SAMPLE COLLECTION AND TREATMENT

General considerations

Many of the dissolved ions normally present in natural waters may be lost from the water sample before it is analyzed in the laboratory because of such chemical and physical reactions as oxidation, reduction, precipitation, adsorption, and ion exchange. Therefore, some properties or constituents such as specific conductance, temperature, dissolved oxygen, alkalinity, and bacteria may change dramatically within a few minutes or hours after sample collection. Immediate analysis in the field is required if accurate results for these parameters are to be obtained. Samples for other constituents may be stabilized by preservative treatment. Some examples of preservative treatment are refrigeration to minimize chemical and biological change due to biologic activity and the addition of acid to prevent the precipitation of cations.

Analysis for "total recoverable" and "total" constituents requires a raw (unfiltered) sample of the water sediment mixture; analysis for "dissolved" constituents requires a filtered sample (generally, through a 0.45 micrometer membrane filter). Other analyses may require bottom material, residue of a filtered sample, or biological material obtained on an artificial substrate. The type of sample treatment required is designated by the U.S. Geological Survey Central Laboratory and defined in their "Service Catalog." Specified sample containers also are listed. Preservatives and bottles are available upon request from the Central Laboratory. Policies of contract laboratories may differ somewhat regarding preservatives and sample containers.

Samples are to be shipped from the field to the laboratory with no delay--preferably the day they were collected. An exception might be when samples are collected near the end of the week and there is reason to believe the shipment will arrive and be held in the Post Office over the weekend. In such instances the nutrients, and other samples requiring cooling, must be held in a dark, refrigerated condition. Another exception to the immediate shipment of samples involves daily samples collected by field observers for the analysis of specific conductance. For practicality, these samples are shipped to the District Laboratory on a monthly basis.

Methods of ground-water sampling

The unstable nature of many chemical and physical properties in ground water requires special collection procedures for samples. In addition, the geochemical controls and nature of the aquifer system may further complicate the method by which samples are collected. The following are general guidelines to use in collection of samples from springs and wells. More detailed information can be found in Wood (1976).

Sampling from springs

For sampling springs in unconsolidated deposits, a well point or slotted pipe can be driven into the ground to a depth of 1 meter or less adjacent to the spring. If the flow is not artesian, the sample can be collected using a small pitcher pump. Plastic pipe and plastic well screen are used for trace metal samples. To sample large upwelling springs, submersible electric pumps placed at the mouth of the spring by hand or attached to a pole generally work well. When sampling for trace metals, plastic is used for the pump housing, pump impellers, and tubing.

Sampling from wells

Wells are pumped prior to sampling to ensure that stagnant water is flushed from the system and the sample is representative of water in the aquifer. Samples are not collected until temperature, specific conductance, and pH remain at constant values. The sample is collected near the wellhead before the water has gone through pressure tanks, water softeners, or other treatment. When wells are not equipped with pumps, a submersible pump with an outside power source is preferred. A pitcher pump may be used if the water level is within about 7 meters of the surface. If pumping cannot be done, a small-diameter point sampler can be used, but only after the well has been bailed until temperature, specific conductance, and pH are constant. Bailers and point samplers usually contaminate the sample with oxygen.

Well packers can be used to sample from individual aquifers tapped by multi-screen or open-hole wells receiving water from several aquifers. Such wells often are avoided in sampling for geochemical studies because of greater costs involved in the use of packers.

Methods of surface-water depth-integrating sample collection

Proper sampling techniques are important to ensure that a sample is representative of the flow in the cross section. The most complete discussion of sampling techniques is found in the report "Field Methods for Measurement of Fluvial Sediment," (Guy and Norman, 1970). Some aspects of sampling are included also in other Geological Survey Techniques of Water-Resources Investigations manuals (see list of references) and quality of water technical memorandums (unpublished).

The number of verticals to be sampled at a site relates primarily to the collection of a representative sample in the cross section and secondarily to the volume of the sample required. With few exceptions, samples that are to be analyzed for suspended sediment or total recoverable constituents need to be collected by using water-sediment, depth-integrating samplers. Instances where use of these samplers are not required are as follows:

1. Extreme low flow where the use of the sampler is impractical. Samples may be collected by immersing the bottle by hand (dip).

2. Under extreme cold temperatures when freezing conditions preclude the use of the normal sampler. In such instances the tubular insert sampler is used. To the degree that is possible, sampling methodology is to be compatible with that used with other type samplers; that is, depth integration and multiple verticals.

3. Samples collected for dissolved chemical constituents that are well mixed within the section. If field measurements of specific conductance show the water to be well mixed, a sample obtained at a single vertical near the centroid of flow may be assumed to be representative of the total flow.

4. Collection of sterile aseptic samples for bacteria work. These samples may be collected at midstream by hand dipping if the stream is wadeable, or otherwise by using the tubular insert sampler with a sterile sample container inserted.

Samples collected at remote sites by automatic samplers need to be retrieved at the earliest possible time. Samples collected in this manner will be analyzed only for constituents that do not require onsite preparation and will be assumed to be representative of that particular flow event. Except for suspended sediment, an aliquot from each bottle collected will be composited to form one sample per event; the appropriate begin and end dates and times for the flow event will be entered into storage, thus indicating a composite sample of the event. When possible, adequate cross-section samples are to be obtained and analyzed for nutrients, bacteria and other scheduled constituents such as suspended organic carbon (SOC), total organic carbon (TOC), and dissolved organic carbon (DOC).

Samples collected by automatic samplers for suspended-sediment concentrations will be analyzed individually and the specific conductance will be measured for each sample. Cross-section samples are to be collected at appropriate intervals, using either the equal-discharge-increment (EDI) method or the equal-width-increment (EWI) method to obtain cross-section coefficients. The coefficients are then applied to the concentration determined at a single vertical to obtain a value that is representative of the average concentration in the cross section.

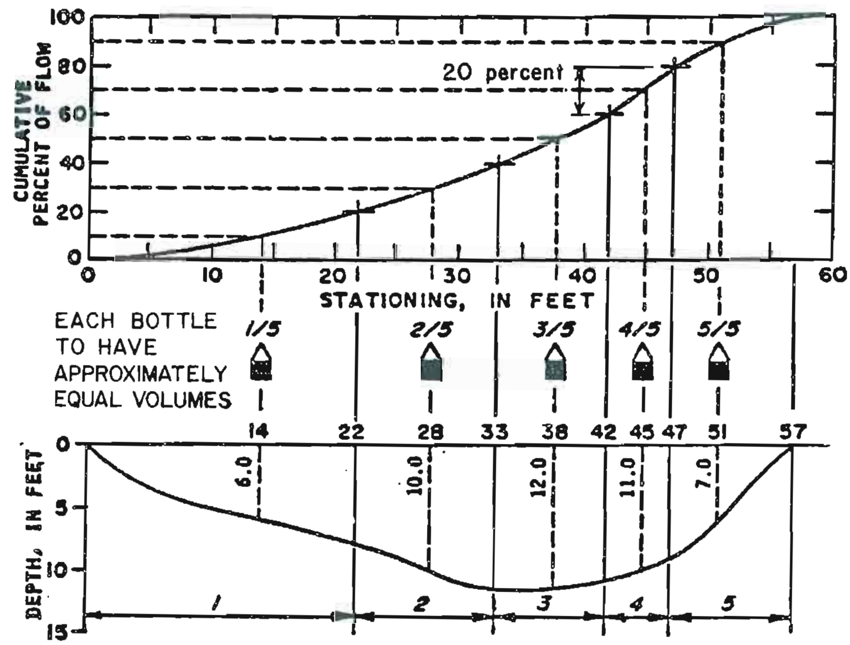
If a representative sample can be obtained by sampling at one vertical, then obtain the volume of sample required at one vertical near the centroid of flow. However, if samples are to be collected at a single vertical for suspended sediment or any of the total or total recoverable chemical constituents, sufficient data must be available to document that materials suspended in the flow are uniformly distributed throughout the cross section. If such data are not available or if flow conditions dictate that suspended materials are not uniformly distributed throughout the cross section, multiple verticals need to be sampled using either the EDI method or the EWI method.

EDI method of sampling for suspended sediment, total recoverable and dissolved chemical constituents, and phytoplankton

The EDI method, in which samples are obtained at the centroids of equal discharge increments, is usually limited to streams having stable channels where discharge rating curves vary little during a year. This method requires that field personnel have knowledge of the streamflow distribution in the cross section before sampling verticals can be selected. If such information can be obtained, the EDI method can save time and labor over the EWI method, especially on larger streams, because fewer verticals are required. To select sampling verticals for the EDI method when prior knowledge of the flow is available, graphs of cumulative discharge in percent of total discharge versus distance from the left or right bank are prepared for low-, medium-, and high-flow conditions for the site. For streams where the EDI method is applicable, these graphs are used as sampling instructions that can be kept in the shelter at the site and in the field vehicle.

The number of equal-discharge increments required to divide the cross section will depend on the size of the river and will generally range from 4 to 10 (fig. 1).

Sampler D-49: nozzle size 3/16-inch ID. Stream width 57 feet; maximum stream depth 12 feet; maximum velocity, 5.0 feet per second; width of section containing 20 percent of flow; variable, 5 to 22 feet; 20 percent of flow per section will give five sampling verticals; transit rate (from nomograph) variable, 0.3-2.0 feet per second.



[ft, feet; ft/s, feet per second; s, seconds]

Increment No.	Percent discharge	Increment width (ft)	Increment depth (width)	Velocity (ft/s)	Maximum transit rate (ft/s)	Transit rate[1] (ft/s)	Total transit time[1] (s)
1	20	22	6	2.0	1.2	0.3	42
2	20	11	10	4.0	1.6	1.1	14
3	20	9	12	5.0	2.0	1.6	9
4	20	5	11	4.0	1.6	1.2	13
5	20	10	7	3.0	1.2	.6	25

[1]Using pint sample container and filling to about 85 percent of capacity

Figure 1.--The equal-discharge-increment (EDI) sampling method.

The initial selection of parts into which the cross section is to be divided for the EDI method is not governed by any predetermined number of sampling points, but rather is chosen on the basis of the following:

1. A discharge measurement is made at the cross section where sampling is to be done. From this measurement, a graph can be constructed using cumulative percent discharge plotted against cross-section stationing. If the cross section is stable, the graph may be used to determine sampling points without having to make a discharge measurement. However, this graph needs to be verified occasionally with computations from recent discharge measurements. Commonly a series of discharge measurements representing low, medium, and high flows is plotted on a single graph and used throughout the range. An example of this type of graph is shown as figure 2.

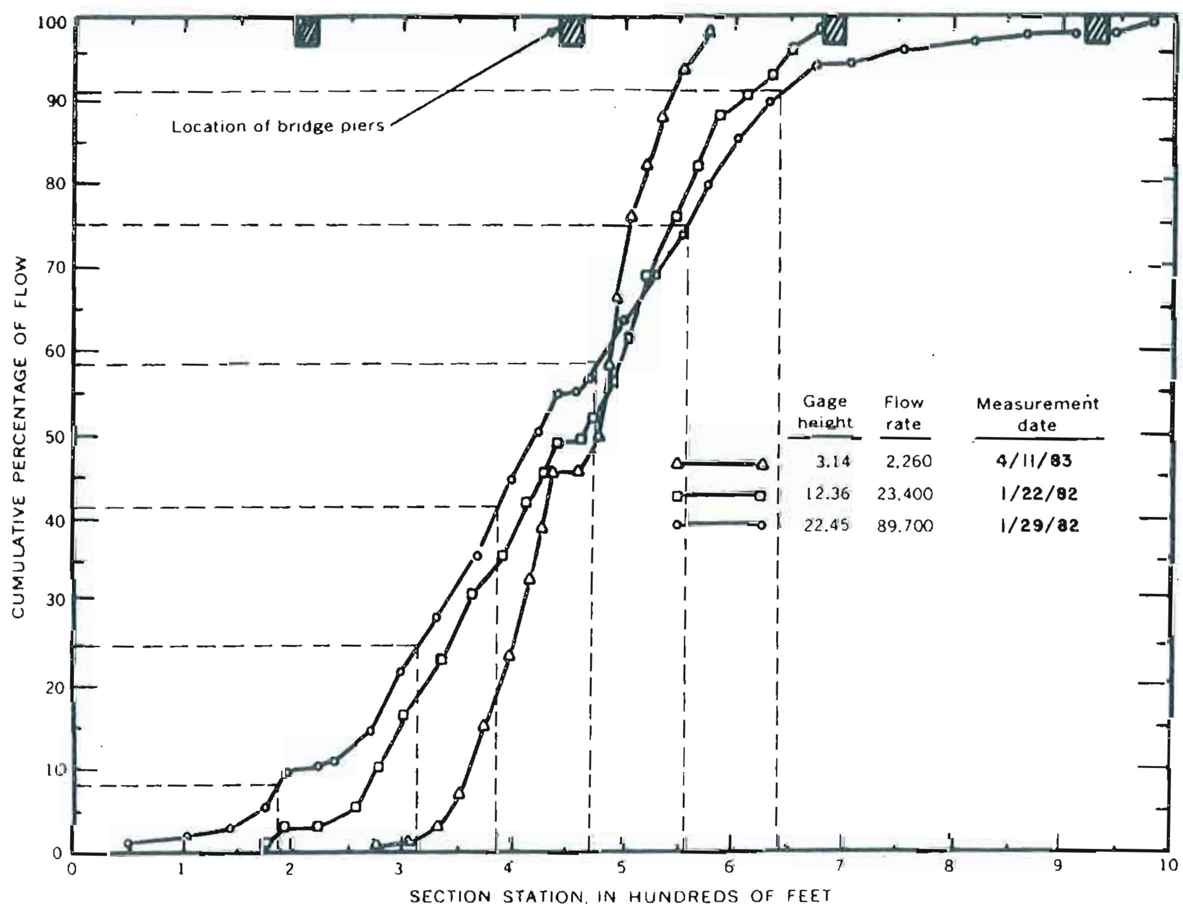


Figure 2.--Cumulative percentage of the total water discharge for three rates of flow with distance across the stream section. Broken lines indicate the stationing of centroids for six eqaul-discharge increments during high flow. Gage height in feet; flow rate in cubic feet per second.

2. A visual inspection of the cross section is made noting the location, if any, of still-water areas or filaments of faster than normal flow, and piers or other obstructions. Cross-sectional surveys of specific conductance, temperature, pH, and dissolved oxygen are made on a seasonal basis to determine if mixing is a problem.

3. Based on the information from the discharge measurement, the visual inspection of the cross section, previous cross sectional surveys, and other information such as laboratory considerations, the decision is made, usually in the relatively calm atmosphere of the office, as to the number of parts needed to adequately define the concentration of suspended sediment in transport through the cross section. The larger the variability in the section and the larger the stream, the more increments will be selected. The final decision as to the number of increments will rest with the District Water Quality Specialist.

Using the EDI method, samples are then collected at the center of each increment of flow as determined from a streamflow measurement or from a cumulative discharge graph. Each bottle is filled to no more than 3 inches from the top. Overfilling can cause secondary circulation, resulting in enrichment of heavy particles in the sample that is not representative of the water-sediment mixture flowing down the stream. Care is needed not to bump the sampler against the streambed causing bed material to rise and enter the bottle. Each bottle is visually inspected; if found to contain excess amounts of large particles, it is emptied, rinsed, and refilled.

[BECAUSE BOTTLES REPRESENT EQUAL PORTIONS OF FLOW, EACH BOTTLE MUST CONTAIN APPROXIMATELY EQUAL VOLUMES OF WATER-SEDIMENT MIXTURE]

The length of immersion time of the sampler can be determined from figure 3. General guidelines for the EDI method of sampling are as follows:

1. Determine the number and locations of verticals to be sampled on the basis of flow conditions and the volume of water needed for analysis. For many streams about four to eight verticals will be sufficient. For example, if six verticals are selected, each of the verticals (stations) needs to be at the centroid of 16.7 percent increments of the discharge--that is, at stations of cumulative discharges of 8.3, 25, 41.7, 58.3, 75 and 91.7 percent. If any of the stations selected are at or near bridge piers or other obstructions where turbulence interferes with the streamflow lines, the sampling station is to be moved a sufficient distance from the obstruction to minimize the effects of the turbulence.

2. After the locations of the sampling stations have been determined, select and assemble the proper sampling and support equipment and safety equipment, such as cones and signs.

3. Read and record the gage height and time at which sampling is begun.

4. Move sampling and support equipment to first station to be sampled.

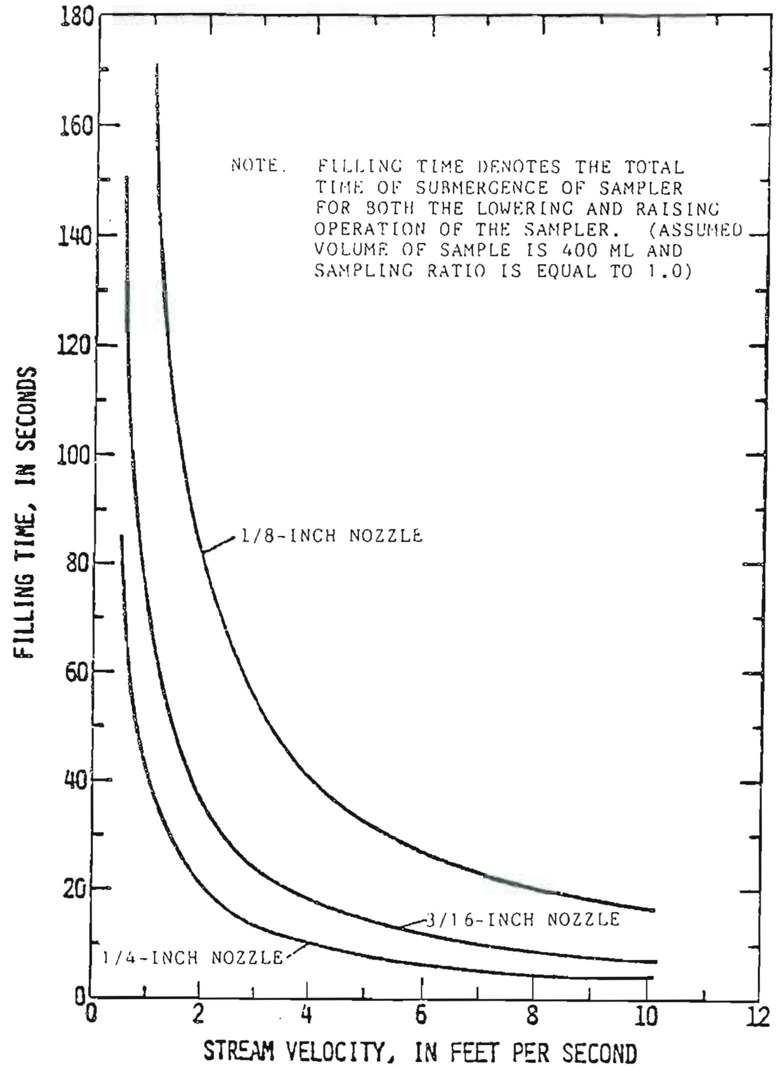


Figure 3.--Time for a suspended-sediment sample bottle of 1-pint capacity to be filled to about 85 percent of capacity.

5. Estimate the sampler transit rates and times from the depths and velocities of flow in each vertical. The transit rate in a vertical needs to be kept constant throughout at least a single direction of travel in that vertical when using the EDI method. The relationship between stream velocity and corresponding filling time (time of submergence of the sampler) for both the pint and quart bottles is shown in figures 3 and 4. A nomograph is given in figure 5 for which the average sampler transit rate and filling time can be determined, given the depth of the vertical and the mean velocity of flow in the vertical.

6. If concentrations of suspended sediment and chemical constituents are to be determined for the stream, collect from each vertical a separate 1-pint

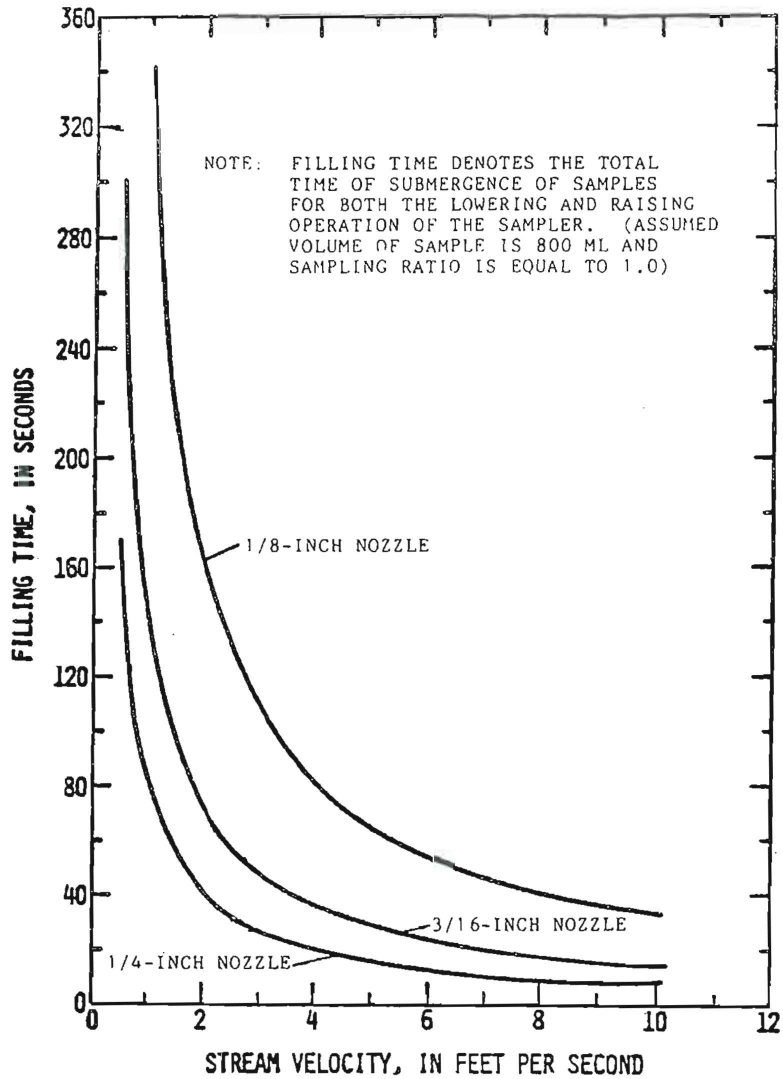
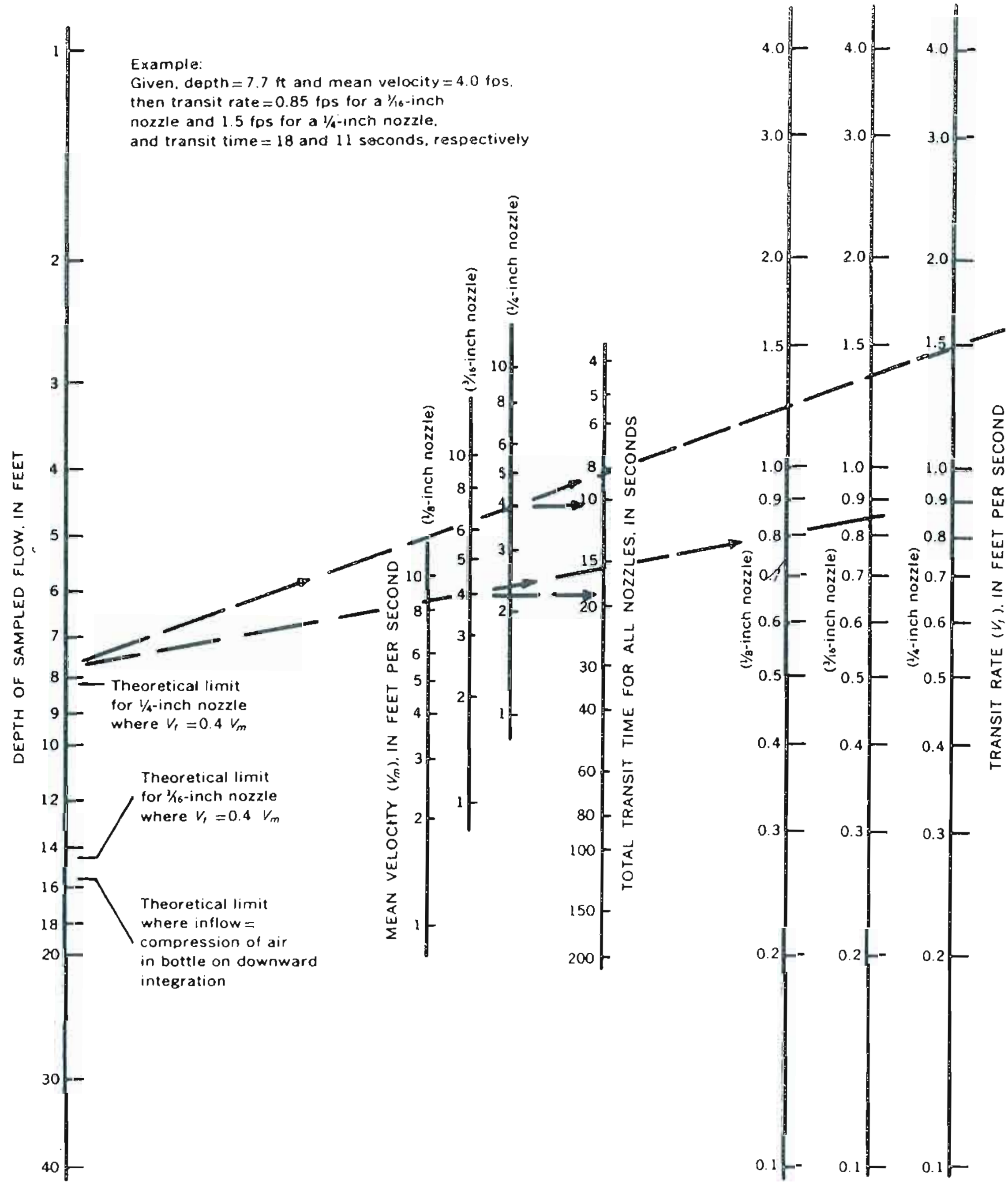


Figure 4.--Time for a suspended-sediment sample bottle of 1-quart capacity to be filled to about 85 percent of capacity.

sample for suspended sediment and 1-pint or 1-quart samples for chemical constituents. The same pint or quart glass bottle is used for each vertical in the cross section for chemical constituents. (Swirl the pint or quart sample gently to keep sediment suspended and pour into churn after sampling each vertical).

[THE INDIVIDUAL DEPTH-INTEGRATED SAMPLES FOR THE DETERMINATION OF DISSOLVED OR TOTAL CHEMICAL CONSTITUENTS (EXCEPT THOSE FOR TOC, DOC, SOC, O&G, BACTERIA, AND PESTICIDES) ARE TO BE COMPOSITED IN THE CHURN SPLITTER]



ROUND TRIP (STREAM SURFACE TO BED AND RETURN) SUSPENDED-SEDIMENT SAMPLER TRANSIT RATE AND TRANSIT TIME FOR 1/8-, 3/16-, AND 1/4-INCH INTAKE NOZZLES, GIVEN THE SAMPLING DEPTH AND MEAN VELOCITY OF FLOW.

Figure 5.--Sampler transit rate and transit time for a 1-pint sample container to be filled to about 85 percent of capacity.

The volume of the sample collected at a vertical is dependent primarily upon the stream velocity and the depth. Because the operator has no control over these factors, the volume of the sample is regulated by selecting a nozzle of appropriate size or by varying the total time of submergence of the sampler. However, the operator has the option of making any number of up and down trips in each vertical.

7. If either the pint or quart container becomes completely filled during a sampling operation, discard the sample, as it will not be representative, and collect another sample.

8. Label each of the pint samples for suspended sediment analysis with the following information:

   a. Station number, name, and location of the stream.
   b. Date.
   c. Mean time and gage height (or discharge) for the period of sample collection (after step 10).
   d. Sampling location (location in the vertical section).
   e. Water temperature.
   f. Initials of sample collector.

9. Read and record the gage height and time at which sample collection was completed.

10. Calculate and record on the field notes the mean time and gage height for the period of sample collection.

11. Complete field measurements, filtration, and preservation of samples as applicable.

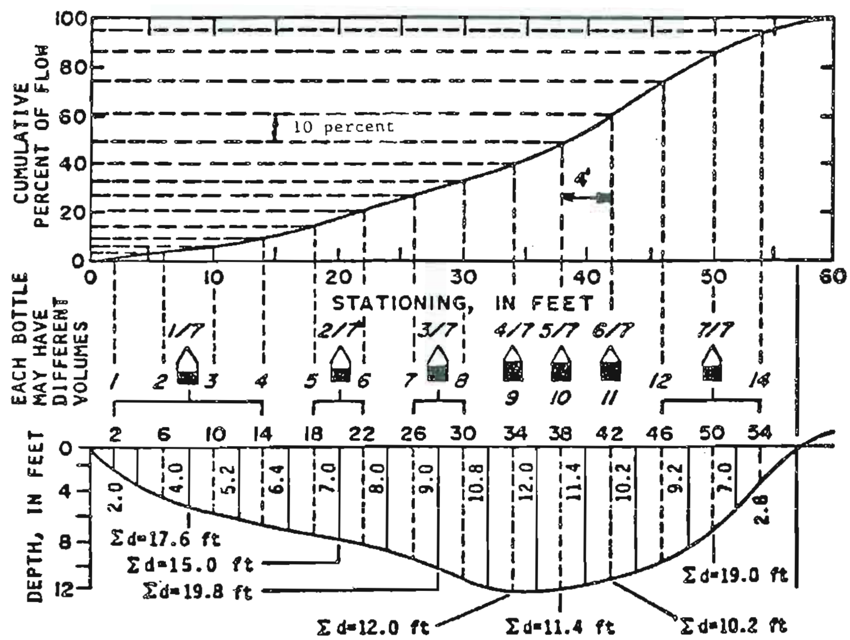
12. Disassemble and clean samplers as described in the section "Methods of Cleaning Samplers and Support Equipment."

EWI method of sampling for suspended sediment, total recoverable and dissolved chemical constituents, and phytoplankton

On wadeable streams and any stream that is subject to a shifting channel, sampling is generally easiest using the EWI method, formerly called ETR or equal-transit-rate method. A shifting channel makes it impossible to establish a set of percentage-discharge curves applicable from one visit to the next. Thus, if a water-discharge measurement is not made immediately before collection of water-sediment samples at these sites, the EWI method is to be used.

The EWI method requires equal spacing of several verticals across the cross section (fig. 6) and an equal transit rate, both up and down, in all verticals. In the EWI method, the width of the stream is determined by reference to a tagline across the stream or to the markings on a bridge rail or a cableway. The stream width is then divided into a number of intervals of equal width, the number of intervals being dependent on channel width, apparent uniformity of lateral sediment distribution, and depth and velocity distribution across the stream.

Sampler D-49; nozzle size 1/4-inch ID; width 57 feet; maximum depth 12 feet; average velocity, 3.5 feet per second; width of section containing 10 percent of flow at deep fast section 4.0 feet; 4 feet wide sections will give 14 sampling verticals; transit rate (3.5 ft/s x 0.4) 1.4 feet per second.



Sampling vertical No.	Percent of flow	Station No.	Width of increment (ft)	Transit rate (ft/s)	Percent of sample
1	2	2	4	1.4	--
2	4	6	4	1.4	--
3	6	10	4	1.4	--
4	10	14	4	1.4	16.6
5	16	18	4	1.4	--
6	22	22	4	1.4	14.2
7	28	26	4	1.4	--
8	34	30	4	1.4	18.7
9	42	34	4	1.4	11.3
10	50	38	4	1.4	10.8
11	62	42	4	1.4	10.2
12	76	46	4	1.4	--
13	88	50	4	1.4	--
14	96	54	4	1.4	18.2

Figure 6.--The equal-width-increment (EWI) sampling method.

The intervals used in EWI sampling are not selected on any predetermined number of sampling points, but rather on the basis of the following: 1) Visually inspect the stream from bank to bank, observing the velocity and depth distribution as well as apparent distribution of sediment in the cross section, 2) determine the size of interval that represents approximately 10 percent of the flow at that part of the cross section where the "unit width discharge" is largest or the greatest concentration of sediment is moving. This interval size must then be used for the ENTIRE EWI cross section and will govern the number of intervals used. The number of sections is generally not less than 10 nor more than 20.

Sampling verticals are at the center of the selected intervals unless obstructions such as piers are present. For example, in a stream 57 feet wide that has been divided into 14 intervals of 4 feet each, the first sampling vertical would be 2 feet from the water's edge and subsequent verticals would be at 6 feet, 10 feet, 14 feet, and so forth, from the starting point water edge. Even if the flow is divided, as in a braided channel, the sampling intervals must be identical from channel to channel and an identical transit rate must be used at each sampling vertical.

Figure 2 may be used as a guideline in selecting transit rates. The proper transit rate is one that gives a full bottle at the vertical having the greatest "unit width discharge." The maximum transit rate must not exceed 0.4 times the mean velocity, and the minimum rate must be sufficiently fast to keep from overfilling any of the sample bottles. Consequently, the transit rate to be used is limited by conditions (depth and velocity) at the sampling vertical containing the largest discharge per foot of width (largest product of depth times velocity).

A vertical transit rate not exceeding 40 percent of the stream velocity will satisfy all the limitations expressed for vertical transit rate (Guy and Norman, 1970). At this transit rate and with the axis of the sampler parallel to the flow, the resultant angle of approach of flow to the nozzle is about 20 degrees. According to the report (p. 32), the sampling error of concentration will be about 1 percent for 0.45-mm particles when the angle of approach is 20 degrees.

After selection of the sampling intervals, the vertical transit rate, the proper sampler, and proper nozzle size, sampling may be started from either bank. The sampler containing the sample bottle is lowered from the surface of the water to the streambed and immediately raised back to the surface, all at a constant rate and with the nozzle pointed directly into the flow. Care is needed not to disturb the streambed by bumping the sampler onto it or material dislodged from the bed may enter the nozzle, giving erroneous results. Each bottle is to be inspected and if coarse bed material is present, the bottle is emptied, rinsed, and resampled using the same sampling intervals or stations.

Several verticals may be sampled using the same bottle until the bottle is filled to within about 3 inches from the top. Do not fill the bottle more than this, as secondary circulation and enrichment of heavy particles may occur and the sediment concentration in the bottle will not be the same as the water-sediment mixture flowing in the stream. If overfilling does occur, the bottle is emptied, rinsed, and resampled using the same sampling intervals or stations.

When no more verticals can be safely sampled without overfilling the bottle, replace the full bottle with an empty one and continue sampling in the same manner until all verticals have been sampled. This procedure is the same whether sampling by wading methods or by reel and cable suspensions.

General guidelines for the EWI method of sampling are as follows:

1. Set out safety equipment where applicable (such as cones and signs) and assemble sampling equipment.

2. Locate the vertical containing the largest discharge per foot of width (largest product of the depth times velocity) by sounding for depth and estimating the velocity at several verticals near the center of flow.

3. If pint samples for suspended sediment and quart samples for chemical constituents are to be collected, determine the transit rates at the maximum discharge vertical for both the pint and quart containers.

   [ONCE DETERMINED, THIS TRANSIT RATE MUST BE USED FOR ALL OTHER VERTICALS]

4. From observations of depth, width, velocity, and sediment characteristics of the streamflow and a knowledge of the volume of sample required for analysis, determine the number of verticals to be sampled.

5. Determine the width of the segment to be sampled or the distance between verticals by dividing the stream width by the number of verticals decided upon. The stream width is determined from a tagline or from station markings on cableways and bridge railings. For example, if the stream width is 164 feet and the number of verticals is 10, the width of each segment to be sampled is 16.4 feet. For practical purposes, a vertical spacing of 16 feet is used. Thus, the location of the first vertical to be sampled would be at 8 feet. The second vertical would be located at 8 + 16 = 24 feet and so on (8, 24, 40, 56, 72, 88, 104, 120, 136, and 152 feet).

6. After determining the sampler transit rate and the number and locations of the verticals to be sampled, read and record the gage height and the time at which sampling is begun.

7. Move sampling and support equipment to first station to be sampled.

8. If concentrations of suspended sediment and chemical constituents are to be determined for the stream, collect separate samples for suspended sediment (in pint milk bottles) and chemical constituents (in quart bottles). A pint or quart bottle may be used to obtain samples from several verticals, provided the containers do not become completely filled. The individual suspended-sediment samples are not composited in the churn splitter by field personnel. The same quart glass bottle for chemical constituents is used for each vertical in the cross section. (Swirl the quart sample gently to keep sediment suspended and pour into churn after sampling each or several verticals.)

9. If either the pint or the quart container becomes completely filled during a sampling operation, discard the sample, as it will not be representative, and collect another sample.

[THE VOLUME OF THE SAMPLE WILL VARY CONSIDERABLY FROM VERTICAL TO VERTICAL WHEN USING THE EWI METHOD]

If the depth and velocity vary greatly within the cross section, the volume of sample from some of the verticals will be very small. Thus, the total volume in the churn spitter, after all verticals have been sampled, may be insufficient for analytical requirements. If so, a second set of samples all at the same transit rate will be needed for all verticals. It must be remembered that complete sets of samples are to be collected--that is, sampling cannot be terminated until the far side of the stream is reached.

10. After sampling has been completed, label each of the pint sediment samples with the following information:

    a. Station number, name, and location of the stream.
    b. Date.
    c. Mean time and gage height (or discharge) for the period of sample collection (after step 12).
    d. Sampling location (location in vertical section).
    e. Water temperature.
    f. Initials of sample collector.

11. Read and record the gage height and time at which sample collection was completed.

12. Calculate and record on the field notes the mean time and gage height for the period of sample collection.

13. Complete field measurements, filtration, and preservation of samples as applicable.

14. Disassemble and clean samplers as described in the section "Methods of cleaning samplers and support equipment."

Other methods of surface-water sample collection

Because of Central Laboratory requirements for samples, and the possibility of contamination from the churn splitter and other circumstances, samples for some analyses may be collected by depth-integration samplers at a reduced number of verticals.

Organic constituents (to be analyzed by the Central Laboratory).--The possibility of contamination from the churn splitter precludes its use for compositing and splitting of samples for the analysis of organic constituents. All samples for analysis of organic constituents are to be collected in glass sample bottles. The Central Laboratory requires a 1-liter sample each for herbicides and insecticides. Both samples may be collected with a depth-integrating sampler with a nylon nozzle and silicone rubber gasket from a single vertical near the centroid of flow. If the depth and velocity permit the collection of a multivertical sample