5. SAMPLING

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Associated Appendices

Related Websites

Agency-wide Quality System Documents: http://www.epa.gov/quality/qa_docs.html

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5. A. Evaluation of Permittee Sampling Program and Compliance Sampling

Wastewater sampling/analysis is an integral part of the National Pollutant Discharge Elimination System (NPDES) Compliance Monitoring Program. NPDES permits contain specific and legally enforceable effluent limitations and monitoring requirements.

Objectives and Requirements

When evaluating the permittee sampling program, the inspector should:

- Verify that the permittee's sampling program complies with the permit
- Verify that the permittee's sampling program complies with:
  - 40 *Code of Federal Regulations (CFR)* 136.1 to 136.5 and Appendices A, B, and C (Guidelines for Establishing Test Procedures for the Analysis of Pollutants) for wastewater samples and
  - 40 *CFR* Part 503 which requires that for biosolids samples, metal analyses be done in accordance with SW-846 methods (in Test Methods for Evaluating Solid Waste Physical/Chemical Methods) and Standard Methods for the Examination of Water and Wastewater.
- Document violations to support enforcement action.

In addition, specific objectives of the sampling conducted by inspectors include the following:

- Verify compliance with effluent limitations
- Verify accuracy of reports and program self-monitoring
- Support enforcement action
- Support permit development reissuance and/or revision
- Determine the quantity and quality of effluent.

Sampling, analysis, preservation technique, sample holding time, and sample container requirements are provided under 40 *CFR* Part 136 as authorized by Section 304(h) of the Clean Water Act (CWA). Chapter Seven contains more information on required analytical procedures "Laboratory Analyses Techniques Evaluation." See the checklist for use in evaluating the permittee's sampling program at the end of this chapter.

For all NPDES permittees the inspector should include a review of sampling procedures and quality control measures the facility uses to ensure the integrity of sample data.

To evaluate sampling procedures, assess the following seven areas:

- Sample collection techniques

- Field measurements
- Sample labeling (including location(s)) and documentation
- Sample preservation and holding time
- Transfer of custody and shipment of samples
- Quality control
- Data handling and reporting.

Significant Industrial User Monitoring Program

It is the responsibility of the permitted Publicly Owned Treatment Works (POTW) with a pretreatment program to oversee sampling procedures of industrial users and to conduct compliance monitoring of its own. Therefore, during a Pretreatment Compliance Inspection (PCI) or audit, the inspector may also need to evaluate POTW sampling procedures for significant industrial users who discharge to the POTW in addition to evaluating the sampling procedures of any permitted POTW. According to the General Pretreatment Regulations, 40 *CFR* 403.12(o), industrial users and POTWs subject to 40 *CFR* 403.12 reporting requirements must maintain the following monitoring records:

- Date, exact place, method and time of sampling, and name of sampler
- Date of analysis
- Name of analyst
- Analytical techniques/methods used
- Analytical results.

During a PCI or an audit, the inspector evaluates the POTW industrial user monitoring program with respect to the criteria specified in the POTW pretreatment program. Elements of the sampling scheme will include the seven areas addressed above and any other areas specifically addressed in the particular pretreatment program. Chapter Nine, "Pretreatment," discusses the focus of this evaluation in greater detail.

Biosolids Monitoring Program

Chapter Ten discusses evaluation of a permittee's biosolids monitoring program. In addition, Appendix L lists approved analytical methods, sample containers, preservation techniques, and holding times for biosolids samples.

Toxicity Testing Program

Chapter Eight discusses evaluation of a permittee's whole effluent toxicity testing program. In addition, for methods manuals for Whole Effluent Toxicity testing go to http://www.epa.gov/owm, as well as http://www.epa.gov/waterscience/WET.

Storm Water Program

Chapter Eleven provides considerations for performing storm water sampling.

5. B. Sampling Procedures and Techniques

Whether an inspector is evaluating a permittee's sampling program or conducting compliance sampling on the permittee's effluent, that inspector must be familiar with the procedures and techniques necessary for accurate sampling of wastewaters. The following discussion details the procedures for sample collection, preservation, transfer, quality control, and data handling.

Wastewater Sample Collection Techniques

Sample collection is an important part of the compliance monitoring program. Without proper sample collection procedures, the results of such monitoring programs are neither useful nor valid, even with the most precise and accurate analytical measurements.

Selection of Representative Sampling Sites

Normally, samples should be collected at the location specified in the permit. In some instances, the sampling location specified in the permit or the location chosen by the permittee may not be adequate for the collection of a representative sample. In that case, the inspector should determine the most representative sampling point available and collect a sample at both locations. If the facility disagrees the reason for the conflict must be documented for later resolution by the permitting authority.

Influent Samples. Document and take these samples at points of high turbulence flow to ensure good mixing. In some instances, the most desirable location may not be accessible. Ensure sampling equipment sampling points are above plant return lines, and sampling equipment should be placed so that it does not interfere with flow measuring devices. The preferred sampling points for raw wastewater are:

- Waste flowing from last process in a manufacturing operation
- Pump wet well (if turbulent)
- Upstream collection lines, tank, or distribution box following pumping from the wet well or sump
- Flume throat
- Aerated grit chamber
- Upstream siphon following the comminutor (in absence of grit chamber).

If it is not possible to sample at a preferred point, choose an alternative location and document the basis for choosing that location.

Effluent Samples. Collect these samples at the site the permit specifies or, if the permit does not specify a site then the inspector should select the most representative site after final treatment and downstream from all entering wastestreams before they enter the receiving waters. Occasionally, municipal plant permits may specify sampling prior to chlorination. For these plants, monitor all parameters at the upstream location except fecal coliforms, pH, and total residual chlorine. Collect wastewater for use in bioassays at the location specified in the facility's NPDES permit.

Collect samples either manually (grab or composite) or with automatic samplers (continuous or composite). The following general guidelines apply when taking samples:

- Take samples at a site specified in the NPDES permit and/or at a site selected to yield a representative sample.
- Use a sampling method (grab, composite, continuous) as required in the permit. Some parameters that are not to be collected by automatic samplers, but must be hand collected are dissolved oxygen, total residual chlorine, oil and grease, coliforms, purgeable organics, sulfides, cyanide, and total phenols.
- Avoid collecting large nonhomogeneous particles and objects.
- Collect the sample facing upstream to avoid contamination.
- Do not rinse sample container with sample when collecting oil and grease and microbiological samples, but fill it directly to within 2.5 to 5 cm from the top.
- Fill the container completely if the sample is to be analyzed for purgeable organics, oxygen, ammonia, hydrogen sulfide, free chlorine, pH, hardness, sulfite, ammonium, ferrous iron, acidity, or alkalinity.
- Collect sufficient volume to allow for quality assurance testing. (Table 5-1 provides a guide to numerous sample volumes, but additional volumes may be necessary for quality assurance testing.)

The following general guidelines apply when using automatic samplers:

- Collect samples where the wastewater is well mixed. Collect the sample near the center of the flow channel at 0.4 to 0.6 depth (mid-depth).
- Obtain a sufficient volume of sample to perform all required analyses plus any additional amount for quality control. Individual portions of a composite sample should be at least 100 milliliters in order to minimize sampler solids bias.
- For automatic samplers which use a peristaltic pump, obtain adequate flow rates in the sampler tubing to effectively transport the suspended solids. To avoid solids bias, the velocity of the wastewater in sample tubing should be at least 2 fps and the tubing diameter should be at least 0.25 inch.
- Time of sample collection begins when the last aliquot is dispensed into the composite sample container.

Table 5-1

Volume of Sample Required for Determination of the Various Constituents of Industrial Wastewater (Associated Water and Air Resource Engineers, Inc. 1973 *Handbook for Monitoring Industrial Wastewater.* USEPA Technology Transfer.)

Tests	Volume of Sample, (1) ml
PHYSICAL	
Color and Odor(2)	100 to 500
Corrosivity(2)	Flowing sample
Electrical conductivity(2)	100
pH, electrometric(2)	100
Radioactivity	100 to 1,000
Specific gravity(2)	100
Temperature(2)	Flowing sample
Toxicity(2)	1,000 to 20,000
Turbidity(2)	100 to 1,000
CHEMICAL	
Dissolved Gases:	
Ammonia,(3) NH(3)	500
Carbon dioxide,(3) free $C0_2$	200
Chlorine,(3) free Cl_2	200
Hydrogen,(3) H_2	1,000
Hydrogen sulfide,(3) H_2S	500
Oxygen,(3) O_2	500 to 1,000
Sulfur dioxide,(3) free SO_2	100
Miscellaneous:	
Acidity and alkalinity	100
Bacteria, iron	500
Bacteria, sulfate-reducing	100
Biochemical oxygen demand (BOD)	100 to 500
Carbon dioxide, total $C0_2$ (including $C0_3^{--}$, $HC0_3^-$, and free)	200
Chemical oxygen demand (dichromate)	50 to 100
Chlorine requirement	2,000 to 4,000
Chlorine, total residual Cl_2 (including OCl^-, HOCl, NH_2Cl, $NHCl_2$, and free)	200
Chloroform-extractable matter	1,000
Detergents	100 to 200
Hardness	50 to 100
Hydrazine	50 to 100
Microorganisms	100 to 200
Volatile and filming amines	500 to 1,000
Oily matter	3,000 to 5,000
Organic nitrogen	500 to 1,000
Phenolic compounds	800 to 4,000
pH, colorimetric	10 to 20
Polyphosphates	100 to 200
Silica	50 to 1,000
Solids, dissolved	100 to 20,000
Solids, suspended	50 to 1,000
Tannin and lignin	100 to 200

Table 5-1

Volume of Sample Required for Determination of the Various Constituents of Industrial Wastewater (Continued)

Tests	Volume of Sample, (1) ml
Cations:	
Aluminum, Al^{+++}	100 to 1,000
Ammonium,(3) $NH4^{+}$	500
Antimony, Sb^{+++} to Sb^{+++++}	100 to 1,000
Arsenic, As^{+++} to As^{+++++}	100 to 1,000
Barium, Ba^{++}	100 to 1,000
Cadmium, Cd^{++}	100 to 1,000
Calcium, Ca^{++}	100 to 1,000
Chromium, Cr^{+++} to Cr^{++++++}	100 to 1,000
Copper, Cu^{++}	200 to 4,000
Iron,(3) Fe^{++} and Fe^{+++}	100 to 1,000
Lead, Pb^{++}	100 to 4,000
Magnesium, Mg^{++}	100 to 1,000
Manganese, Mn^{++} to $Mn^{+++++++}$	100 to 1,000
Mercury, Hg^{+} and Hg^{++}	100 to 1,000
Potassium, K^{+}	100 to 1,000
Nickel, Ni^{++}	100 to 1,000
Silver, Ag^{+}	100 to 1,000
Sodium, Na^{+}	100 to 1,000
Strontium, Sr^{++}	100 to 1,000
Tin, Sn^{++} and Sn^{++++}	100 to 1,000
Zinc, Zn^{++}	100 to 1,000
Anions:	
Bicarbonate, HCO_3^{-}	100 to 200
Bromide, Br^{-}	100
Carbonate, CO_3^{--}	100 to 200
Chloride, Cl^{--}	25 to 100
Cyanide, CN^{-}	25 to 100
Fluoride, Fl^{-}	200
Hydroxide, OH^{-}	50 to 100
Iodide, I^{-}	100
Nitrate, NO_3^{-}	10 to 100
Nitrite, NO_2^{--}	50 to 100
Phosphate, ortho, PO_4^{--}, HPO_4^{--}, $H_2PO_4^{-}$	50 to 100
Sulfate, SO_4^{--}, HSO_4	100 to 1,000
Sulfide, S^{--}, HS^{-}	100 to 500
Sulfite, SO_3^{--}, HSO_3^{-}	50 to 100

(1) Consider volumes specified in this table as guides for the approximate quantity of sample necessary for a particular analysis. The exact quantity used should be consistent with the volume prescribed in the standard method of analysis, whenever a volume is specified.
(2) Use aliquots for other determinations.
(3) Obtain samples for unstable constituents in separate containers, preserved as prescribed; containers must be completely filled and sealed against air exposure.

Sample Types

Two types of sample techniques are used: grab and composite. For many monitoring procedures, 40 *CFR* Part 136 does not specify sampling type. For these procedures, the NPDES permit writer determines the appropriate sample type and specifies them in the NPDES permit.

Grab Samples. Grab samples are individual samples collected over a period of time not exceeding 15 minutes and are representative of conditions at the time the sample is collected. The sample volume depends on the type and number of analyses to be performed. The collection of a grab sample is appropriate when a sample is needed to:

- Sample an effluent that does not discharge on a continuous basis
- Provide information about instantaneous concentrations of pollutants at a specific time
- Allow collection of a variable sample volume
- Corroborate composite samples
- Monitor parameters not amenable to compositing (e.g., pH, temperature, dissolved oxygen, chlorine, purgeable organics, oil and grease, coliform bacteria, and others specified by the NPDES permit, which may include phenols, sulfites, and hexavalent chromium). Volatile organics, sulfides, phenols, and phosphorus samples can be composited. If you composite use special handling procedures.

Composite Samples. Collect these samples over time, either by continuous sampling or by mixing discrete samples, and represent the average characteristics of the wastestream during the compositing period use. Composite samples are used when stipulated in a permit and when:

- Average pollutant concentration during the compositing period is determined
- Mass per unit time loadings is calculated
- Wastewater characteristics are highly variable.

Various methods for compositing samples are available, select one based on either time or flow proportioning. Table 5-2 lists the advantages and disadvantages of various methods. The permit may specify which type of composite sample to use. Collect composite samples either manually or with automatic samplers. Inspectors should consider variability in wastestream flow rate and parameter concentrations carefully when choosing compositing methods, sampling equipment (tubing and containers), and quality assurance procedures. The compositing methods are as follows:

- Time Composite Sample—This method requires discrete sample aliquots collected in one container at constant time intervals. This method is appropriate when the flow of the sampled stream is constant (flow rate does not vary more than ±10 percent of the average flow rate) or when flow monitoring equipment is not available.

Table 5-2

Compositing Methods

Method	Advantages	Disadvantages	Comments
Time Composite			
Constant sample volume, constant time interval between samples	Minimal instrumentation and manual effort; requires no flow measurement	May lack representativeness, especially for highly variable flows	Widely used in both automatic samplers and manual handling
Flow-Proportional Composite			
Constant sample volume, time interval between samples proportional to stream flow	Minimal manual effort	Requires accurate flow measurement reading equipment; manual compositing from flowchart	Widely used in automatic as well as manual sampling
Constant time interval between samples, sample volume proportional to total stream flow at time of sampling	Minimal instrumentation	Manual compositing from flowchart in absence of prior information on the ratio of minimum to maximum flow; chance of collecting too small or too large individual discrete samples for a given composite volume	Used in automatic samplers and widely used as manual method
Constant time interval between samples, sample volume proportional to total stream flow since last sample	Minimal instrumentation	Manual compositing from flow chart in absence of prior information on the ratio of minimum to maximum flow; chance of collecting either too small or too large individual discrete samples for a given composite volume	Not widely used in automatic samplers but may be done manually
Sequential Composite			
Series of short period composites, constant time intervals between samples	Useful if fluctuations occur and time history is desired	Requires manual compositing of aliquots based on flow	Commonly used; however, manual compositing is labor intensive
Series of short period composites, aliquots taken at constant discharge increments	Useful if fluctuations occur and the time history is desired	Requires flow totalizer; requires manual compositing of aliquots based on flow	Manual compositing is labor intensive
Continuous Composite			
Constant sample volume	Minimal manual effort, requires no flow measurement highly variable flows	Requires large sample capacity; may lack representativeness for highly variable flows	Practical but not widely used
Sample volume proportional to stream flow	Minimal manual effort, most representative especially for highly variable sample volume, variable pumping capacity and power	Requires accurate flow measurement equipment, large sample volume, variable pumping capacity, and power	Not widely used

- Flow-Proportional Composite Sample—There are two methods used for this type of sample. One method collects a constant sample volume at varying time intervals proportional to stream flow (e.g., 200 milliliters sample collected for every 5,000 gallons of flow). In the other method, collect the sample by increasing the volume of each aliquot as the flow increases, while maintaining a constant time interval between the aliquots.

- Sequential Composite Sample—This method requires discrete samples collected in individual containers at constant time intervals or discharge increments—for example, samples collected every 15 minutes, composited into separate containers each hour. The discrete samples can then be manually flow-proportioned to form the composite sample. Alternatively, take a constant sample volume at constant discharge increments, as measured with a totalizer.

- Continuous Composite Sample— Collect this sample continuously from the wastestream. The sample may be constant volume, or the volume may vary in proportion to the flow rate of the wastestream.

Sample Volume

The volume of samples collected depends on the type and number of analyses needed, as reflected in the parameters to be measured. Obtain the volume of the sample sufficient for all the required analyses plus an additional amount to provide for any split samples or repeat analyses. Table 5-1 provides a guide to sample volumes required for determining the constituents in wastewater. Consult the laboratory receiving the sample for any specific volume required. EPA's *Methods for Chemical Analysis of Water and Wastes* (USEPA 1979b) and *Handbook for Sampling and Sample Preservation of Water and Wastewater* (USEPA 1982), and the current Environmental Protection Agency (EPA)-approved edition of *Standard Methods for the Examination of Water and Wastewater* [American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF)] contain specific recommended minimum sample volumes for different pollutant parameters.

Sample Containers

The 40 *CFR* Part 136 describes required sample containers, sample preservation, and sample holding time. Table 5-3 includes this material. It is essential that the sample containers be made of chemically resistant material unaffected by the concentrations of the pollutants measured. In addition, sample containers must have a closure that will protect the sample from contamination. Collect wastewater samples for chemical analysis in plastic (polyethylene) containers. Exceptions to this general rule are oil and grease samples, pesticides, phenols, polychlorinated biphenyls (PCBs), and other organic pollutant samples. Collect these in properly cleaned glass jars or bottles and sealed. Collect bacteriological samples in properly sterilized plastic or glass containers. Collect samples that contain constituents that will oxidize when exposed to sunlight (such as iron cyanide complexes) in dark containers.

Ensure sample containers are clean and uncontaminated. Check analytical procedures to determine if they specify container cleaning procedures. Use precleaned and sterilized disposable containers (e.g., polyethylene cubitainers). If these are not used or if the analytical method does not specify procedures, use the following procedures for cleaning sample containers:

- Wash with hot water and detergent.
- Rinse with acid (e.g., nitric for metals).
- Rinse with tap water, then rinse three or more times with organic-free water.
- Rinse glass containers with an interference-free, redistilled solvent (such as acetone or methylene chloride for extractable organics).
- Dry in contaminant-free area.

Table 5-3

Required Containers, Preservation Techniques, and Holding Times (Excerpt from 40 *CFR* Part 136, Table II)

Parameter	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
BACTERIAL TESTS			
Coliform, fecal and total	P,G	Cool, 4°C 0.008% $Na_2S_2O_3$[5]	6 hours
Fecal streptococci	P,G	Cool, 4°C 0.008% $Na_2S_2O_3$[5]	6 hours
INORGANIC TESTS			
Acidity	P,G	Cool, 4°C	14 days
Alkalinity	P,G	Cool, 4°C	14 days
Ammonia	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
Biochemical oxygen demand	P,G	Cool, 4°C	48 hours
Biochemical oxygen demand, carbonaceous	P,G	Cool, 4°C	48 hours
Bromide	P,G	None required	28 days
Chemical oxygen demand	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
Chloride	P,G	None required	28 days
Chlorine, total residual	P,G	None required	Analyze immediately
Color	P,G	Cool, 4°C	48 hours
Cyanide, total and amenable to chlorination	P,G	Cool, 4°C NaOH to pH>12 0.6 g ascorbic acid[5]	14 days[6]
Fluoride	P	None required	28 days
Hardness	P,G	HNO_3 to pH<2, H_2SO_4 to pH<2	6 months
Hydrogen ion (pH)	P,G	None required	Analyze immediately
Kjeldahl and organic nitrogen	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
METALS[7]			
Chromium VI	P,G	Cool, 4°C	24 hours
Mercury	P,G	HNO_3 to pH<2	28 days
Metals except above	P,G	HNO_3 to pH<2	6 months

Table 5-3

Required Containers, Preservation Techniques, and Holding Times
(Excerpt from 40 *CFR* Part 136, Table II)
(Continued)

Parameter	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
INORGANIC TESTS (Continued)			
Nitrate	P,G	Cool, 4°C	48 hours
Nitrate-nitrite	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
Nitrite	P,G	Cool, 4°C	48 hours
Oil and grease	G	Cool, 4°C HCl, H_2SO_4 to pH<2	28 days
Organic carbon	P,G	Cool, 4°C HCl, H_2SO_4 to pH<2	28 days
Orthophosphate phosphorus	P,G	Filter immediately Cool, 4°C	48 hours
Dissolved oxygen Probe Winkler	 G bottle & top G bottle & top	 None required Fix onsite and store in the dark	 Analyze immediately 8 hours
Phenols	G	Cool, 4°C H_2SO_4 to pH<2	28 days
Phosphorus (elemental)	G	Cool, 4°C	48 hours
Phosphorus, total	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
Residue, total	P,G	Cool, 4°C	7 days
Residue, filterable	P,G	Cool, 4°C	7 days
Residue, nonfilterable (TSS)	P,G	Cool, 4°C	7 days
Residue, settleable	P,G	Cool, 4°C	48 hours
Residue, volatile	P,G	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific conductance	P,G	Cool, 4°C	28 days

Table 5-3

Required Containers, Preservation Techniques, and Holding Times
(Excerpt from 40 *CFR* Part 136, Table II)
(Continued)

Parameter	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
INORGANIC TESTS (Continued)			
Sulfate	P,G	Cool, 4°C	28 days
Sulfide	P,G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH >9	7 days
Sulfite	P,G	None required	Analyze immediately
Surfactants	P,G	Cool, 4°C	48 hours
Temperature	P,G	None required	Analyze immediately
Turbidity	P,G	Cool, 4°C	48 hours
ORGANIC TESTS[8]			
Purgeable halocarbons	G, teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[5]	14 days
Purgeable aromatic hydrocarbons	G, teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[5] HCl to pH 2[9]	14 days
Acrolein and acrylonitrile	G, teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[5] Adjust pH to 4-5[10]	14 days
Phenols[11]	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[5]	7 days until extraction 40 days after extraction
Benzidenes[11]	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[5]	7 days until extraction[13]
Phthalate esters[11]	G, teflon-lined cap	Cool, 4°C	7 days until extraction; 40 days after extraction
Nitrosamines[11,14]	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[5] Store in the dark	7 days until extraction; 40 days after extraction
Polychlorinated biphenyls (PCBs)[11]	G, teflon-lined cap	Cool, 4°C	7 days until extraction; 40 days after extraction
Nitroaromatics and isophorone[11]	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[5] Store in the dark	7 days until extraction; 40 days after extraction

Table 5-3

Required Containers, Preservation Techniques, and Holding Times
(Excerpt from 40 *CFR* Part 136, Table II)
(Continued)

Parameter	Container[1]	Preservative[2,3]	Maximum Holding Time[4]
ORGANIC TESTS[8] (Continued)			
Polynuclear aromatic hydrocarbons[11]	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[5] Store in the dark	7 days until extraction; 40 days after extraction
Haloethers[11]	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
Chlorinated hydrocarbons[11]	G, teflon-lined cap	Cool, 4°C	7 days until extraction; 40 days after extraction
2,3,7,8-tetrachlorodibenzo-p-dioxin[11]	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
PESTICIDES TEST			
Organochlorine pesticides[11]	G, teflon-lined cap	Cool, 4°C pH 5-9[15]	7 days until extraction; 40 days after extraction
RADIOLOGICAL TEST			
Alpha, beta, and radium	P,G	HNO_3 to pH<2	6 months
WHOLE EFFLUENT TOXICITY TESTS			
Acute and Chronic, for NPDES Compliance	P,G	Cool, 0-6°C NO ADDITIONS	36 Hours to test initiation

[1] Polyethylene (P) or glass (G).

[2] Perform sample preservation steps immediately upon sample collection. For composite chemical samples, preserve each aliquot at the time of collection. When use of an automatic sampler makes it impossible to preserve each aliquot, then preserve chemical samples by maintaining at 4°C until compositing and sample splitting are completed.

[3] When shipping any sample by common carrier or sent through the United States mail, comply with the Department of Transportation Hazardous Materials Regulations (49 *CFR* Part 172). See fact sheet in Appendix N. The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of this Table, 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 (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); sulfuric acid (H_2SO_4) 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 0.08% by weight or less (pH about 12.3 or less).

Table 5-3

Required Containers, Preservation Techniques, and Holding Times
(Excerpt from 40 *CFR* Part 136, Table II)
(Continued)

[4] Analyze samples as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time and has received a variance from the Regional Administrator under § 136.3(e). 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 knowledge exists to show that this is necessary to maintain sample stability.

[5] Used only in the presence of residual chlorine.

[6] Maximum holding time is 24 hours when sulfide is present. Optionally, test all samples with lead acetate paper before pH adjustments to determine whether sulfide is present. If sulfide is present, remove by the addition of cadmium nitrate powder until a negative spot test is obtained. Filter the sample then NaOH is added to pH 12.

[7] Filter samples should be filtered immediately onsite before adding preservative for dissolved metals.

[8] Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific organic compounds.

[9] Analyze samples receiving no pH adjustment within 7 days of sampling.

[10] pH adjustment is if not needed if not measuring acrolein. Analyze samples for acrolein receiving no pH adjustment within 3 days of sampling.

[11] When the extractable analytes of concern fall within a single chemical category, observe the specified preservation and maximum holding times for optimum safeguarding of sample integrity. When the analytes of concern fall within two or more chemical categories, preserve the sample by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to between 6 and 9; hold samples preserved in this manner for 7 days before extraction and for 40 days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re: the requirement for thiosulfate reduction of residual chlorine) and footnotes 12 and 13 (re: 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] Store extracts up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

[14] For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to between 7 and 10 with NaOH within 24 hours of sampling.

[15] Perform the pH adjustment upon receipt at the laboratory and omit if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

EPA Sample Identification Methods

Identify each sample accurately and completely. Use labels or tags to identify the samples that are moisture-resistant and able to withstand field conditions. Use a waterproof pen to complete the labels or tags. A numbered label or tag associated with a field sample data sheet containing detailed information on the sample is preferable to using only a label or tag for information[1]. The information for each sample should include the following:

- Facility name/location
- Sample site location
- Sample number
- Name of sample collector
- Date and time of collection
- Indication of grab or composite sample with appropriate time and volume information
- Identification of parameter to be analyzed
- Preservative used.

Wastewater Sample Preservation and Holding Time

In most cases, wastewater samples contain one or more unstable pollutants that require immediate (e.g., within 15 minutes) preservation and/or analysis. Provide appropriate chemical preservation before transferring samples to the laboratory. Procedures used to preserve samples include cooling, pH adjustment, and chemical treatment. For some parameters such as cyanide and phenols, add preservatives to sample bottles prior to or immediately following sample collection. For many samples, if preservatives are not appropriately used, bacteria can quickly degrade certain constituents (such as phenols and phosphorus). Other constituents may volatilize (such as volatile organics and sulfides) or may react to form different chemical species (hexavalent chromium, for example). Proper preservation and holding times are essential to ensure sample integrity. (See Table 5-3 and refer to 40 *CFR* Part 136.)

Analysis of samples within one day ensures against error from sample deterioration. However, such prompt analysis is not feasible for composite samples in which portions may be stored for as long as 24 hours. Where possible, provide sample preservation during compositing, usually by refrigeration to 4°C (or icing). If using an automatic sampler with ice, replace the ice as necessary to maintain low temperatures. This is a particular limitation of automatic samplers used during the summer when ice must be frequently replaced.

The 40 *CFR* Part 136 indicates maximum sample holding times. Times listed are the maximum holding times between sample collection and analysis that are allowed for the sample to be considered valid. Typically, the holding time limitations begin upon combination of the last aliquot in a sample. When use of an automatic sampler makes it impossible to preserve each aliquot, the preservation (chemical) should be done immediately following the composite (40 *CFR* 136.3).

[1]Note: Preprinted labels, data sheets, chain-of-custody forms, etc., can be done in the field using software developed by the Superfund Program.

Transfer of Custody and Shipment of Samples

To ensure the validity of the permit compliance sampling data in court, written records must accurately trace the custody of each sample through all phases of the monitoring program. The primary objective of this chain-of-custody is to create an accurate written record (see an example chain-of-custody form in Appendix M) that can be used to trace the possession and handling of the sample from the moment of its collection through its analysis and introduction as evidence.

- Use sample seals to protect the sample's integrity from the time of collection to the time it is opened in the laboratory. The seal should indicate the collector's name, the date and time of sample collection, and sample identification number.

- Pack samples properly to prevent breakage. Seal or lock the shipping container to readily detect any evidence of tampering can be readily detected. Use of tamper proof evidence tape is recommended.

- Place samples on ice or synthetic ice substitute that will maintain sample temperature at 4°C throughout shipment.

- Accompany every sample with a sample tag and a chain-of-custody record that has been completed, signed, and dated. The chain-of-custody record should include the names of sample collectors, sample identification numbers, date and time of sample collection, location of sample collection, and names and signatures of all persons handling the sample in the field and in the laboratory.

- The responsibility for proper packaging, labeling, and transferring of possession of the sample lies with the inspector.

- Accompany all sample shipments with the chain-of-custody record and other pertinent forms. The originator retains a copy of these forms. Also, the originator must retain all receipts associated with the shipment.

- EPA Inspectors with the responsibility of working with hazardous materials that are placed in commerce (transporting/shipping) must have hazardous materials training as required by the Department of Transportation (See Appendix N).

- When transferring possession of samples, the transferee must sign and record the date and time on the chain-of-custody record (use the currently approved record). In general, make custody transfers for each sample, although samples may be transferred as a group, if desired. Each person who takes custody must fill in the appropriate section of the chain-of-custody record.

- Pack and ship samples in accordance with applicable International Air Transportation Association (IATA) and/or DOT regulations. See Table 5-3, footnote 3.

Quality Control

Conduct control checks during the actual sample collection to determine the performance of sample collection techniques. In general, the most common monitoring errors usually are improper sampling methodology, improper preservation, inadequate mixing during compositing and splitting, and excessive sample holding time. In addition, collect and analyze the following samples to check sample collection techniques:

Blanks

- **Trip Blank**. This is a sample vial(s) filled at the laboratory with deionized water. The blank(s) follows the same handling and transport procedures as the samples collected during the event. The blank(s) functions as a check on sample contamination originating from sample transport, shipping and from site conditions.

  Note: Expose the trip blank vial(s), to the same environmental conditions (i.e., light, temperature, etc.) of the sample vial(s) but do not open until it is time for analysis.

- **Field Blank/Field Reagent Blank**. These are similar to the trip blanks except they are prepared in the field with deionized water exactly as the sample(s) that are collected. Field blanks are used to check for analytical artifacts and/or background introduced by sampling and analytical procedures.

- **Equipment/Rinsate Blank**. Collect a blank when using an automatic sampler or other non-dedicated equipment during the sampling process. The blank is a check of the equipment cleanliness. For automatic samplers, prepare blanks prior to collecting samples, by pumping deionized organic free water through the sampler and collecting the discharge purge water in a sample container for analysis for the constituents of concern.

Field Duplicate. Collect this sample simultaneously from the same source at selected stations on a random time frame by grab samples or from two sets of field equipment installed at the site. Duplicate samples check analytical precision as well as evaluate the “representativeness” of the sample aliquot.

Split Samples. These are samples that have been divided into two containers for analysis by separate laboratories. These samples provide an excellent means of identifying discrepancies in the permittee’s analytical techniques and procedures. When filling split samples from a single composite jug, shake the composited sample well and half fill the EPA sample container, then shake the composite again and fill half of the permittee’s container. Repeat the procedure for each parameter collected.

The laboratories performing the sample analyses should also use the following control measures:

Prep/Reagent Blank. A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps to error in the observed value.

Quality Control Sample. This is an uncontaminated sample matrix spiked with known amounts of analytes from a source independent from the calibration standards. Use this sample to establish intra laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurements' system.

Matrix Spike/Matrix Spike Duplicate (MS/MSD). This sample is three times the normal volume required for a specific chemical analysis to which a known quantity of analyte has been added prior to all sample preparation. The laboratory utilizes the MS/MSD samples as part of their Quality Assurance/Quality Control Program.

- Use a matrix spike to verify accuracy of the analytical procedures.

- A matrix spike duplicate is a duplicate of a matrix spike sample. It measures the precision of the analysis in terms of relative percent difference.

Table 5-4 indicates quality control procedures for field analyses and equipment. Quality control is discussed in greater detail in Chapter Seven of this manual and EPA's *NPDES Compliance Inspector Training Laboratory Analyses Manual*, April 1990.

Table 5-4

Quality Control Procedures for Field Analysis and Equipment

Parameter	General	Daily	Frequency
Dissolved Oxygen			
Membrane Electrode	• Enter the make, model, and serial and/or ID number for each meter in a logbook. • Report data to nearest 0.1 mg/l.	• Calibrate meter using manufacturer's instructions or Winkler-Azide method. • Check membrane for air bubbles and holes. Change membrane and KCl if necessary. • Check leads, switch contacts, etc., for corrosion and shorts if meter pointer remains off-scale.	• Quarterly, check instrument calibration and linearity using a series of at least three dissolved oxygen standards. • Quarterly, take all meters to the laboratory for maintenance, calibration, and quality control checks.
Winkler-Azide method	• Record data to nearest 0.1 mg/l.	• Duplicate analysis should be run as a precision check. Duplicate values should agree within ±0.2 mg/l.	
pH			
Electrode Method	• Enter the make, model, and serial and/or ID number for each meter in a logbook.	• Calibrate the system against traceable standard buffer solutions of known pH value which closely bracket the actual sample pH (e.g., 4, 7, and 10 at the start of a sampling run). • Periodically check the buffers during the sample run and record the data in the logbook. • Be on the alert for erratic meter response arising from weak batteries, cracked electrodes, fouling, etc. • Check response and linearity following highly acidic or alkaline samples. Allow additional time for equilibration. • Check against the closest reference solution each time a violation is found. • Rinse electrodes thoroughly between samples and after calibration. Blot dry.	

Table 5-4

Quality Control Procedures for Field Analysis and Equipment (Continued)

Parameter	General	Daily	Frequency
Conductivity			
	• Enter the make, model, and serial and/or ID number for each meter in a logbook.	• Standardize with KCl standards having similar specific conductance values to those anticipated in the samples. Calculate the cell constant using two different standards. • Rinse cell after each sample to prevent carryover.	• Quarterly, take all meters to lab for maintenance, calibration, and quality control checks. • Quarterly, check temperature compensation. • Quarterly, check date of last platinizing, if necessary. • Quarterly, analyze NIST or EPA reference standard, and record actual vs. observed readings in the logbook.
Residual Chlorine			
Amperometric Titration	• Enter the make, model, and ID and/or serial number of each titration apparatus in a logbook. Report results to nearest 0.01 mg/l.	• Refer to instrument manufacturer's instructions for proper operation and calibration procedures.	• Biweekly, return instrument to lab for maintenance and addition of fresh, standardized reagents.

Table 5-4

Quality Control Procedures for Field Analysis and Equipment (Continued)

Parameter	General	Daily	Frequency
Manual Thermometer	• Enter the make, model, and serial and/or ID number and temperature range. • All standardization should be against a traceable NIST or NIST calibrated thermometer. Reading should agree within ±1°C. If enforcement action is anticipated, calibrate the thermometer before and after analysis. All data should be read to the nearest 1°C. Report data between 10° and 99°C to two significant figures.	• Check for air spaces of bubbles in the column, cracks, etc. Compare with a known source if available.	• Biweekly, check at two temperatures against a NIST or equivalent thermometer. Enter data in logbook. • Temperature readings should agree within ±1°C or the thermometer should be replaced or recalibrated. • Initially and biannually, determine accuracy throughout the expected working range of 0°C to 50°C. A minimum of three temperatures within the range should be used to verify accuracy. Preferable ranges are 5-10°C, 15-25°C, and 35-45°C.
Thermistors, Thermographs	• Enter the make, model, and serial and/or ID number of the instrument in a logbook. All standardization shall be against a NIST or NIST calibrated thermometer. Reading should agree within ±1°C. If enforcement action is anticipated, refer to the procedure listed above.	• Check thermistor and sensing device for response and operation according to the manufacturer's instruction. Record actual vs. standard temperature in logbook.	• Initially and biannually, determine accuracy throughout the expected working range of 0°C to 50°C. A minimum of three temperatures within the range should be used to verify accuracy. Preferable ranges are 5-10°C, 15-25°C, and 35-45°C.
Flow Measurement			
	• Enter the make, model, and serial and/or ID number of each flow measurement instrument in a logbook.	• Install the device in accordance with the manufacturer's instructions and with the procedures given in owner's manual.	• Annually affix record of calibration (NIST, manufacturer) to the instrument log.

Table 5-4

Quality Control Procedures for Field Analysis and Equipment (Continued)

Parameter	General	Daily	Frequency
Automatic Samplers			
	• Enter the make, model, and serial and/or ID number of each sampler in a logbook.		• Check intake velocity vs. head (minimum of three samples), and clock time setting vs. actual time interval.

Quality Assurance Project Plan

The EPA has developed the Quality Assurance Project Plan (QAPP) as a tool for project managers and planners to document the type and quality of data needed for the agency to make environmental decisions and to describe the methods for collecting and assessing those data. The QAPP is required for all EPA projects resulting in the generation, collection, and use of environmental data. The development, review, approval and implementation of the QAPP is an integral part of an Agency-wide Quality System, which is required per the authority of EPA Order 5360.1 A2.

If the EPA is to have confidence in the quality of data used to support environmental decisions, there must be a systematic planning process in place. A product of the systematic planning process is the QAPP. An example of the systematic planning process endorsed by the EPA is the Data Quality Objectives (DQO) Process. The QAPP ensures that the needed management and technical practices are in place so that environmental data used to support agency decisions are of adequate quality and usability for their intended purpose.

Prior to the start of data collection, a QAPP defining the goals and scope of the project, the need for sample collection, a description of the data quality objectives and QA/QC activities to ensure data validity and usability must be developed by the project officer. Thereafter, a review by all parties to the sampling effort, such as a Quality Assurance (QA) Officer, must be conducted. Also, EPA laboratories will require a copy of an approved QAPP prior to conducting any sample analysis. This QAPP requirement applies to both EPA staff and outside contractors. The process for approval of the QAPP and other documents related to the data collection activity should be outlined in the lead organization's Quality Management Plan (QMP).

For further information on the QAPP's please visit the Office of Environmental Information (OEI) web page at: www.epa.gov/quality. Then click on the radio button for "documents" which contains valuable information. There is also a section on Guidance on the same web-site.

Data Handling and Reporting

Verified analytical results are normally entered into a laboratory data management system of some type. The system should contain the sampling data, including time and exact location, analysis dates and times, names of analysts, analytical methods/techniques used, and analytical results. Data are then reported to the project officer (inspector) for inclusion into the compliance report. The quality assurance manual by EPA (*Handbook for Analytical Quality Control in Water and Wastewater Laboratories*, USEPA 1979) and the article by J.J. Delfino ("Quality Assurance In Water and Wastewater Analysis Laboratories," Delfino 1977) provide useful information to the inspector on a number of data management techniques.

5. C. References and Permittee Sampling Inspection Checklist

References

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PERMITTEE SAMPLING INSPECTION CHECKLIST

A. PERMITTEE SAMPLING EVALUATION

Yes	No	N/A	1.	Take samples at sites specified in permit.
Yes	No	N/A	2.	Locations adequate for representative samples.
Yes	No	N/A	3.	Flow proportioned samples obtained when required by permit.
Yes	No	N/A	4.	Complete sampling and analysis on parameters specified by permit.
Yes	No	N/A	5.	Conduct sampling and analysis in frequency specified by permit.
Yes	No	N/A	6.	Permittee uses method of sample collection required by permit. Required method:_____ If not, method being used is: ( ) Grab ( ) Manual composite ( ) Automatic Composite
			7.	Sample collection procedures adequate:
Yes	No	N/A		a. Samples refrigerated during compositing.
Yes	No	N/A		b. Proper preservation techniques used.
Yes	No	N/A		c. Containers and sample holding times before analyses conform to 40 *CFR* 136.3.
Yes	No	N/A		d. Samples analyzed in time frame needed.
Yes	No	N/A	8.	Facility performs monitoring and analyses more often than required by permit; if so, results reported in permittee's self-monitoring report.
Yes	No	N/A	9.	Samples contain chlorine.
Y es	No	N/A	10.	Use contract laboratory for sample analysis.
Yes	No	N/A	11.	POTW collects samples from industrial users in pretreatment program.

B. SAMPLING INSPECTION PROCEDURES AND OBSERVATIONS

Yes	No	N/A	1.	Obtain grab samples.
Yes	No	N/A	2.	Obtain composite sample. Compositing Frequency:___ Preservation: _____
Yes	No	N/A	3.	Refrigerate sample during compositing.
Yes	No	N/A	4.	Obtain flow proportioned sample.
Yes	No	N/A	5.	Obtain sample from facility sampling device.
Yes	No	N/A	6.	Sample representative of volume and nature of discharge.
Yes	No	N/A	7.	Sample split with permittee.
Yes	No	N/A	8.	Employ chain-of-custody procedures.
Yes	No	N/A	9.	Samples collected in accordance with permit.
Yes	No	N/A	10.	Observe excessive foam, grease, floating solids at the outfall.

C. AUTOMATIC SAMPLER PROCEDURES AND OBSERVATIONS

Yes	No	N/A	1.	Sample intake tubing place in a well mixed, representative location (0.4 to 0.6 depth).
Yes	No	N/A	2.	Individual aliquot volume checked and at least 100ml.

PERMITTEE SAMPLING INSPECTION CHECKLIST (Continued)

C. AUTOMATIC SAMPLER PROCEDURES AND OBSERVATIONS (Continued)

Yes	No	N/A	3.	Proper sample tubing (teflon for organics, otherwise tygon) and tubing at ID at least 0.25 inch.
Yes	No	N/A	4.	Proper composite sample container (glass for organics, otherwise plastic.
Yes	No	N/A	5.	Proper refrigeration (4^0C or ice), with required documentation.
Yes	No	N/A	6.	Proper wastewater velocity in the sample tubing (at least 2 fps).