERS

GENERAL

The use of radioactive material for measuring discharge by tracer

	Basic measurements data				Observations of ionic wave					
Item	Symbol	Value	Units	Time t	$\%_0$ P	Time t	$\%_0$ P	Time t	$\%_0$ P
1 Volume of initial solution	V_1	0.0300	m³	0 00"	0	6 15"	52	12 30"	3
				15"	1	30"	48	45"	2
2 Volume of river water for dilution	W_0	10000	ml	30"	3	45"	44	13 00"	2
3 Volume of initial solution for dilution	W_1	1	ml	45"	7	7 00"	40	15"	1
4 Dilution ratio $\dfrac{W_0}{W_1}$	n	10000	—	1 00"	13	15"	37	30"	1
				15"	20	30"	33	45"	1
5 Resistance of river water flow	R_0	969	ohms	30"	32	45"	29	14 00"	1
				45"	43	8 00"	26	15"	1
6 Resistance of river water in tank	R	969	ohms	2 00"	56	15"	23	30"	1
				15"	66	30"	21	45"	1
7 Resistance of mixture	R_t	691	ohms	30"	75	45"	19	15 00"	0
				45"	81	9 00"	18	15"	0
8 Relative electrical conductivity of mixture on rheochord	P_t	402	$\%_0$	3 00"	85	15"	15	30"	0
				15"	88	30"	13	45"	0
9 Or from formula $P_t (\frac{R}{R_t} - 1) 1000\%_0$	P_t	402	$\%_0$	30"	90	45"	12	16 00"	0
				45"	91	10 00"	10	15"	0
				4 00"	90	15"	9	30"	0
10 Relative electrical conductivity of initial solution $P_p \cdot P_t \, n$	P_p	4020000	$\%_0$	15"	88	30"	8	45"	0
				30"	85	45"	7	17 00"	0
Discharge calculation				45"	81	11 00"	6	15"	
11 Time between observations	Δt	15	sec	5 00"	77	15"	5	30	
12 Sum of ordinates of ionic wave graph	ΣP	1933	$\%_0$	15"	72	30"	5	45"	
				30"	66	45"	4	18 00"	
13 Product $F = \Delta t(\Sigma P)$	F	28,995	$\%_0$ sec	45"	61	12 00"	3		
				6 00"	56	15"	3		
14 Correction $\Delta F = \dfrac{P_1 - P_n}{2}(t_n - t_1) = 0$			$\%_0$ sec	$\Sigma P =$	1 428	$\Sigma P =$	491	$\Sigma P =$	14
15 Area of ionic wave graph $F \pm \Delta F$		28995	$\%_0$ sec						
16 Water discharge $Q = \dfrac{V_1 \cdot P_p}{F \pm \Delta F} = \dfrac{(0.03)(4020000)}{28995}$				4 16 m³/sec					

FIGURE 127.—Sample computation of discharge using salt dilution in the sudden injection method. (From World Meteorological Organization, 1962, p. 49.)

dilution will not be described in detail, because the method is still (1980) considered to be in the experimental stage. Radioactive tracers should be ideal for the dilution method because concentrations as low as 10^{-9} ci/L may be accurately determined with a counter or count-rate meter whose sensing probe is immersed in the stream.

The radioactive element that has been most commonly used is gold 198, which has a half-life of 2.7 d. Tests have also been made using sodium 24, which has a half-life of 14.9 hr. It is necessary that the radioactive tracer have a short half-life so that the radioactivity introduced into the stream will decay to an insignificant level in a short
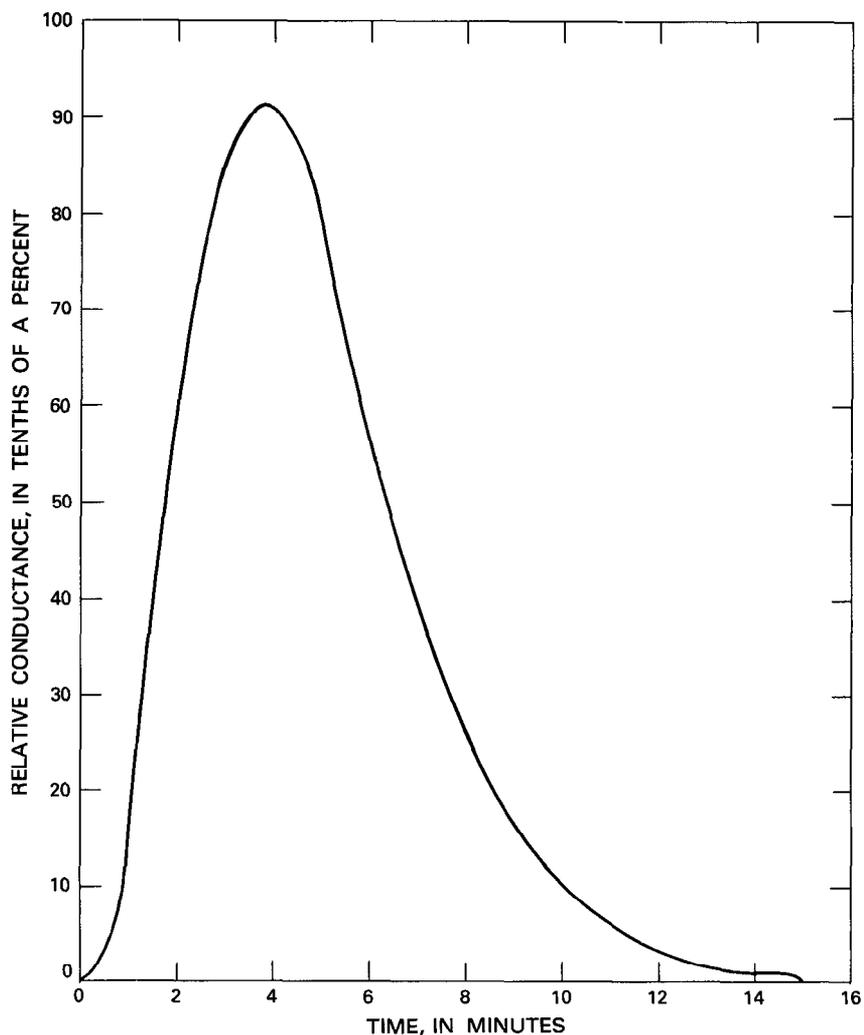

FIGURE 128.—Curve of relative conductance versus time for the ionic wave in the sample problem. (From World Meteorological Organization, 1962, p. 48.)

time. That requirement introduces a problem in logistics, in that the radioactive element must arrive from the nuclear plant and be used at the measurement site at the scheduled time, so that excessive decay of the radiation does not occur before the discharge measurement is made. Another factor that tends to discourage the use of radioactive tracers is the requirement of a government license merely to handle the material; radiation shielding must be provided while shipping and handling the material because of the potential threat to public health. In addition, approval must usually be obtained at all government levels, including the local level, before the radioisotope can be used in a stream, and local fear of radioactive pollution is often difficult to overcome.

METHODOLOGY

A measurement reach of channel is selected, using one of the equations, 28 to 32 (p. 221–222), as a guide in determining the length of reach needed for satisfactory mixing. Before the measurement is started, the instrument for counting gamma-ray emissions—Geiger or scintillation counter—is calibrated, taking into account the exact conditions under which the counter will be used.

A measured quantity of the radioisotope is introduced into the stream at the injection site by being quickly poured out of a bottle; or more frequently, a glass bottle containing the radioisotope is placed in a wire-screen container that is then lowered into the stream, after which the glass bottle is shattered to release the isotope for mixing in the streamflow. At the sampling site downstream, where the probe of the Geiger or scintillation counter is immersed in the stream, gamma-ray emissions are continuously counted. The counters are started well before the arrival of the isotope-stream mixture so that the counts received from natural (background) radiation sources may be measured. The counters continue to count throughout the passage of the isotope-stream mixture until the count returns to the background level. The total net count (N) is equal to the gross count obtained minus the background count accumulated during the period of the gross count.

The discharge is computed from the equation

$$Q = \frac{FA}{N},\qquad(41)$$

where

Q =   stream discharge (volume per unit time),
F =   a calibration factor for the probe and counting system,
A =   total quantity of radioactivity introduced into the stream, and
N =   total net count recorded by the counter.

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