

EXHIBIT 3-17. RECOMMENDED OPERATING PROCEDURES FOR TAKING GRAB SAMPLES

- Label sample containers before sampling event
- Take a cooler with ice to the sampling point
- Take the grab from the horizontal and vertical center of the channel
- Avoid stirring up bottom sediments in the channel
- Hold the container so the opening faces upstream
- Avoid touching the inside of the container to prevent contamination
- Keep the sample free from uncharacteristic floating debris
- Transfer samples into proper containers (e.g., from bucket to sample container), however, fecal coliform, fecal streptococcus, phenols and O&G should remain in original containers
- If taking numerous grabs, keep the samples separate and labelled clearly
- Use safety precautions (see Chapter 6)

3.3 GRAB SAMPLE COLLECTION

Section 3.1.2 discussed both the parameters that must be monitored by grab sample and the conditions under which grab sampling is required. This section explains how to collect grab samples. The entire sample is collected at an uninterrupted interval (i.e., grabbed at one time). A grab sample provides information on the characterization of storm water at a given time and may be collected either manually or automatically as discussed below.

3.3.1 HOW TO MANUALLY COLLECT GRAB SAMPLES

A manual grab is collected by inserting a container under or downcurrent of a discharge with the container opening facing upstream. Generally, simplified equipment and procedures can be used. In most cases, the sample container itself may be used to collect the sample. Less accessible outfalls may require the use of poles and buckets to collect grab samples. To ensure that manual grab samples are representative of the storm water discharged, the procedures set forth in Exhibit 3-17 should be followed.

Specialized equipment and procedures may be needed, particularly in situations where storm water discharges are inaccessible or where certain parameters are monitored. For example:

- When sampling for O&G and VOCs, equipment that safely and securely houses O&G bottles or VOC vials should be used. This may be necessary because: (1) O&G will adhere to containers and thus should not be transferred from one container to another; and (2) excessive aeration during sampling may result in the partial escape of VOCs.
- Since facilities sometimes use sample bottles that already contain preservatives (as provided by contract laboratories), extreme care should be taken when filling them to avoid spills, splatters, or washout of the preservatives.

All equipment and containers that come into contact with the sample must be clean to avoid contamination. Additionally, sample collection equipment and container materials should be totally unreactive to prevent leaching of pollutants. Cleaning procedures are discussed in detail in Section 3.5.

3.3.2 HOW TO COLLECT GRAB SAMPLES BY AUTOMATIC SAMPLER

Grab samples can also be collected using programmed automatic samplers. Automatic samplers come equipped with computers that can be programmed to collect grab samples. Programming for grabs is specific to the type of automatic sampler. Some samplers are portable and have been developed specifically to sample for storm water discharges. These samplers are frequently attached to a rain gauge and/or a flow sensor. Such samplers can be programmed to initiate sample collection by one or more of the following conditions: (1) depth of flow in a channel; (2) rainfall in inches; (3) flow rate; (4) time; (5) external signal; and (6) combinations of the first three conditions. For example, an automatic sampler could be used to collect a sample at 15-minute intervals after its sensors indicate that rainfall has begun.

When using an automatic sampler, planning is very important. First, all equipment must be properly cleaned, particularly the tubing and the sample containers. There are several different types of tubing available, including rubber and Tygon tubing. Tygon tubing is commonly used since it generally does not leach contaminants. Deionized water should be drawn through the sampler to remove any remaining pollutant residuals prior to taking samples. Tubing should also be replaced periodically to avoid algae or bacterial growth.

Sampling personnel should also use adequate and appropriate containers and ensure they are properly cleaned. Section 3.5 contains information on cleaning procedures which should be followed for all equipment. Additionally, the utilization of blanks (a control used to verify the accuracy of analytical results) is recommended to determine if cross-contamination of sampling equipment has occurred. Samplers should also be programmed, set up, and supplied with a source of power. Properly charged batteries should be readily available for portable samplers in advance of a storm event and, as a backup power supply in case of power failure. Finally, although automatic samplers may be useful in some situations, several parameters are not amenable to collection by automatic sampler. These pollutants include fecal streptococcus, fecal coliforms, oil and grease and VOCs which should be collected manually, not automatically, as discussed in Section 3.1.2.

3.4 FLOW-WEIGHTED COMPOSITE SAMPLE COLLECTION

Composite samples are samples simply comprised of a series of individual sample aliquots that have been combined to reflect average pollutant concentrations of the storm water discharge during the sampling period. Composite samples can be developed based on time or flow rate. There are four different types

EXHIBIT 3-20. CONSTANT TIME - VOLUME PROPORTIONAL TO FLOW RATE

(Q)

V = volume of sample collected

DENOTES COLLECTION OF A SAMPLE
WHERE VOLUME IS PROPORTIONAL TO THE
RATE OF FLOW. THE INDIVIDUAL SAMPLES
ARE COMPOSITED INTO ONE CONTAINER

TIME (t)

Method of compositing samples proportional to flow rate

Source: Methodology for the Study of Urban Storm Generated Pollution and Control, U.S. EPA
600/2-76-145, August 1976.

(Q)

DENOTES SAMPLES OF EQUAL
VOLUME (SAME LENGTH ARROWS)
AT EQUAL TIME INTERVALS

TIME (t)

Method of compositing samples on a fixed volume-fixed time interval basis

Source: Methodology for the Study of Urban Storm Generated Pollution and Control, U.S. EPA
600/2-76-145, August 1976.

of composite samples, as follows:

- Constant Time - Constant Volume - Samples of equal volume are taken at equal increments of time and composited to make an average sample (similar to Exhibit 3-18). This method is not acceptable for samples taken for compliance with the storm water permit application regulations.
- Constant Time - Volume Proportional to Flow Increment - Samples are taken at equal increments of time and are composited proportional to the volume of flow since the last sample was taken (see Exhibit 3-19).
- Constant Time - Volume Proportional to Flow Rate - Samples are taken at equal increments of time and are composited proportional to the flow rate at the time each sample was taken (see Exhibit 3-20).
- Constant Volume - Time Proportional to Flow Volume Increment - Samples of equal volume are taken at equal increments of flow volume and composited (see Exhibit 3-21).

Generally, flow-weighted composite samples must be collected for most parameters. The methods for generating flow-weighted composite samples are discussed in the following sections.

For storm water discharge permit applications, the aliquots for flow-weighted composite samples must be collected during a representative storm for the first 3 hours, or for the duration of the storm event if it is less than 3 hours long. The storm water application regulations allow for flow-weighted composite samples to be collected manually or automatically. For both methods, equal volume aliquots may be collected at the time of sampling and then flow-proportioned and composited in the laboratory, or the aliquot may be collected based on the flow rate at the time of sample collection and composited in the field. When composite samples are collected, the regulations require that each aliquot collection be separated by a minimum of 15 minutes and that a minimum of three sample aliquots be taken within each hour of the discharge. See Exhibit 3-22

<p>EXHIBIT 3-19. CONSTANT TIME - VOLUME PROPORTIONAL TO FLOW INCREMENT</p>
<p>(V)</p> <p>TIME (t)</p> <p>Method of compositing samples proportional to flow volume at constant time interval</p>
<p>Source: Methodology for the Study of Urban Storm Generated Pollution and Control, U.S. EPA 600/2-76-145, August 1976.</p>

EXHIBIT 3-21. CONSTANT VOLUME - TIME PROPORTIONAL TO FLOW VOLUME INCREMENT

(V)

DENOTES SAMPLES OF EQUAL VOLUME
(SAME LENGTH ARROWS) AT CONSTANT
FLOW INCREMENTS (VARIABLE TIME)

TIME (t)

Method of compositing samples of equal volume at equal increments of flow

Source: Methodology for the Study of Urban Storm Generated Pollution and Control, U.S. EPA
600/2-76-145, August 1976.

EXHIBIT 3-22. EXAMPLE OF SAMPLING INTERVALS

Suppose that a storm water discharge began at 2:15 p.m. and lasted until 5:15 p.m. on a Friday. The field staff person wants to collect the samples at regular intervals, so s/he plans to collect an aliquot with a volume that is proportional to the flow every 20 minutes. After the third hour of collection, the field staff person must deliver the samples to the laboratory (which is 10 minutes away). The laboratory closes at 5:00 p.m. So, s/he should take the last sample at 4:45 p.m. One way of doing this would be to collect samples (in hour three) at 4:15, 4:30, and 4:45 p.m. This would comply with the three-sample minimum in hour three (4:15-5:15 p.m.) and the required 15-minute minimum interval between collections. It would also allow the field staff person to get the samples to the lab before it closes for the weekend. On the other hand, if s/he missed the sample collection at 4:15 p.m. and instead, collected the sample at 4:20 p.m., then s/he would have to collect the next sample at 4:35 p.m. and the last sample at 4:50 p.m., and the field staff person would not be able to deliver the sample until Monday (by which time the required maximum holding time would be exceeded), and the sampling would need to be repeated.

for an example of how this requirement may be fulfilled.

The provisions set forth in 40 CFR 122.21(g)(7) for collecting flow-weighted composite samples establish specific requirements for minimum time duration between sample aliquots. Where these conditions cannot be met, the permitting authority may allow alternate protocols with respect to the time duration between sample aliquots (see Chapter 5). However, permission from the permitting authority must be obtained before changes are initiated. Considerations applicable to the collection of flow-weighted composites by automatic and manual techniques are discussed in the following sections.

3.4.1 HOW TO MANUALLY COLLECT FLOW-WEIGHTED COMPOSITE SAMPLES

Manually collected, flow-weighted composite samples may be appropriate for a facility that prefers not to invest in automatic equipment. This technique is cost-effective for short-term monitoring programs and for facilities where few outfalls are being sampled. The fundamental requirement for facilities that use these methodologies is that they should have personnel available to perform the sampling when needed. Those facilities where VOCs analysis of storm water discharges are required should manually collect composite samples since these parameters may not be amenable to sampling by automatic samplers. Compositing of VOC samples should be conducted in the laboratory as discussed in Section 3.5.2.

The manual collection of a flow-weighted sample is performed in the same manner as taking manual grab samples (see Section 3.3.1). The only difference is that a series of samples (or aliquots) will be collected. As discussed in the previous section, there are two ways to manually collect and combine the aliquots for a flow-weighted sample:

- Collect sample aliquot volumes based on the flow at the time of sampling which can immediately be combined to make the composite sample in the field (see Exhibit 3-23)
- Collect equal volume sample aliquots at the time of sampling and then flow-proportion and composite the aliquots in the laboratory (see Exhibit 3-24).

EXHIBIT 3-23. EXAMPLE OF HOW TO COLLECT SAMPLE ALIQUOT VOLUMES BASED ON FLOW, AND PROPORTION AND COMPOSITE IN THE FIELD

Step 1: Determine the necessary volume for compositing purposes.

Example: To fulfill analyses for all parameters in Section VII.A of Form 2F for which composite samples are required [Biochemical Oxygen Demand (BOD₅), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), Total Kjeldahl Nitrogen (TKN), nitrate plus nitrite, and phosphorous] a total composite sample volume of 5,000 ml is needed by the contract laboratory.

Step 2: Determine an appropriate interval for collection of samples.

Example: Manually collected flow-weighted composite samples must consist of at least three sample aliquots collected per hour and must be gathered at least 15 minutes apart. For this example, sample aliquots will be collected exactly 20 minutes apart.

Step 3: Estimate or measure the volume of discharge for each sampling event.

Example: A discharge flow volume of 4.8 cubic feet will be used here.

Step 4: Convert the discharge flow volume to liters.

Example: To convert cubic feet to liters, use the conversion factor of 28.32 liters per 1 cubic foot as set forth in the following formula:

$$\text{Volume (liters)} = \text{Volume (cubic feet)} \times \frac{28.32 \text{ liters}}{1 \text{ cubic foot}}$$

$$\text{Volume} = 4.8 \text{ cubic feet} \times \frac{28.32 \text{ liters}}{1 \text{ cubic foot}} = 136 \text{ liters}$$

Step 5: Using Steps 3 and 4, volumes that have been discharged between the collection of each aliquot can be calculated.

(Note that the discharge volumes provided for aliquot numbers 2-9 have already been given for the purposes of this exhibit.)

Example: The procedures set forth in Section 3.2 may be used to calculate discharge volumes. The following table presents aliquot numbers, time of aliquot collection, and discharge volumes.

Aliquot Number	Time of Aliquot Collection	Discharged Volume
1	2:15 p.m.	136 liters
2	2:35 p.m.	200 liters
3	2:55 p.m.	122 liters
4	3:15 p.m.	178 liters
5	3:35 p.m.	156 liters
6	3:55 p.m.	117 liters
7	4:15 p.m.	94 liters
8	4:30 p.m.	21 liters
9	4:45 p.m.	12 liters

**EXHIBIT 3-23. EXAMPLE OF HOW TO COLLECT SAMPLE ALIQUOT VOLUMES
BASED ON FLOW, AND PROPORTION AND COMPOSITE IN THE
FIELD (Continued)**

Step 6: Determine the appropriate minimum aliquot volume as the basis for collecting other aliquot samples which together will provide adequate volume to fulfill the analytic requirements.

Example: In Step 1, it was determined that at least 5,000 ml of sample were required for flow-weighted composite sample analytical testing. As discussed in Section 3.4.1, basing the sample collection on a minimum aliquot volume of 1,000 ml gathered every interval (i.e., every 15 minutes) should result in adequate sample volume.

Step 7: Calculate the volume of the sample aliquot which must be collected during each aliquot sample period using the following formula:

$$\text{Aliquot volume (ml)} = \text{Minimum aliquot volume (ml)} \times \frac{\text{Aliquot's discharge volume (liters)}}{\text{Initial discharge volume (liters)}}$$

Step 6 shows that the minimum aliquot volume is 1,000 ml.

$$\text{Aliquot \#1 volume (ml)} = 1,000 \text{ ml} \times \frac{136 \text{ liters}}{136 \text{ liters}} = 1,000 \text{ ml}$$

$$\text{Aliquot \#2 volume (ml)} = 1,000 \text{ ml} \times \frac{200 \text{ liters}}{136 \text{ liters}} = 1,471 \text{ ml}$$

$$\text{Aliquot \#3 volume (ml)} = 1,000 \text{ ml} \times \frac{122 \text{ liters}}{136 \text{ liters}} = 897 \text{ ml}$$

$$\text{Aliquot \#4 volume (ml)} = 1,000 \text{ ml} \times \frac{178 \text{ liters}}{136 \text{ liters}} = 1,309 \text{ ml}$$

$$\text{Aliquot \#5 volume (ml)} = 1,000 \text{ ml} \times \frac{156 \text{ liters}}{136 \text{ liters}} = 1,147 \text{ ml}$$

$$\text{Aliquot \#6 volume (ml)} = 1,000 \text{ ml} \times \frac{117 \text{ liters}}{136 \text{ liters}} = 860 \text{ ml}$$

$$\text{Aliquot \#7 volume (ml)} = 1,000 \text{ ml} \times \frac{94 \text{ liters}}{136 \text{ liters}} = 691 \text{ ml}$$

$$\text{Aliquot \#8 volume (ml)} = 1,000 \text{ ml} \times \frac{21 \text{ liters}}{136 \text{ liters}} = 154 \text{ ml}$$

$$\text{Aliquot \#9 volume (ml)} = 1,000 \text{ ml} \times \frac{12 \text{ liters}}{136 \text{ liters}} = 88 \text{ ml}$$

A table of these calculations follows:

Aliquot Number	Discharged Volume	Aliquot Volume
1	136 liters	1,000 ml
2	200 liters	1,471 ml
3	122 liters	897 ml
4	178 liters	1,309 ml
5	156 liters	1,147 ml
6	117 liters	860 ml
7	94 liters	691 ml
8	21 liters	154 ml
9	12 liters	88 ml

In conclusion, a combination of the above sample aliquots result in a composite of 7,617 ml.

EXHIBIT 3-24. EXAMPLE OF HOW TO MANUALLY COLLECT EQUAL SAMPLE ALIQUOTS WHICH ARE LATER FLOW-PROPORTIONED AND COMPOSITED IN THE LABORATORY

Step 1: Determine the necessary volume for compositing purposes.

Example: To fulfill analyses for all parameters in Section VII.A of Form 2F for which composite samples are required (BOD₅, COD, TSS, TKN, nitrate plus nitrite, and phosphorous) a total composite sample volume of 5,000 ml is needed by the contract laboratory.

Step 2: Determine an appropriate interval for collection of samples.

Example: Manually collected flow-weighted composite samples must consist of at least nine sample aliquots and must be gathered at least 15 minutes apart; only three or four samples per hour may be taken. For convenience, the minimum number of three is chosen. Sample aliquots will be collected every 20 minutes.

Step 3: Determine the aliquot which should be taken during each sampling event.

Example: At least 5,000 ml of sample is required for flow-weighted composite sample analytical testing. As discussed in Section 3.4.1, a minimum aliquot volume of 1,000 ml gathered every interval (i.e., every 15 minutes) should result in adequate sample volume to be used for later flow-weighted compositing.

Step 4: Estimate or measure the volume of discharge for each sampling event while collecting a discrete 1,000-ml aliquot, as discussed in Step 3, for later compositing.

Example: Section 3.2 discusses methods to calculate total discharge volumes. A discharge flow volume of 4.8 cubic feet will be used here.

Step 5: Convert the discharge flow volume to liters.

Example: To convert cubic feet to liters, use the conversion factor of 28.32 liters per 1 cubic foot as set forth in the following formula:

$$\text{Volume (liters)} = \text{Volume (cubic feet)} \times \frac{28.32 \text{ liters}}{1 \text{ cubic foot}}$$

$$\text{Volume} = 4.8 \text{ cubic feet} \times \frac{28.32 \text{ liters}}{1 \text{ cubic foot}} = 136 \text{ liters}$$

EXHIBIT 3-24. EXAMPLE OF HOW TO MANUALLY COLLECT EQUAL SAMPLE ALIQUOTS WHICH ARE LATER FLOW-PROPORTIONED AND COMPOSITED IN THE LABORATORY (Continued)

Step 6: Using Steps 3 and 4, calculate the volumes that have been discharged between the collection of each aliquot.

Example: The procedures set forth in Section 3.2 may be used to calculate discharge volumes. The following table presents aliquot numbers, time of aliquot collection, and discharge volumes (note that the discharge volumes provided for aliquot numbers 2-9 were chosen for purposes of this exhibit).

Aliquot Number	Time of Aliquot Collection	Discharged Volume
1	2:15 p.m.	136 liters
2	2:35 p.m.	200 liters
3	2:55 p.m.	122 liters
4	3:15 p.m.	178 liters
5	3:35 p.m.	156 liters
6	3:55 p.m.	117 liters
7	4:15 p.m.	94 liters
8	4:30 p.m.	21 liters
9	4:45 p.m.	12 liters

Step 7: Determine the aliquot sample which is associated with the greatest discharge volume.

Example: Aliquot number 2 was taken when the volume was 200 liters. This is the largest discharge volume.

Step 8: Calculate the volume of sample aliquot which must be used subsequent to the sample event to comprise a flow-weighted composite sample. The following formula should be used:

$$\text{Aliquot volume (ml)} = \text{Minimum aliquot volume (ml)} \times \frac{\text{Aliquot's discharge volume (liters)}}{\text{Largest discharge volume (liters)}}$$

Step 3 shows that the minimum aliquot volume is 1,000 ml. Using this value and the data determined as part of Steps 6 and 7, the following can be calculated:

$$\text{Aliquot \#1 volume (ml)} = 1,000 \text{ ml} \times \frac{136 \text{ liters}}{200 \text{ liters}} = 680 \text{ ml}$$

$$\text{Aliquot \#2 volume (ml)} = 1,000 \text{ ml} \times \frac{200 \text{ liters}}{200 \text{ liters}} = 1,000 \text{ ml}$$

$$\text{Aliquot \#3 volume (ml)} = 1,000 \text{ ml} \times \frac{122 \text{ liters}}{200 \text{ liters}} = 610 \text{ ml}$$

$$\text{Aliquot \#4 volume (ml)} = 1,000 \text{ ml} \times \frac{178 \text{ liters}}{200 \text{ liters}} = 890 \text{ ml}$$

$$\text{Aliquot \#5 volume (ml)} = 1,000 \text{ ml} \times \frac{156 \text{ liters}}{200 \text{ liters}} = 780 \text{ ml}$$

$$\text{Aliquot \#6 volume (ml)} = 1,000 \text{ ml} \times \frac{117 \text{ liters}}{200 \text{ liters}} = 585 \text{ ml}$$

EXHIBIT 3-24. EXAMPLE OF HOW TO MANUALLY COLLECT EQUAL SAMPLE ALIQUOTS WHICH ARE LATER FLOW-PROPORTIONED AND COMPOSITED IN THE LABORATORY (Continued)

$$\text{Aliquot \#7 volume (ml)} = 1,000 \text{ ml} \times \frac{94 \text{ liters}}{200 \text{ liters}} = 470 \text{ ml}$$

$$\text{Aliquot \#8 volume (ml)} = 1,000 \text{ ml} \times \frac{21 \text{ liters}}{200 \text{ liters}} = 105 \text{ ml}$$

$$\text{Aliquot \#9 volume (ml)} = 1,000 \text{ ml} \times \frac{12 \text{ liters}}{200 \text{ liters}} = 60 \text{ ml}$$

A table of these calculations follows

Aliquot Number	Discharged Volume	Aliquot Volume
1	136 liters	680 ml
2	200 liters	1,000 ml
3	122 liters	610 ml
4	178 liters	890 ml
5	156 liters	780 ml
6	117 liters	585 ml
7	94 liters	470 ml
8	21 liters	105 ml
9	12 liters	60 ml

In conclusion, a combination of the above sample aliquots results in a composite sample of **5,100 ml**.

When uniform time intervals are used between the collection of the sample aliquots, the volumes of each aliquot used in the composite sample can be determined based on either volumes of flow or the flow rate, as they will result in similar proportions. However, when there are different time intervals between the sample aliquots, the individual sample aliquot volumes should be based on the runoff volume (calculated from the individual flow rates and durations) associated with each sample aliquot.

Generally, 1,000 ml for each aliquot collected should provide enough sample volume, when composited, for pollutant analyses of the required parameters contained in Section VII.A of Form 2F (see Section 3.6). More aliquot volume may be required if sampling is conducted for additional parameters. The laboratory conducting the analyses should always be contacted prior to a sampling event to determine how much sample volume they will require.

Manually collected flow-weighted composite samples can also be prepared by collecting sample aliquots of equal volume where the collection times are related to the volume of discharge which has passed since the last sample aliquot collection. However, this method is subject to fluctuating flow rates and volumes which may dictate that samples be taken prior to the 15-minute interval required by the regulations. In that case, the alternative sampling protocol would have to be approved by the permitting authority.

3.4.2 HOW TO COLLECT FLOW-WEIGHTED COMPOSITE SAMPLES BY AUTOMATIC SAMPLER

The typical automatic sampler collects sample aliquots after a specific interval. These aliquots can be flow-weight composited by the automatic sampler; or by hand in the laboratory. The automatic sampler may be programmed in one of three ways: (1) to collect a sample at equal time intervals and varying aliquot volumes commensurate with the flow (either rate or volume) that has passed; (2) to collect equal volume aliquots at varying time intervals commensurate with the flow volume that has passed; or (3) to collect equal volume aliquots of sample at equal time intervals.

The first two methods automatically composite the sample but require that the sampler be connected to a flow meter such that the sampler determines either the flow rate or the amount of volume that passes. Since these methods automatically composite samples, one main sample container may be used to receive all aliquots. The third method automatically collects the sample aliquots but does not automatically flow-weight composite the sample. As such, discrete sample containers must be used, and manual flow-weighted compositing must be conducted after the aliquots are collected. Exhibits 3-23 and 3-24 in Section 3.4.1 describe the manual compositing procedures that should be followed.

Manufacturers' instructions for the use of an automatic sampler provide the best explanation of programming options and should be consulted for information on programming samplers for storm water collection. Some of the points regarding automatic samplers discussed in Section 3.3.2 should also be considered.

3.5 SAMPLE HANDLING AND PRESERVATION

Samples must be handled and preserved in accordance with 40 CFR Part 136. This section describes acceptable analytical methods, including requirements regarding sample holding times, containers,

sizes, and preservation requirements. For each pollutant or parameter that may have to be analyzed, 40 CFR Part 136 includes information on:

- Container types to be used to store the samples after collection
- Procedures to correctly preserve the samples
- The maximum holding time allowed for each parameter.

The following sections present a detailed discussion of preservation techniques and sample handling procedures. Technical Appendix C presents a matrix of required containers, preservation techniques, and holding times for each parameter. Most laboratories can provide clean sample containers, preservatives, sealing, chain-of-custody forms and can advise further on sample handling and preservation.

3.5.1 DECONTAMINATION OF SAMPLE EQUIPMENT CONTAINERS

Storm water sample containers should be cleaned and prepared for field use according to the procedures set forth in 40 CFR Part 136. A summary of the procedures is presented below for plastic containers, any or all of which may be performed by the laboratory or container distributor:

- Nonphosphate detergent and tap water wash
- Tap water rinse
- 10 percent nitric acid rinse (only if the sample is to be analyzed for metals)
- Distilled/deionized water rinse
- Total air dry.

To clean glass containers, the same steps should be taken; but, after the distilled/deionized water rinse, the containers should be rinsed with solvent if appropriate prior to total air drying. After the decontamination procedures have been accomplished, the sample containers should be capped or sealed with foil, and the sampling device should be protected and kept clean. It is a good idea to label sample containers after cleaning. The laboratory should keep a record of the technician performing the cleaning procedure as well as the date and time. This begins the required chain-of-custody procedure for legal custody (see Section 3.10 for more information). A chain-of-custody record accompanies each sample to track all personnel

handling the sample. This record is essential to trace the sample integrity in the event that quality control checks reveal problems. For this reason, as well as to avoid problems if contamination issues arise, it is suggested that the laboratory performing the analysis perform the cleaning.

3.5.2 SAMPLE PRESERVATION AND HOLDING TIMES

Preservation techniques ensure that the sample remains representative of the storm water discharge at the time of collection. Since many pollutants in the samples collected are unstable (at least to some extent), the sample should be analyzed immediately or preserved or fixed to minimize changes between the time of collection and analysis. Because immediate analysis is not always possible, most samples are preserved regardless of the time of analysis.

Problems may be encountered when flow-weighted composite samples are collected. Since sample deterioration can take place during the compositing process, it is necessary to preserve or stabilize the samples during compositing in addition to preserving aggregate samples before shipment to the laboratory. Preservation techniques vary depending on the pollutant parameter to be measured; therefore, familiarity with 40 CFR Part 136 (see Technical Appendix C) is essential to ensure effective preservation. It is important to verify that the preservation techniques for one parameter do not affect the analytical results of another in the same sample. If this is the case, two discrete samples should be collected and preserved accordingly.

Sample preservation techniques consist of refrigeration, pH adjustment, and chemical fixation. pH adjustment is necessary to stabilize the target analyte (e.g., addition of NaOH stabilizes cyanide); acidification of total metal samples ensures that metal salts do not precipitate. Refrigeration is the most widely used technique because it has no detrimental effect on the sample composition (i.e., it does not alter the chemistry of the sample), and it does not interfere with most analytical methods. Refrigeration requires the sample to be quickly chilled to a temperature of 4°C. This technique is used at the beginning of sample collection in the field, and is continued during sample shipment, and while the sample is in the laboratory. Even though samples taken for compositing purposes are taken over time each individual sample must be refrigerated. If taken manually, the samples can be placed in an ice box. If taken by a automatic sampler, the sampler unit should have refrigeration capabilities. The analytical laboratory may provide chemicals necessary for fixation, or may tell sampling personnel where they can be purchased.

In addition to preservation techniques, 40 CFR Part 136 indicates maximum holding times. A detailed list of holding times appears in Technical Appendix C. The holding time is the maximum amount of time that samples may be held before analysis and still be considered valid. Samples exceeding these holding times are considered suspect and sample collection may have to be repeated.

Although Technical Appendix C provides required sample containers, preservation techniques, and holding times, some of the more commonly monitored parameters warrant additional discussion. The following provides a more detailed discussion of considerations pertaining to cyanide, VOCs, organics and pesticides, O&G, pH, total residual chlorine, fecal coliform, fecal streptococcus, and 5-day Biochemical Oxygen Demand (BOD₅).

Cyanide

Cyanide is very reactive and unstable. If the sample cannot be analyzed immediately, it must be preserved by pH adjustment after collection. However, prior to pH adjustment, procedures to eliminate residual chlorine and sulfides must be followed immediately.

Where chlorine has the possibility of being present, the sample should be tested for residual chlorine by using potassium iodide-starch test paper previously moistened with acetate buffer. If the sample contains residual chlorine (a blue color indicates the need for treatment), ascorbic acid must be added 0.6 gram (g) at a time until the tests produce a negative result; then, an additional 0.6 g of ascorbic acid should be added to the sample.

Samples containing sulfides may be removed, in which case the holding time is extended to 14 days. Sulfides must be removed as follows:

- Use lead acetate paper moistened with an acetic acid buffer solution to test for the presence of sulfide. Darkening of the lead acetate paper indicates sulfide is present in the sample.
- Add cadmium nitrate to be added to the sample in a manner similar to the ascorbic acid until the test is negative.
- Filter with a 0.45 micrometer (µm) filter and prefilter combination immediately after.

After chlorine and sulfide residuals have been eliminated, the pH must be adjusted to greater than 12.0 standard units (s.u.) and chilled to 4°C.

If cyanide is suspected to be present, the sampling personnel should bring all materials mentioned above to the sampling location.

VOCs

Sampling for VOCs requires the use of a glass vial. The vial should contain a teflon-coated septum seal. Volatiles will escape from the water to the air if any air is entrapped in the container. Therefore, the sample should be collected so that there are no air bubbles in the container after the screw cap and septum seal are applied. To ensure that air bubbles are not trapped in the vial, the following procedures should be followed:

- Fill the vial until a reverse meniscus forms above the top of the vial
- Screw on the cap (the excess sample will overflow)
- Invert the vial to check for the presence of air bubbles
- If air bubbles are observed, the vial should be opened, emptied, then completely refilled, and the first three actions should be repeated.

VOC samples should not be composited in the field. To composite a sample, the sampling personnel would have to mix it thoroughly. This mixing action would aerate the sample and cause volatiles to be lost. Therefore, VOC samples should be sent to the laboratory where they can be immediately, and carefully, composited and analyzed with minimal volatilization as per method Nos. 502.1, 502.2, 524.1, and 524.2 as described at 40 CFR 141.24(f)(14)(iv) and (v). There are two ways flow-weighted compositing of VOCs can be accomplished—mathematical compositing or procedural compositing as discussed below.

Mathematical Compositing

In this method, the grab samples are analyzed separately. The sampling personnel collect the requisite number of samples and send them to the laboratory. The laboratory performs the individual analyses on each sample. Five ml (or 25 ml if greater sensitivity is required) of each grab sample are placed into the purge vessel of the GC or GC/MS for analysis. Special precautions must be made to maintain zero headspace in the syringe used to transfer the VOC sample into the purge vessel of the GC or GC/MS. These analytical results are mathematically flow-weight composited using the calculation in Exhibit 3-24. The concentrations (C) should be adjusted by using the following formula:

$$\text{Adjusted Concentration} = \frac{\text{Individual Aliquot Volume}}{\text{Total Composite Sample}} \times C$$

Each sample concentration should be adjusted, and all adjusted concentrations added, to obtain the flow-weighted VOC composite using this method.

Procedural Compositing

For the second method, sampling personnel collect the requisite number of samples and provide the laboratory with flow-weighted values for each sample using the calculation in Exhibit 3-24. The laboratory technician then draws the necessary volume from each aliquot into an adequately sized syringe, physically combining the samples to result in a flow-weighted composite sample for VOC analysis. Necessary volumes are drawn into the syringe with a volume control fitting. The samples are thus composited directly in the syringe and then placed in the purge vessel of the GC or GC/MS. The advantage of this procedure is that only one analysis on the GC or GC/MS has to be performed.

Although the applicant is required to report only flow-weighted composite concentrations, the mathematical compositing method may provide more information, as it will indicate the concentrations of each separate grab sample. For example, if the procedural compositing method is employed and one of the samples has a high concentration and the other three have non-detectable concentrations, the result will be an average which does not represent the concentration in any of the separate grab samples. In certain cases it may be important to know the concentration of each grab as well as the composite concentration. The mathematical compositing method would be the most appropriate compositing method in these cases.

Organics and Pesticides

The procedures affecting organics and pesticides [base/neutral/acids and pesticide polychlorinated biphenyls (PCBs)] are less complex than VOC procedures. Glass containers must be used for sample collection purposes, amber glass should be used to eliminate the potential for reactivity caused by light. These samples should be maintained at 4°C during storage and shipment. A preservative in the form of 0.008 percent sodium thiosulfate (Na₂S₂O₃) must be added to organic samples if residual chlorine is present. To determine if chlorine is present, a small color indicator test kit can be used. Eighty ml of Na₂S₂O₃ per liter of sample must then be added and mixed well until chlorine tests indicate a negative result

as per methods 604 and 625 of 40 CFR Part 136 Appendix A. The pH of pesticide samples must be adjusted to between 5 and 9 s.u.

Oil and Grease

O&G tends to adhere to the surfaces that it contacts. Therefore, it should not be transferred from one container to another; rather, a 1-liter container should be used to take the sample. The container used for O&G must be made of glass. A teflon insert should be included in the glass container's lid. However, if teflon is not available, aluminum foil extending out from under the lid may be used. Samples for O&G must be preserved by adding sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) to a pH of less than 2 s.u. and then stored at 4°C.

Additional Considerations

Some pollutants have specific analysis requirements due to short holding times that the applicant must consider. For example:

- Requirements to analyze immediately (pH, total residual chlorine, temperature, sulfite, and dissolved oxygen)
- Requirements to preserve immediately and analyze within 6 hours (fecal coliform and fecal streptococcus)
- Requirements to analyze within 48 hours (BOD_5).

Because of these requirements, field testing equipment may need to be purchased, borrowed, or rented for those parameters that may require field analysis. If the laboratory is located nearby, analysis in the field may not be required.

Laboratories do not always operate in the evenings or on weekends. As a result, holding times for samples taken in the late afternoon or on a Friday may be exceeded. To prevent this from occurring, close coordination with laboratories is necessary. The latest date and time of delivery should be established to avoid taking samples, only to discover they cannot be accepted by the laboratory and analyzed in accordance with 40 CFR Part 136 requirements.

3.6 SAMPLE VOLUMES

presents minimal suggested sample volumes for specific parameters. This exhibit should be consulted so that the proper volume is collected for analysis of each pollutant of concern. This exhibit may not include all parameters; if a particular parameter is not listed, refer to 40 CFR Part 136.

3.7 SAMPLE DOCUMENTATION

Information should be submitted to the laboratory with the sample to ensure proper handling by the laboratory. Exhibit 3-26 is an example form which can be used to document the following information.

- Unique Sample or Log Number - All samples should be assigned a unique identification number. If there is a serial number on the transportation case, the sampling personnel should add this number to the field records.
- Date and Time of Sample Collection - Date and time of sample collection (including notation of a.m. or p.m.) must be recorded. In the case of composite samples, the sequence of times and aliquot size should be noted.
- Source of Sample, Including Facility Name and Address - Use the outfall identification number from the site map with a narrative description; a diagram referring to the particular site where the sample was taken should be included.
- Name of Sampling Personnel - The names and initials of the persons taking the sample must be indicated. For a composite sample, the names of the persons installing the sampler and the names of the persons retrieving the sample should be included.
- Sample Type - Each sample should indicate whether it is a grab or composite sample. If the sample is a composite, the volume and frequency of individual aliquots should be noted.
- Preservation Used - Any preservatives (and the amount) added to the sample should be recorded. The method of preservation (e.g., refrigeration at 4°C) should be indicated.
- Analysis Required - All parameters for which the sample must be analyzed at the laboratory should be specified.

- Flow - If flow is measured at the time of sampling, the measurement must be recorded and accompanied by a description of the flow measurement method and calculations.
- Date, Time, and Documentation of Sample Shipment - The shipment method (e.g., air, rail, or bus) as well as the shipping papers or manifest number should be noted.
- Comments - All relevant information pertaining to the sample or the sampling site should be recorded. Such comments could include the condition of the sample site, observed characteristics of the sample, environmental conditions that may affect the sample, and problems encountered during sampling.

3.8 SAMPLE IDENTIFICATION AND LABELING

Prior to collection of the sample, a waterproof, gummed sample identification label or tag should be attached to the sample container. This label should contain relevant information for sample analysis, such as:

- Facility name
- Name of the sample collector
- Sample identification number
- Date and time of sample collection
- Type of analysis required
- Location of sample collection
- Preservatives used
- Type of sample (grab or composite).

Sample lids should be used to protect the sample's integrity from the time it is collected to the time it is opened in the laboratory. The lid should contain the collector's name, the date and time the sample was collected, and a sample identification number. Information on the seal must be identical to the information on the label. In addition, the lid should be taped shut so that the seal must be broken to open the sample container. Caution should be taken to ensure that glue from tape and label tag wires do not contaminate samples, particularly those containing volatile organics and metals. Also, waterproof ink should be used to avoid smearing on the label from melted ice used for cooling.

3.9 SAMPLE PACKAGING AND SHIPPING

If the samples are not hand-delivered to the laboratory or analyzed in an onsite laboratory, they should be placed in a transportation case (e.g., a cooler) along with the chain-of-custody record form, pertinent field records, and analysis request forms, and shipped to the laboratory. Glass bottles should be wrapped in foam rubber, plastic bubble wrap, or other material to prevent breakage during shipment. The wrapping can be secured around the bottle with tape. The container lid should also be sealed with tape. Samples should be placed in ice or a synthetic ice substitute that will maintain the sample temperature at 4°C throughout shipment. Ice should be placed in double-wrapped watertight bags so the water will not leak from the shipping case. Metal or heavy plastic ice chests make good sample transportation cases. Filament tape wrapped around each end of the ice chest ensures that it will not open during transport. Sampling records (preferably laminated or waterproof) can be placed in a waterproof envelope and taped to the inside of the transportation case to avoid getting them wet in case a sample container or an ice bag leaks. Shipping containers should also be sealed to prevent tampering. A copy of all sampling records should be kept onsite in case they are requested by the permitting authority.

Most samples will not require any special transportation precautions except careful packaging to prevent breakage and/or spillage. If the sample is shipped by common carrier or sent through the U.S. mail, it must comply with Department of Transportation Hazardous Materials Regulations (49 CFR Parts 171-177). Air shipment of hazardous materials samples may also be covered by requirements of the International Air Transport Association (IATA). Before shipping a sample, the facility should be aware of, and follow, any special shipping requirements. Special packing and shipping rules apply to substances considered hazardous materials as defined by IATA rules. Storm water samples are not generally considered hazardous materials, but in the event of a spill, leakage, etc., at the collection site hazardous materials may be present in the samples. Be aware, before sampling, of what hazardous materials may be in the discharge drainage area. If the presence of hazardous materials is suspected, do not sample unless properly trained.

3.10 CHAIN-OF-CUSTODY PROCEDURES

Once samples have been obtained and collection procedures are properly documented, a written record of the chain of custody of that sample should be made. This is recommended so the applicant can be confident that the samples have not been tampered with and that the sample once analyzed is representative of the storm water discharge. "Chain-of-custody" refers to the documented account of changes in possession that occur for a particular sample or set of samples. The chain-of-custody record allows an accurate step-by-step recreation of the sampling path, from origin through analysis. Information necessary in chain-of-custody is:

- Name of the persons collecting the sample
- Sample ID numbers
- Date and time of sample collection
- Location of sample collection
- Names and signatures of all persons handling the samples in the field and in the laboratory.

To ensure that all necessary information is documented, a chain-of-custody form should be developed. An example of such a form is found in Exhibit 3-27 Chain-of-custody forms should be printed on carbonless, multipart paper so all personnel handling the sample receive a copy. All sample shipments should be accompanied by the chain-of-custody record and a copy of these forms should be retained by the originator. In addition, all receipts associated with the shipment should be retained. Carriers typically will not sign for samples; therefore, seals must be used to verify that tampering has not occurred during shipment.

EXHIBIT 3-27. EXAMPLE OF CHAIN-OF-CUSTODY FORM

Source: U.S. EPA, Region 8

When transferring possession of samples, the transferee should sign and record the date and time on the chain-of-custody record. In general, custody transfers are made for each sample, although samples may be transferred as a group. Each person who takes custody should fill in the appropriate section of the chain-of-custody record.