

## **WASTEWATER SAMPLING PROCEDURES**

The analytical results of a sample are only as accurate as the quality of the sample taken. If your technique for collecting samples is poor, then no matter how accurate your lab procedures are, the results will be poor. By sampling according to set procedures, you reduce the chance of error and increase the accuracy of your sample results.

This is a document compiled from information obtained from the Environmental Protection Agency, Water Environment Federation, Florida Dept. of Environmental Protection and ISCO Manufacturing publications. It will cover the proper methods of sampling, sample preparation, documentation and sampler cleaning.

### **The Six Criteria For Quality Data**

1. Collecting Representative Samples
2. Formulating The Objectives Of The Sampling Program
3. Proper Handling And Preservation Of Water Samples
4. Proper Chain-Of-Custody And Sample Id Procedures
5. Field Quality Assurance
6. Proper Analysis

### **Collecting Representative Samples**

#### **I. Flow Measurement**

##### **A. Devices and Methods:**

1. **Portable Flow Meters**-These meters need some type of primary measuring device in the stream such as a flume or weir to get accurate results. The flow meter then measures the water depth with a pressure sensor. The manufacturers instructions must be followed for accurate measurement.
2. **Consumption Meter**- Some sample locations are not suitable for placing a portable flow meter. In those cases, the consumption meter will need to be read before and after the sample period. This will give you a quantity that will probably be somewhat higher than the actual waste flow but will be more accurate than most other methods. If the sample site uses water to irrigate lawns or has other uses that do not require the water to go down the sewer avoid sampling on those days if possible.
3. **Manning Formula**-The rate of flow in an open channel can be determined, if the conditions are right, without the use of a primary measuring device. The cross section of the pipe must be uniform and the slope and roughness of the pipe is known. The flow can only be by gravity. The formula is in *Isco Open Channel Flow Measurement Handbook, third edition*. The required formula and tables can also be found on the Internet, (<http://wilkes1.wilkes.edu/~whitman/ENV322/LEC/open1.html>). Some flow meters can be programmed to measure flow using the Manning formula.

Manning Formula: 
$$Q = \frac{KAR^{2/3}S^{1/2}}{N}$$

Q = flow rate  
 A = cross sectional area of flow  
 R = hydraulic radius  
 S = slope of the hydraulic Gradient  
 n = Manning coefficient of roughness  
 K = constant dependent upon units

**Location: Example**

**Date:**

n-roughness	0.014	
S-slope	0.02	
d-depth of flow in dec.	0.1875	
D-diameter	12	
D-diameter in ft.	1	
d/D	0.015625	*Table 6-2 page 110
A/D <sup>2</sup>	0.08	
A	0.08	
R/D	0.098	Table 6-2 page 110
R	0.098	
Gallons/min	114.9177508	
Gallons/8 hr day	55160.52	

\*Isco Open Channel Flow Measurement Book

4. **Flow Insert**-These devices are inserted into the end of a pipe that flows into to an open channel pipe. These inserts work like a weir and must have a relatively level channel to be used.

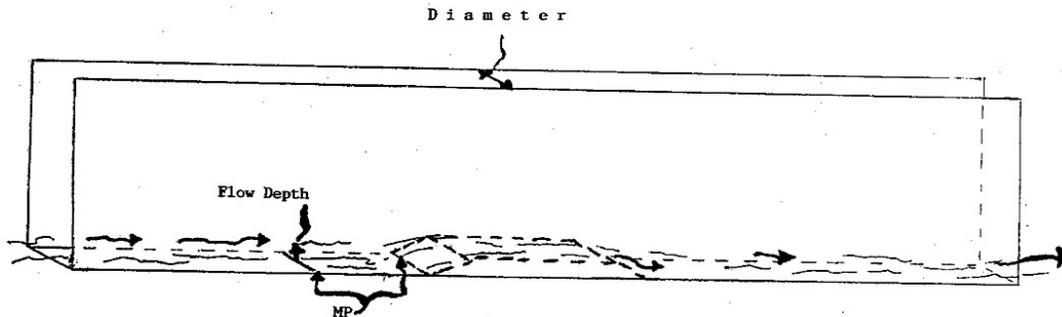
**B. Calibrations:**

1. **Calibrating Flow Meters**- When the flow sensor is placed in the stream it must be calibrated to the stream's actual depth. This is done by measuring the stream's depth at the spot where the flow sensor is located. Use a stiff measuring stick. To make it easier to read the water depth, use indicator paste to see where the water level mark is. When using the flow meter with a Palmer-Bowles flume there are

two measurements needed to get an accurate flow reading. The first one establishes the measuring point by dividing the diameter of the pipe or channel by 2 and measure back from the bottom of the upper transition ( $D/2$ =measuring point). The second measurement is the depth of flow, at the measuring point. The flow depth is then put in the following formula (Flow depth at measuring point -  $D/6$ =actual depth), (see: *Isco Open Channel Flow Measurement Handbook, third edition and the Palmer-Bowlus Flume diagram*). This value represents the depth of flow over the flume. The flow meter can be calibrated from this value. This procedure is only for use with Palmer-Bowles flumes. For other flow measuring devices, see the calibration procedure for that instrument.

### Palmer-Bowlus Flume Flow Measurement

PALMER - BOWLUS FLUME  
FLOW MEASUREMENT



Diameter =  $D$  ( $D/2$ ) = Measuring Point (MP)

Flow Depth =  $F$  ( $F-D/6$ ) = Actual Flow Depth

2. **Manning Formula Measurements**-Depth measurements will need to be done periodically and then averaged for use in the formula.
3. **Zeroing The Flow Insert**-The flow insert must be connected to the flow meter and zeroed before it is inserted into the sewer line.

## II. Sample Collection

### A. Devices and Methods:

1. **Automatic Samplers**-These devices collect samples by periodically pumping a sample into a sample bottle or sample bottles. The sampler is triggered to sample by a set time or by the amount of liquid that passes by a flow-measuring device.
2. **Sample Dip Poles**- Plastic or aluminum rods that are expandable to lengths of 20 ft. They have devices on the end to hold a sample bottle securely.
3. **Sample Types**-
  - a. **Grab**-Each sample shows the characteristics of the water at the time of sampling only and should not exceed a sampling time of 15 minutes. Grab sampling is done for such procedures as batch discharge, constant wastestream characteristics and when the parameter tested deteriorates rapidly such as cyanides, volatile organic compounds and phenols (See 40 CFR, Part 403 Appendix E).
  - b. **Composite**-These are individual samples taken and deposited in the same collection bottle. There are two methods that are most common to collecting composite samples. Time paced is when samples are collected at set increments of time. Flow paced samples are taken when a measured volume of water flows over the sensor of a flow meter. The preferred method of sampling is by flow pacing. This gives the most representative sample. Metals, Base/Neutral/Acid Organics, BOD and TSS samples may be collected by this method.
  - c. **Grab Composite**- This procedure is not commonly used but is useful for such parameters as total oil and grease released to the sewer system in a 24-hour period. Individual samples are grabbed in the field and then composited in the lab or in the field for analysis. Another variation on grab composite is the flow-proportioned grab composite. Samples are grabbed in the usual manner but the flow level is recorded at the time of sampling. After all the predetermined times of sampling are done the composite is made with portions of each grab sample according to the amount of flow at the time of sampling.
  - d. **Volatile Organic Compounds Grab**- These samples are collected in a clean glass beaker and transferred to 40-milliliter vials, usually with HCl acid for a preservative. The cap has a flexible septum in it. There must not be any air bubbles in the vial, so the cap must not have an air space under it. The vial must be filled until the liquid crowns and the cap screwed until the septum bulges.
  - e. **Discrete Sampling**- This method is used when you want to look at the characteristics of the wastewater flow at certain times of the day, for certain parameters, such as high or low pH, or for high or low flow events. Samples are taken in individual bottles at the time of the event and each sample is analyzed. This method can also be used for flow composites if the flow rate is recorded at the time of sampling.

## B. Sampler Programming:

### 1. Tubing

- a. **Length & diameter-** The sample volume is determined by the length, type and diameter of the sample tube. The computer program built into most samplers will do this calculation.
  - b. **Type-** Vinyl tubing is to be used for metals, BOD and TSS samples. Teflon tubing can be used for all samples, including organics samples that are not volatile. It cannot be used for oil and grease samples.
2. **Flow-paced sample frequency-** An idea of total daily flow is needed to calculate how much flow passes the sample tube before the sample is taken. Too low a flow estimate will mean the sampler will fill its bottle or bottles before the 24 hour sampling period is done and too high a flow estimate will mean the sampler will collect too few samples in the 24 hour period.
  3. **Sample volume-** The volume of the sample collection vessel must be known so that the amount of each sample taken can be determined. For example: If the collection container is 10,000 milliliters and 125 samplings will occur, the sample volume can be no more than 80 milliliters or the collection container will overflow or the sampler will shut-off when it reaches 10,000 milliliters.

### **Formulating The Objectives Of The Sampling Program**

#### **I. To Fulfill the Sampling Requirements of the IPP Program**

##### **A. Self monitoring:**

1. **Review and schedule-** Schedule and review the SIU's yearly sampling requirements.
2. **Monitor the results-** Make sure the sample results come in on time and that the results are within permit limits.
3. **Sample collection training-** Periodically go over the sampling procedures with the SIU's.

##### **B. Compliance monitoring:**

1. **Collecting samples-** Collect the necessary samples from the SIU's waste streams.
2. **Records-** Keep accurate records of the sampling events and the results.
3. **Verify-** The results of the compliance monitoring should verify if the SIU is collecting accurate data when they collect their self-monitoring.

#### **II. To Fulfill the Sampling Requirements of the NPDES Permit**

##### **A. Permit required plant sampling:**

1. **Collecting samples-** Collect the necessary samples from the WPCF waste streams.
2. **Records-** Keep accurate recorders of the sampling events and the results.
3. **Representative-** Make sure samples are a true representation of the effectiveness of the treatment plant processes.
4. **Identify Pollutants-** Identify pollutants of concern for local limit development.

5. **Determine Removal Rates-** Determine pollutants of concern removal rate through the Water Pollution Control Facility.
6. **Reporting-** Sample results are to be the State and Environmental Protection Agency.

### III. For Waste Treatment Plant Operation

#### A. Process control sampling:

1. **Collecting samples-** Collect the necessary samples from the WPCF waste streams to operate and monitor plant processes.
2. **Records-** Keep accurate records of the routine and unique sampling events and the results.
3. **Representative-** Make sure samples are a true representation of the effectiveness of the treatment plant processes.

### Proper Handling And Preservation Of Water Samples

#### I. Proper Handling Of Samples

##### A. Equipment cleaning:

1. **Sampler cleaning-** The case can be cleaned with soap and water and rinsed thoroughly. The sampler head can be cleaned in the same manner if the connector terminals are covered. The optional cage and float assembly can be removed, on some samplers, and cleaned like the case or it can be left off but the sampler will not shut off when the sample bottle is full. Removal of the cage and float assembly will reduce the chances of contamination from previous samples when the sample has very low parameter limits.
2. **Tubing cleaning-** Vinyl tubing should not be re-used after sampling. Pump tubing should be medical grade because it does not contain any organic materials. Inspect it for wear and replace if necessary.
  - a. **Pump tubing cleaning-**
    - Rinse the tubing by running hot water through it for 2 minutes. Soap, such as Liqui-Nox, Alconox, Citranox or the appropriate equivalent, must be used.
    - Rinse the tubing with reagent grade 20% hydrochloric acid, reagent grade nitric acid or 2% solution of Citranox for 2 minutes.
    - Rinse the tubing with hot water for 2 minutes.
    - Rinse the tubing with distilled water for 2 minutes.
    - Place Parafilm M over the ends.
  - b. **Teflon tubing cleaning-**
    - Rinse twice with a minimum of at least spectra-grade or pesticide grade acetone.

- Rinse thoroughly with hot tap water. Use a tube brush if necessary, to clean particles out of the tubing. Rinse 3 times.
- Acid wash with 20% hydrochloric, nitric acid or 2% solution of Citranox.
- Rinse 3 times with tap water and 3 times with distilled water.
- Petroleum ether may used to dry the tubing by rinsing it with the ether and pulling room air through the tubing.
- If possible, dry in an oven (less than 150 deg. F) overnight.
- Place Para film M over the ends.

**c. Collection Sample Container cleaning-**

**1) Plastic (polyethylene)**

- Wash with hot water (detergent optional).
- Rinse with acid (nitric for metals) or a 2% solution of Citranox.
- Rinse with tap water, then three times with Distilled water.

**2) Glass**

- Wash with hot water (detergent optional).
- Rinse with acid (nitric for metals) or a 2% solution of Citranox.
- Rinse with tap water, then three times with Distilled water.
- Dry in contamination-free area.
- Rinse glass containers with an interference-free, redistilled solvent (e.g., acetone, isopropanol or methylene chloride) for extractable organics.
- Rinse glassware for volatile organics with isopropanol.
- Rinse with tap water, then at least three times with DI water.
- Dry in contaminant-free area.

**3) Ice Chests**

- Wash the exterior and interior of all ice chests with laboratory detergent after each use and rinse with tap water and air dry.

**d. Recycling-**

- Only Teflon tubing, pump tubing and composite sample jugs should be recycled for more use in sampling. Every other container and tubing should be discarded.

**e. Disposable Polyethylene Bags-**

- These bags can be ordered from various vendors and can be used for collecting BOD and TSS samples. These bags can not be reused.

**II. Preservation Of Water Samples**

**A. 40 CFR Preservation Chart:**

<b>EPA Required Containers, Preservation Techniques, and Holding Times</b>			
<b>PARAMETER NO./ NAME</b>	<b>CONTAINER (1)</b>	<b>PRESERVATION (2,3)</b>	<b>MAXIMUM HOLDING TIME (4)</b>
<b>Table IA – Bacteria Tests</b>			
1-4 Coliform, Fecal & Total	P, G	Cool, 4C, 0.008% <sup>5</sup>	6 hours
5 Fecal Streptococci	P, G	Cool, 4C, 0.008% <sup>5</sup>	6 hours
<b>Table IA – Aquatic Toxicity Tests</b>			
6-10 Toxicity, Acute & Chronic	P, G	Cool, 4C <sup>16</sup>	36 hours
<b>Table IB – Inorganic Tests</b>			
1. Acidity	P, G	Cool, 4C	14 days
2. Alkalinity	P, G	Cool, 4C	14 days
4. Ammonia	P, G	Cool, 4C, H2SO4 to pH<2	28 days
9. Biochemical Oxygen Demand	P, G	Cool, 4C	48 hours
10. Boron	P, PFTE or Quartz	HNO3 to pH<2	6 months
11. Bromide	P, G	None Required	28 days
14. Biochemical Oxygen Demand, Carbonaceous	P, G	Cool, 4C	48 hours
15. Chemical Oxygen Demand	P, G	Cool, 4C, H2SO4 to pH<2	28 days
16. Chloride	P, G	None Required	28 days
17. Chlorine, Total Residual	P, G	None Required	Analyze immediately
21. Color	P, G	Cool, 4C	48 hours
23 – 24. Cyanide, Total and Amenable to Chlorination	P, G	Cool, 4C, NaOH to pH>12, 0.6g Ascorbic Acid <sup>5</sup>	14 days <sup>6</sup>
25. Fluoride	P	None Required	28 days
27. Hardness	P, G	HNO3 to pH<2, H2SO4 to pH<2	6 months
28. Hydrogen Ion (pH)	P, G	None Required	Analyze immediately
31, 43. Kjeldahl & Organic Nitrogen.	P, G	Cool, 4C, H2SO4 to pH<2	28 days

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<b>Metals:</b> <sup>7</sup>			
18. Chromium VI	P, G	Cool, 4C	24 hours
35. Mercury	P, G	HNO <sub>3</sub> to pH<2	28 days
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, G	HNO <sub>3</sub> to pH<2	6 months
38. Nitrate	P, G	Cool, 4C	48 hours
39. Nitrate-Nitrite	P, G	Cool, 4C, H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
40. Nitrite	P, G	Cool, 4C	48 hours
41. Oil & Grease	G	Cool, 4C, HCL or H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
42. Organic Carbon	P, G	Cool, 4C, HCL or H <sub>2</sub> SO <sub>4</sub> or H <sub>3</sub> PO <sub>4</sub> to pH<2	28 days
44. Orthophosphate	P, G	Filter Immediately, Cool, 4C	48 hours
46. Oxygen, Dissolved Probe	G Bottle & Top	None Required	Analyze immediately
47. Winkler	G Bottle & Top	Fix on Site and Store in Dark	8 hours
48. Phenols	G only	Cool, 4C, H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
49. Phosphorus	G	Cool, 4C	48 hours
50. Phosphorus, Total	P, G	Cool, 4C, H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days
53. Residue, Total	P, G	Cool, 4C	7 days
54. Residue, Filterable	P, G	Cool, 4C	7 days
55. Residue, Nonfilterable (TSS)	P, G	Cool, 4C	7 days
56. Residue, Settleable	P, G	Cool, 4C	48 hours
57. Residue, Volatile	P, G	Cool, 4C	7 days
61. Silica	P, PFTE or Quartz	Cool, 4C	28 days
64. Specific Conductance	P, G	Cool, 4C	28 days
65. Sulfate	P, G	Cool, 4C	28 days
66. Sulfide	P, G	Cool, 4C, add Zinc & Acetate Plus Sodium Hydroxide to pH>9	7 days
67. Sulfite	P, G	None Required	Analyze immediately
68. Surfactants	P, G	Cool, 4C	48 hours
69. Temperature	P, G	None Required	Analyze
73. Turbidity	P, G	Cool, 4C	48 hours

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<b>Table IC – Organic Tests</b>			
13, 18-20, 22, 24-28, 34-37 39-43, 45-47, 56, 76, 104, 105, 108-111, 113. Purgeable Halocarbons	G, Teflon- lined Septum	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup>	14 Days
6, 57, 106. Purgeable Aromatic Hydrocarbons	G, Teflon- lined Septum	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup> , HCL to pH <sup>2</sup> <sup>9</sup>	14 Days
3, 4. Acrolein & Acrylonitrile	G, Teflon- lined Septum	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup> , Adjust pH to 4-5 <sup>10</sup>	14 Days
23, 30, 44, 49, 53, 77, 80, 81, 98, 100, 102. Phenols <sup>11</sup>	G, Teflon- Lined Cap	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup>	7 Days Until Extraction; 40 Days After Extraction
7, 38. Benzidines <sup>11</sup>	G, Teflon- lined Septum	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup>	7 Days Until Extraction <sup>13</sup>
14, 17, 48, 50-52. Phthalate Esters <sup>11</sup>	G, Teflon- lined Septum	Cool, 4C	7 Days Until Extraction; 40 Days After Extraction
82-84. Nitrosamines <sup>11, 14</sup>	G, Teflon- lined Septum	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup> , Store in Dark	7 Days Until Extraction; 40 Days After Extraction
88-94. PCBs <sup>11</sup>	G, Teflon- lined Septum	Cool, 4C	7 Days Until Extraction; 40 Days After Extraction
54, 55, 75, 79. Nitroaromatic & Isophorone	G, Teflon- lined Septum	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup> , Store in Dark	7 Days Until Extraction; 40 Days After Extraction
1, 2, 5, 8-12, 32, 33, 58, 59, 74, 78, 99, 101. Polynuclear Aromatic Hydrocarbons <sup>11</sup>	G, Teflon- lined Septum	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup> , Store in Dark	7 Days Until Extraction; 40 Days After Extraction
15, 16, 21, 31, 87. Haloethers	G, Teflon- lined Septum	Cool, 4C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup> ,	7 Days Until Extraction; 40 Days After Extraction
29, 35-37, 63-65, 73, 107. Chlorinated Hydrocarbons <sup>11</sup>	G, Teflon- lined Septum	Cool, 4C	7 Days Until Extraction; 40 Days After

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			Extraction
60-62, 66-72, 85, 86, 95-97, 102, 103. CDDs/CDFs <sup>11</sup> Aqueous: Field and Lab	G	Cool, 0- 4C, pH<9, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <sup>5</sup>	1 year
Solids, Mixed Phase, and Tissue: Field Preservation	G	Cool, 4C	7 days
Solids, Mixed Phase, and Tissue: Lab Preservation	G	Freeze, <-10C	1 year
<b><u>Table ID – Pesticides Tests</u></b>			
1-70. Pesticides <sup>11</sup>	G	Cool, 4C, pH 5-9 <sup>15</sup>	1 year
<b><u>Table IE – Radiological Tests</u></b>			
1-5. Alpha, beta and Radium	P, G	HNO <sub>3</sub> to pH<2	6 months

**Table II Notes**

<sup>1</sup> Polyethylene (P) or glass (G). For microbiology, plastic sample containers must be made of sterilizable materials (polypropylene or other autoclavable plastic).

<sup>2</sup> Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4 deg. C until compositing and sample splitting is completed.

<sup>3</sup> When any sample is to be shipped by common carrier or sent through the United States Mails, 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 (HNO<sub>3</sub>) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 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).

<sup>4</sup> Samples should be analyzed 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 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 Sec. 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. See Sec. 136.3(e) for details. The term "analyze immediately" usually means within 15 minutes or less of sample collection.

<sup>5</sup> Should only be used in the presence of residual chlorine.

<sup>6</sup> Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

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<sup>7</sup> Samples should be filtered immediately on-site before adding preservative for dissolved metals.

<sup>8</sup> Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

<sup>9</sup> Sample receiving no pH adjustment must be analyzed within seven days of sampling.

<sup>10</sup> 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.

<sup>11</sup> 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. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4 deg. 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 of residual chlorine), and footnotes 12, 13 (re the analysis of benzidine).

<sup>12</sup> If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 $\pm$ 0.2 to prevent rearrangement to benzidine.

<sup>13</sup> Extracts may be stored up to seven days before analysis if storage is conducted under an inert (oxidant – free) atmosphere.

<sup>14</sup> For the analysis of diphenylnitrosamine, add 0.008% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and adjust pH to 7-10 with NaOH within 24 hours of sampling.

<sup>15</sup> 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% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

<sup>16</sup> 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 4C temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature can not 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 that show that the toxicity of the effluent samples is not reduced because of the increased holding temperature.

**Proper Chain-of-Custody and Sample Identification Procedures**

**I. Chain-of-Custody**

**A. Form:**

CITY OF GREELEY  
CHAIN OF CUSTODY

300 E 8th Street, Greeley, CO 80631  
(970) 350-9363

WATER POLLUTION CONTROL FACILITY  
WASTEWATER TREATMENT DIVISION

PROJECT NAME: **XYZ, Inc. 1<sup>st</sup> QUARTER SELF-MONITORING**

PROJECT CONTACT NAME: **Joe Sampler**

PROJECT CONTACT TELEPHONE: **555-555-5555**

SAMPLERS: (PRINT) **B. Joe Sampler**

ANALYSTS REQUESTED  
40 CFR 136 Methods

**BOD, TSS**  
**Total Metals: Cr, Cu, Ni, Ag, Hg, Cd, Zn**  
**Cyanide, Total**  
**OIL AND GREASE**  
**VOC METHOD EPA 624**

REMARKS  
**EXAMPLE**

DATE	TIME	COMP	GRAB	STATION LOCATION	NUMBER OF CONTAINERS	DATE	TIME	DATE	TIME	SPLIT SAMPLES:
7-8-02	10:30-10:35	X		XYZ, Inc. OUTFALL 02	2, 500mL/p	X	X			Metals preserved with HNO <sub>3</sub> BOD, TSS preserved @ 4°C
7-9-02	10:40		X	"	1, 500mL/p		X			Preserved with NaOH to pH>12 Preserved with H <sub>2</sub> SO <sub>4</sub> @ 4°C.
7-8-02	10:02		X	"	1, 1L. glass			X		
7-9-02	1030-1630	X		"	4, 40mL. glass				X	Composite each vial equally
REINQUISHED BY: (SIGNATURE) _____ DATE: _____ TIME: _____ RECEIVED BY: (SIGNATURE) _____ DATE: _____ TIME: _____ SPLIT SAMPLES: _____										
REINQUISHED BY: (SIGNATURE) _____ DATE: _____ TIME: _____ RECEIVED BY: (SIGNATURE) _____ DATE: _____ TIME: _____ SPLIT SAMPLES: _____										
REINQUISHED BY: (SIGNATURE) _____ DATE: _____ TIME: _____ RECEIVED BY: (SIGNATURE) _____ DATE: _____ TIME: _____ SPLIT SAMPLES: _____										
REINQUISHED BY: (SIGNATURE) _____ DATE: _____ TIME: _____ RECEIVED BY: (SIGNATURE) _____ DATE: _____ TIME: _____ SPLIT SAMPLES: _____										

## **B. Custody Form Procedure:**

1. **(A) Project Number-** Assign a number to the sampling episode that can be used on the bottles to track the samples.
2. **(B) Sampler-** The sampler should print and/or sign their name.
3. **(C) Project Name-** The project name, and if necessary, the project address.
4. **(D) Project Contact Name-** The name of the person who is in charge of the project.
5. **(E) Project Telephone Number-** The phone number of where the project contact person can be received.
6. **(F) Sample Date-**List the dates for grab and composite samples.
7. **(G) Sample Time-**List the sample time for each sample.
8. **(H) Composite-** Check this box for samples collected over a 24-hour period.
9. **(I) Grab-** Check this box for samples that were taken as grab samples.
10. **(J) Station Location-** The site where the sample was taken.
11. **(K) Number of Containers-** List the number and type of containers for each sampling event.
12. **(L) Analysis Requested-** List the analysis needed that is compatible with 40 CFR 136 Methods.
13. **(M) Remarks-** Note any special requirement for the samples for the laboratory.
14. **(N) Relinquished-** When a sample is turned over to a laboratory or second party, it must have the signature, date and time of when it was relinquished and who relinquished it.
15. **(O) Received By-** Must be signed and have the date and time when it is received from the shipping party.
16. **(P) Relinquished-** See (N).
17. **(Q) Received-** See (O).
18. **(R) Split Samples-** When a sample is split into different proportions for analysis, the receiving party can accept or reject the samples and they must sign this box.

## **II. Sample Identification**

### **A. Container Label Requirements:**

1. **Sample Site Location.**
2. **Container Number-**If more than one container/ sample.
3. **Name of Sample Collector.**
4. **Facility name/location.**
5. **Date and Time of Collection.**
4. **Identify as a Grab or Composite.**
5. **Test Parameters-**List analysis to be done.
6. **Preservative Used.**

### **B. Sample Data Sheet:**

A list of the samples collected should be kept. This could be the chain-of-custody form and a copy should be kept after the samples are shipped off or submitted to your lab.

The sheet should include the information in **II, A.**

### **C. Custody Seal:**

This seal should keep the cover of the shipping container from being opened because to do so would ruin the integrity of the seal. The seal should include the shipping or receiving facility name, the collector’s name and the date the container is sealed for shipment.

**Quality Assurance**

**I. Sample Control** – Quality assurance protocols are implemented to ensure that sample collection procedures are not resulting in contamination of samples used to determine compliance. At least 10 percent of all samples collected undergo one of the following quality control events.

- A. Duplicate Samples-** Separate samples taken from the same source at the same time. These provide a check on equipment and technique.
- B. Split Samples-** A sample is divided into two containers for analysis to check handling and analytical procedures.
- C. Equipment Blanks-** After a set number of sampling events a cleaned sampler is taken and DI water is run through the sampler and collected for analysis.
- D. Trip Blanks-** Periodic blank samples are stored for parameters that are required to be sampled and these blanks are analyzed.

**II. Equipment Control**

**A. Clean Equipment:**

- 1. Equipment Labels-** After sampling equipment is cleaned properly a label should be attached to the equipment stated when and how it was cleaned and who cleaned it.
- 2. Equipment Log-** A log should be kept with how the sampler was cleaned, when the sampler was cleaned, who cleaned the sampler and when sample blanks need to be done.
- 3. Reusable Collection Containers-** They must be washed and rinsed according to the proper cleaning procedure and then a label should be attached to the container with the information of who cleaned the container, how it was cleaned, and when it was cleaned.

**Proper Analysis**

**I. Proper Procedures**

**A. Chart:**

**EPA APPROVED TESTING PROCEDURES**

<b>METALS:</b>	<b>METHOD 200.7</b>	<b>METHOD 245.1</b>	<b>METHOD 200.8</b>
	Total Antimony (Sb)	Mercury (Hg)	Total Recoverable Thallium, mg/L
	Total Arsenic (As)		Total Antimony (Sb)
	Total Beryllium (Be)		Total Beryllium (Be)
	Total Cadmium (Cd)		Total Cadmium (Cd)
	Total Chromium (Cr)		Total Chromium (Cr)

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Total Copper (Cu)	Total Copper (Cu)
Total Lead (Pb)	Total Lead (Pb)
Total Nickel (Ni)	Total Nickel (Ni)
Total Selenium (Se)	Total Selenium (Se)
Total Silver (Ag)	Total Thallium (Ti)
Total Thallium (Ti)	Total Cadmium (Cd)
Total Zinc (Zn)	Total Chromium (Cr)
Total molybdenum (Mo)	Total Copper (Cu)
Total Cadmium (Cd)	Total Lead (Pb)
Total Chromium (Cr)	Total Nickel (Ni)
Total Copper (Cu)	
Total Lead (Pb)	
Total Nickel (Ni)	

<b>ORGANICS: METHOD 420.1</b>	<b>METHOD 624</b>	<b>METHOD 8270C</b>	<b>METHOD 608</b>	<b>METHOD 632</b>
Total Phenols (Includes Hexane & Xylene)	Full spectrum (Includes Diazinon)	Full spectrum	Full spectrum (Includes Carbaryl)	Full spectrum

**INORGANIC, NONMETALS:      METHOD 4500**  
Cyanides

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**References:**

Federal Code of Regulations

USEPA, Handbook for Monitoring Industrial Wastewater

ISCO, 3700 Portable Sampler Instruction Manual

State of Florida Cleaning/Decontamination Procedures