

Sample Collection

A sample is a part or piece taken from a larger entity and presented as being representative of the whole. The concept of being “representative” is highly important and required by the permit. All subsequent conclusions, decisions, and action steps will depend to some degree on the validity of the samples initially collected. Without proper sampling techniques, even the most precise and accurate analytical procedures will produce results which do not reflect the actual pollutant levels that are being discharged from the permitted facility.

Sample Collection Plan

Effective sample collection includes development of a sample plan that contains the following items:

- X Parameters to be sampled
- X Required sample containers and caps
- X Identification of proper equipment and procedures for safe, accurate and effective sampling
- X Identification of representative sampling sites
- X Procedures to collect adequate volumes for the required analyses
- X Procedures to preserve samples to maintain integrity
- X Identification of each sample by proper labeling
- X Procedures to ensure that holding times are not exceeded
- X QA/QC and chain of custody procedures
- X Sample transport procedures

In the event a commercial laboratory is hired to collect the samples, the sample collection should be provided by the permittee to the laboratory or the plan can be developed by the laboratory and approved by the permittee. If a commercial laboratory collects the samples, the permittee is responsible for overseeing the sample collection to assure the samples are being collected per the plan.

Sample type

The permit will specify what type of sample is required. The type of sample must be documented.

- X Grab samples are individual samples which are manually collected within 15 minutes. This type of sample represents the condition existing at that particular moment the sample is collected. Certain parameters must be collected by the grab method. Some common parameters for stormwater monitoring which must be collected as grab samples is pH and oil and grease. Grab sample holding times begin when the sample is collected.
- X Composite samples are samples collected over time, either by continuous sampling or by mixing discrete samples collected throughout the sampling period (for example, 24 hours). Composite samples reflect the average wastestream during the compositing period. The NPDES Permit states that all composite samples must be flow weighted, that is, each amount collected is dependent on the flow at the time the individual aliquot was collected. Composite sample holding times begin when the final portion is collected.

Sample containers

Sample containers may be clear glass, amber glass, polypropylene plastic or Teflon. Some samples, such as oil and grease require the bottle cap be Teflon lined. Sample containers can be

either disposable or re-useable.

Containers that are purchased as precleaned and treated must have manufacturer certification stating so. Preservatives may already be in the sample bottles when received. The volumes and types of preservatives must be specified.

When sampling with bottle already containing preservative, care must be taken not to overfill the container or spill the preservative. After collection and preservation with acids or bases, the pH should be verified to assure the target pH is reached. Do not verify pH on oil and grease samples.

Sample Identification

Sample identification must be present on the sample container. Waterproof gummed labels or tags should be attached to all the sample containers. If tags are used, assure the tags do not loosen during transport. Labels or tags should be clearly written in indelible ink and include the following:

- X Exact location the sample was collected
- X Date & time the sample was collected
- X Preservatives used (cooling is a preservative)
- X Sample collector's name
- X Analyses to be performed

Sample Preservation

Sample preservation is required to maintain the sample integrity during sample collection and between sample collection and analysis. Preservatives vary according analyses to be done on the sample. Preservatives include cooling the sample, chemical addition or both. pH samples cannot be preserved and must be analyzed within 15 minutes of sample collection. A table of required sample containers, preservatives and maximum holding time is attached. Pay attention to the footnotes!

Sample Holding Time

Sample holding times depend on the specific parameter. If the maximum allowable holding time is exceeded, the sample is invalid and is not reportable. pH analyses must be done on site so as not to exceed the holding time. Failure to produce a reportable analysis is a violation of the permit.

Sampling Equipment

Sampling equipment must be documented as being clean and free from contaminates. Reusable equipment should be washed with hot water and detergent, rinsed thoroughly with tap water and triple rinsed with organic free water. Further rinsing with acetone is advised only when the type of tubing (e.g., Teflon) is not susceptible to dissolution by the solvent. Sample collection tubing should be changed between sample locations to prevent cross contamination. Pump tubing should also be changed when changing sample locations. A log should be maintained of who cleaned the equipment, the method of cleaning, and the date of cleaning. Re-usable sample equipment requires equipment blanks to demonstrate cleanliness. Disposable, pre-cleaned sampling equipment may eliminate equipment blank requirements.

Chain-of-Custody Procedures

Custody seals should be used on the individual sample containers to prevent tampering and protect the sample integrity. A proper custody seal cannot be removed without showing evidence of tampering. Some seals available through scientific supply companies do not necessarily meet this criteria.

Once a sample has been obtained and properly collected, a written record of the chain of possession of that sample is made. Chain-of-custody (COC) refers to the documented account of changes in possession that occur for a particular sample or set of samples. The COC will also contain information on the sample type, collection methods, dates and times and preservatives used. The COC record allows an accurate step by step re-creation of the sample from collection through analysis to sample destruction. Some of the information that needs to be addressed in the COC is:

- X Name and signature of the individual collecting the sample
- X Sample ID (what type of sample)
- X Date and time of sample collection
- X Exact sampling location
- X Analyses to be performed
- X Printed name(s) and signature(s) of all persons handling the samples in the field, during transit, and in the laboratory.
- X Sample type, sample containers, sample preservation

When transferring possession of samples, the transferee must sign and record the date and time on the COC. The person accepting the sample must also sign the COC and record the date and time the transfer took place. Each person who accepts custody must fill in the appropriate section of the COC. Transfer of all samples must be done in person. When using a common carrier (FedEx, UPS) or courier, the samples should be sealed in an ice chest containing sufficient ice to assure the samples arrive at the laboratory at the required temperature. The courier should not sign the COC. The ice chest should be sealed with tape or stretch wrap and sealed with a custody seal to prevent opening. The laboratory will verify custody intact when received.

Recordkeeping

In addition to other records required by the Permit, sampling and analysis records include:

- § The date, exact place, time and methods of sampling or measurements, and preservatives used.
- § The individuals who collected the sample and performed field measurements.
- § The date(s) and time the analyses were performed.
- § The individual who performed the analyses.
- § The analytical techniques or methods used.
- § The measurements and results of such analyses.
- § Quality control data for the analyses.

Excerpt from 40 CFR 136.3, Table II-Required Containers, Preservation Techniques and Holding Times

Parameter No./name	Container ¹	Preservation ^{2,3}	Maximum holding time ⁴
Table IA—Bacterial Tests:			
1–5. Coliform, total, fecal, and <i>E. coli</i>	PA, G	Cool, <10 °C, 0.0008% Na ₂ S ₂ O ₃ ⁵	6 hours. ^{22,23}
Table IB—Inorganic Tests:			
4. Ammonia	P, FP, G	Cool, ≤6 °C ¹⁸ , H ₂ SO ₄ to pH<2	28 days.
9. Biochemical oxygen demand	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
14. Biochemical oxygen demand, carbonaceous	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
15. Chemical oxygen demand	P, FP, G	Cool, ≤6 °C ¹⁸ , H ₂ SO ₄ to pH<2	28 days.
16. Chloride	P, FP, G	None required	28 days.
17. Chlorine, total residual	P, G	None required	Analyze within 15 minutes.
23–24. Cyanide, total or available (or CATC)	P, FP, G	Cool, ≤6 °C ¹⁸ , NaOH to pH>12 ⁶ , reducing agent ⁵	14 days.
28. Hydrogen ion (pH)	P, FP, G	None required	Analyze within 15 minutes.
Table IB—Metals: ⁷			
18. Chromium VI	P, FP, G	Cool, ≤6 °C ¹⁸ , pH = 9.3–9.7 ²⁰	28 days.
35. Mercury (CVAA)	P, FP, G	HNO ₃ to pH<2	28 days.
35. Mercury (CVAFS)	FP, G; and FP-lined cap ¹⁷	5 mL/L 12N HCl or 5 mL/L BrCl ¹⁷	90 days. ¹⁷
3, 5–8, 12, 13, 19, 20, 22, 26, 29, 30, 32–34, 36, 37, 45, 47, 51, 52, 58–60, 62, 63, 70–72, 74, 75, metals, except boron, chromium VI, and mercury	P, FP, G	HNO ₃ to pH<2, or at least 24 hours prior to analysis ¹⁹	6 months.
38. Nitrate	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
39. Nitrate-nitrite	P, FP, G	Cool, ≤6 °C ¹⁸ , H ₂ SO ₄ to pH<2	28 days.
40. Nitrite	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
41. Oil and grease	G	Cool to ≤6 °C ¹⁸ , HCl or H ₂ SO ₄ to pH<2	28 days.
46. Oxygen, Dissolved Probe	G, Bottle and top	None required	Analyze within 15 minutes.
47. Winkler (dissolved oxygen)	G, Bottle and top	Fix on site and store in dark	8 hours.
48. Phenols	G	Cool, ≤6 °C ¹⁸ , H ₂ SO ₄ to pH<2	28 days.
49. Phosphorous (elemental)	G	Cool, ≤6 °C ¹⁸	48 hours.
50. Phosphorous, total	P, FP, G	Cool, ≤6 °C ¹⁸ , H ₂ SO ₄ to pH<2	28 days.
53. Residue, total (total solids)	P, FP, G	Cool, ≤6 °C ¹⁸	7 days.
54. Residue, Filterable (dissolved solids)	P, FP, G	Cool, ≤6 °C ¹⁸	7 days.
55. Residue, Nonfilterable (TSS)	P, FP, G	Cool, ≤6 °C ¹⁸	7 days.
56. Residue, Settleable	P, FP, G	Cool, ≤6 °C ¹⁸	48 hours.
57. Residue, Volatile	P, FP, G	Cool, ≤6 °C ¹⁸	7 days.
69. Temperature	P, FP, G	None required	Analyze.

1 “P” is polyethylene; “FP” is fluoropolymer (polytetrafluoroethylene (PTFE; Teflon[®]), or other fluoropolymer, unless stated otherwise in this Table II; “G” is glass; “PA” is any plastic that is made of a sterilizable material (polypropylene or other autoclavable plastic); “LDPE” is low density polyethylene.

- 2 Except where noted in this Table II and the method for the parameter, preserve each grab sample within 15 minutes of collection. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), refrigerate the sample at ≤ 6 °C during collection unless specified otherwise in this Table II or in the method(s). For a composite sample to be split into separate aliquots for preservation and/or analysis, maintain the sample at ≤ 6 °C, unless specified otherwise in this Table II or in the method(s), until collection, splitting, and preservation is completed. Add the preservative to the sample container prior to sample collection when the preservative will not compromise the integrity of a grab sample, a composite sample, or an aliquot split from a composite sample; otherwise, preserve the grab sample, composite sample, or aliquot split from a composite sample within 15 minutes of collection. If a composite measurement is required but a composite sample would compromise sample integrity, individual grab samples must be collected at prescribed time intervals (e.g., 4 samples over the course of a day, at 6-hour intervals). Grab samples must be analyzed separately and the concentrations averaged. Alternatively, grab samples may be collected in the field and composited in the laboratory if the compositing procedure produces results equivalent to results produced by arithmetic averaging of the results of analysis of individual grab samples. For examples of laboratory compositing procedures, see EPA Method 1664A (oil and grease) and the procedures at 40 CFR 141.34(f)(14)(iv) and (v) (volatile organics).
- 3 When any sample is to be shipped by common carrier or sent via the U.S. Postal Service, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).
- 4 Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before the start of analysis and still be considered valid (e.g., samples analyzed for fecal coliforms may be held up to 6 hours prior to commencing analysis). Samples may be held for longer periods only if the permittee or monitoring laboratory has data on file to show that, for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional Administrator under §136.3(e). For a grab sample, the holding time begins at the time of collection. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), **the holding time begins at the time of the end of collection of the composite sample**. For a set of grab samples composited in the field or laboratory, the holding time begins at the time of collection of the last grab sample in the set. Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if it knows that a shorter time is necessary to maintain sample stability. See §136.3(e) for details. The date and time of collection of an individual grab sample is the date and time at which the sample is collected. For a set of grab samples to be composited, and that are all collected on the same calendar date, the date of collection is the date on which the samples are collected. For a set of grab samples to be composited, and that are collected across two calendar dates, the date of collection is the dates of the two days; e.g., November 14–15. For a composite sample collected automatically on a given date, the date of collection is the date on which the sample is collected. For a composite sample collected automatically, and that is collected across two calendar dates, the date of collection is the dates of the two days; e.g., November 14–15.
- 5 Add a reducing agent only if an oxidant (e.g., chlorine) is present. Reducing agents shown to be effective are sodium thiosulfate (Na₂S₂O₃), ascorbic acid, sodium arsenite (NaAsO₂), or sodium borohydride (NaBH₄). However, some of these agents have been shown to produce a positive or negative cyanide bias, depending on other substances in the sample and the analytical method used. Therefore, do not add an excess of reducing agent. Methods recommending ascorbic acid (e.g., EPA Method 335.4) specify adding ascorbic acid crystals, 0.1–0.6 g, until a drop of sample produces no color on potassium iodide (KI) starch paper, then adding 0.06 g (60 mg) for each liter of sample volume. If NaBH₄ or NaAsO₂ is used, 25 mg/L NaBH₄ or 100 mg/L NaAsO₂ will reduce more than 50 mg/L of chlorine (see method “Kelada-01” and/or Standard Method 4500–CN[–] for more information). After adding reducing agent, test the sample using KI paper, a test strip (e.g. for chlorine, SenSafe™ Total Chlorine Water Check 480010) moistened with acetate buffer solution (see Standard Method 4500–Cl.C.3e), or a chlorine/oxidant test method (e.g., EPA Method 330.4 or 330.5), to make sure all oxidant is removed. If oxidant remains, add more reducing agent. Whatever agent is used, it should be tested to assure that cyanide results are not affected adversely.
- 6 Sample collection and preservation: Collect a volume of sample appropriate to the analytical method in a bottle of the material specified. If the sample can be analyzed within 48 hours and sulfide is not present, adjust the pH to > 12 with sodium hydroxide solution (e.g., 5% w/v), refrigerate as specified, and analyze within 48 hours. Otherwise, to extend the holding time to 14 days and mitigate interferences, treat the sample immediately using any or all of the following techniques, as necessary, followed by adjustment of the sample pH to > 12 and refrigeration as specified. There may be interferences that are not mitigated by approved procedures. Any procedure for removal or suppression of an interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide. Particulate cyanide (e.g., ferric ferrocyanide) or a strong cyanide complex (e.g., cobalt cyanide) are more accurately measured if the laboratory holds the sample at room temperature and pH > 12 for a minimum of 4 hours prior to analysis, and performs UV digestion or dissolution under alkaline (pH=12) conditions, if necessary.
- 6.1 Sulfur: To remove elemental sulfur (S₈), filter the sample immediately. If the filtration time will exceed 15 minutes, use a larger filter or a method that requires a smaller sample volume (e.g., EPA Method 335.4 or

- Lachat Method 01). Adjust the pH of the filtrate to > 12 with NaOH, refrigerate the filter and filtrate, and ship or transport to the laboratory. In the laboratory, extract the filter with 100 mL of 5% NaOH solution for a minimum of 2 hours. Filter the extract and discard the solids. Combine the 5% NaOH-extracted filtrate with the initial filtrate, lower the pH to approximately 12 with concentrated hydrochloric or sulfuric acid, and analyze the combined filtrate. Because the detection limit for cyanide will be increased by dilution by the filtrate from the solids, test the sample with and without the solids procedure if a low detection limit for cyanide is necessary. Do not use the solids procedure if a higher cyanide concentration is obtained without it. Alternatively, analyze the filtrates from the sample and the solids separately, add the amounts determined (in µg or mg), and divide by the original sample volume to obtain the cyanide concentration.
- 6.2 Sulfide: If the sample contains sulfide as determined by lead acetate paper, or if sulfide is known or suspected to be present, immediately conduct one of the volatilization treatments or the precipitation treatment as follows: Volatilization—Headspace expelling. In a fume hood or well-ventilated area, transfer 0.75 liter of sample to a 4.4 L collapsible container (e.g., Cubitainer™). Acidify with concentrated hydrochloric acid to pH < 2. Cap the container and shake vigorously for 30 seconds. Remove the cap and expel the headspace into the fume hood or open area by collapsing the container without expelling the sample. Refill the headspace by expanding the container. Repeat expelling a total of five headspace volumes. Adjust the pH to > 12, refrigerate, and ship or transport to the laboratory. Scaling to a smaller or larger sample volume must maintain the air to sample volume ratio. A larger volume of air will result in too great a loss of cyanide (> 10%). Dynamic stripping: In a fume hood or well-ventilated area, transfer 0.75 liter of sample to a container of the material specified and acidify with concentrated hydrochloric acid to pH < 2. Using a calibrated air sampling pump or flowmeter, purge the acidified sample into the fume hood or open area through a fritted glass aerator at a flow rate of 2.25 L/min for 4 minutes. Adjust the pH to > 12, refrigerate, and ship or transport to the laboratory. Scaling to a smaller or larger sample volume must maintain the air to sample volume ratio. A larger volume of air will result in too great a loss of cyanide (> 10%). Precipitation: If the sample contains particulate matter that would be removed by filtration, filter the sample prior to treatment to assure that cyanide associated with the particulate matter is included in the measurement. Ship or transport the filter to the laboratory. In the laboratory, extract the filter with 100 mL of 5% NaOH solution for a minimum of 2 hours. Filter the extract and discard the solids. Combine the 5% NaOH-extracted filtrate with the initial filtrate, lower the pH to approximately 12 with concentrated hydrochloric or sulfuric acid, and analyze the combined filtrate. Because the detection limit for cyanide will be increased by dilution by the filtrate from the solids, test the sample with and without the solids procedure if a low detection limit for cyanide is necessary. Do not use the solids procedure if a higher cyanide concentration is obtained without it. Alternatively, analyze the filtrates from the sample and the solids separately, add the amounts determined (in µg or mg), and divide by the original sample volume to obtain the cyanide concentration. For removal of sulfide by precipitation, raise the pH of the sample to > 12 with NaOH solution, then add approximately 1 mg of powdered cadmium chloride for each mL of sample. For example, add approximately 500 mg to a 500-mL sample. Cap and shake the container to mix. Allow the precipitate to settle and test the sample with lead acetate paper. If necessary, add cadmium chloride but avoid adding an excess. Finally, filter through 0.45 micron filter. Cool the sample as specified and ship or transport the filtrate and filter to the laboratory. In the laboratory, extract the filter with 100 mL of 5% NaOH solution for a minimum of 2 hours. Filter the extract and discard the solids. Combine the 5% NaOH-extracted filtrate with the initial filtrate, lower the pH to approximately 12 with concentrated hydrochloric or sulfuric acid, and analyze the combined filtrate. Because the detection limit for cyanide will be increased by dilution by the filtrate from the solids, test the sample with and without the solids procedure if a low detection limit for cyanide is necessary. Do not use the solids procedure if a higher cyanide concentration is obtained without it. Alternatively, analyze the filtrates from the sample and the solids separately, add the amounts determined (in µg or mg), and divide by the original sample volume to obtain the cyanide concentration. If a ligand-exchange method is used (e.g., ASTM D6888), it may be necessary to increase the ligand-exchange reagent to offset any excess of cadmium chloride.
- 6.3 Sulfite, thiosulfate, or thiocyanate: If sulfite, thiosulfate, or thiocyanate is known or suspected to be present, use UV digestion with a glass coil (Method Kelada-01) or ligand exchange (Method OIA-1677) to preclude cyanide loss or positive interference.
- 6.4 Aldehyde: If formaldehyde, acetaldehyde, or another water-soluble aldehyde is known or suspected to be present, treat the sample with 20 mL of 3.5% ethylenediamine solution per liter of sample.
- 6.5 Carbonate: Carbonate interference is evidenced by noticeable effervescence upon acidification in the distillation flask, a reduction in the pH of the absorber solution, and incomplete cyanide spike recovery. When significant carbonate is present, adjust the pH to ≥12 using calcium hydroxide instead of sodium hydroxide. Allow the precipitate to settle and decant or filter the sample prior to analysis (also see Standard Method 4500-CN.B.3.d).
- 6.6 Chlorine, hypochlorite, or other oxidant: Treat a sample known or suspected to contain chlorine, hypochlorite, or other oxidant as directed in footnote 5.
- 7 For dissolved metals, filter grab samples within 15 minutes of collection and before adding preservatives. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), filter the sample within 15 minutes after completion of collection and before adding preservatives. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (e.g., by interchange of a metal between dissolved

- and suspended forms), collect and filter grab samples to be composited (footnote 2) in place of a composite sample collected automatically.
- 8 Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.
- 9 If the sample is not adjusted to pH 2, then the sample must be analyzed within seven days of sampling.
- 10 The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.
- 11 When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity (*i.e.* , use all necessary preservatives and hold for the shortest time listed). When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to ≤ 6 °C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6–9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (regarding the requirement for thiosulfate reduction), and footnotes 12, 13 (regarding the analysis of benzidine).
- 12 If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.
- 13 Extracts may be stored up to 30 days at < 0 °C.
- 14 For the analysis of diphenylnitrosamine, add 0.008% Na₂S₂O₃ and adjust pH to 7–10 with NaOH within 24 hours of sampling.
- 15 The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% Na₂S₂O₃.
- 16 Sufficient ice should be placed with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, it is necessary to immediately measure the temperature of the samples and confirm that the preservation temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature cannot be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of the increased holding temperature.
- 17 Samples collected for the determination of trace level mercury (< 100 ng/L) using EPA Method 1631 must be collected in tightly-capped fluoropolymer or glass bottles and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. A sample collected for dissolved trace level mercury should be filtered in the laboratory within 24 hours of the time of collection. However, if circumstances preclude overnight shipment, the sample should be filtered in a designated clean area in the field in accordance with procedures given in Method 1669. If sample integrity will not be maintained by shipment to and filtration in the laboratory, the sample must be filtered in a designated clean area in the field within the time period necessary to maintain sample integrity. A sample that has been collected for determination of total or dissolved trace level mercury must be analyzed within 90 days of sample collection.
- 18 Aqueous samples must be preserved at ≤ 6 °C, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted as valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification of “ \leq °C” is used in place of the “4 °C” and “ < 4 °C” sample temperature requirements listed in some methods. It is not necessary to measure the sample temperature to three significant figures (1/100th of 1 degree); rather, three significant figures are specified so that **rounding down to 6 °C may not be used to meet the ≤ 6 °C requirement**. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).
- 19 An aqueous sample may be collected and shipped without acid preservation. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. If the sample must be analyzed within 24 hours of collection, add the acid immediately (see footnote 2). Soil and sediment samples do not need to be preserved with acid. The allowances in this footnote supersede the preservation and holding time requirements in the approved metals methods.
- 20 To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.
- 21 **Holding time is calculated from time of sample collection to elution for samples shipped to the laboratory in bulk and calculated from the time of sample filtration to elution for samples filtered in the field.**
- 22 Samples analysis should begin immediately, preferably within 2 hours of collection. The maximum transport time to the laboratory is 6 hours, and samples should be processed within 2 hours of receipt at the laboratory.
- 23 For fecal coliform samples for sewage sludge (biosolids) only, the holding time is extended to 24 hours for the following sample types using either EPA Method 1680 (LTB–EC) or 1681 (A–1): Class A composted, Class B aerobically digested, and Class B anaerobically digested.