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QUALITY ASSURANCE MANUAL
FOR
SELF-MONITORED INDUSTRIES

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1. INTRODUCTION AND PURPOSE

A Quality Assurance (QA) program is a series of planned and systematic activities implemented to provide adequate confidence in the product produced, in this case, self-monitoring data. The California Regional Water Quality Control Board has mandated that the City of Stockton implement a QA program for self-monitored industries. This document presents the elements of the QA program that the City will require to be initiated and maintained by all industrial dischargers.

Self-monitoring results are used for billing purposes and in determining compliance with permit requirements. It is essential that the values obtained through analysis are accurate and reliable.

Quality Assurance (QA): The overall policy, procedures, and assessment structure used to monitor the sampling program from sample collection through sample analysis. The QA program includes the review of sample collection protocols, chain of custody procedures and quality control data.

Quality Control (QC): The operational techniques and activities taken to implement a Quality Assurance Program. Field QC includes appropriate sampling methods, sample containers, preservation, and the collection of duplicate, background and blank samples.

When the practices outlined in this manual are uniformly and consistently applied, the industrial discharger will benefit in two ways: the results of analyses will be legally defensible; and problems with treatment and sample handling are easily identified for correction.

2. SAMPLE COLLECTION AND HANDLING

The importance of QA/QC in sample handling is to ensure the integrity of the sample; i.e., to minimize the possibility of contamination and to accurately reflect the composition of the sample stream at the time of sampling (a representative sample).

Sample Containers and Sampling Apparatus

Appropriate sampling equipment is required. Most samples can be collected in glass (borosilicate) or plastic (polyethylene or polypropylene) containers. Use the information provided in the Code of Federal Regulations, 40 CFR Part 136.3, "Table II – Required Containers, Preservation Techniques, and Holding Times" (Section 8).

Cleanliness of sample containers must be ensured at all times. The collection vessel in the composite sampler is included in this category.

General procedure for cleaning composite sampler containers:

1. Inspect containers. Discard if deteriorated or if contaminated to the extent that they cannot be cleaned.
2. Rinse well with tap water.
3. Wash containers and caps using a non-phosphate detergent, warm water and a brush.

4. Rinse well with tap water.
5. Rinse at least five times with deionized water.
6. Invert and let dry.

Samples sent to contract laboratories for analysis should be collected in the appropriate containers supplied by that laboratory.

Sample Preservation and Storage

Samples must be preserved correctly for the type of analysis they will receive. In addition, analysis must begin within a specified "holding time". Refer to Section 8 for the holding times allowed for specific analyses.

Accountability of Handling

After a sample has been collected, it must be labeled immediately, the sampling information logged into a notebook, and formal chain of custody procedures initiated to ensure sample integrity. From this point on, the sample is always accompanied by its chain of custody form. An example of a chain of custody form is shown in Section 9.

A sample is under proper custody if any of the following apply:

1. It is in your possession.
2. It is in your view, after being in your possession.
3. It was in your possession and then was placed in a secured location to prevent tampering.
4. It is in a designated secured area (requires a locked enclosure).

When the custody of a sample is transferred, the individuals relinquishing and receiving the sample will sign, date and record the time on the chain of custody form.

Sample QC Requirements

In addition to the self-monitoring schedule outlined in the Wastewater Discharge Permit, a minimum number of Quality Control tests will be required for each test specified:

1. Container Blank: This sample contains laboratory pure water which has been held in a prepared sample container. Analysis of this sample determines whether the container may be contaminating the sample. This measures the efficiency of the container preparation procedure. This is necessary for each test where containers are prepared in-house (including composite sampler jugs).

   Required two times per year for monthly monitoring, one time per year if less frequent.

   Not required for containers prepared by outside laboratories.

2. Field Blank: This sample contains laboratory pure water which has been carried through sample collection devices (e.g. pass the water through the composite sampler). Analysis of this sample determines whether the sampling equipment is contaminating the sample.

Required two times per year for monthly monitoring, one time per year if less frequent.

3. Field Duplicate: This is a separate sample collected at the sampling site. It will provide a measure of the homogeneity of the sample material and the consistency of the sampling technique. Results are suspect if not within 10% of one another. This is especially important for grab samples.

Duplicates are required on 10% of all analyses, or one time per year if less than ten analyses are performed in a calendar year.

Sample Analysis

All pretreatment analyses must be performed using prescribed methods listed in 40 CFR Part 136, by a laboratory certified to perform the analysis.

An industry that contracts with a laboratory to perform pretreatment analyses must maintain documentation that the contract laboratory is certified by the State of California to perform the analytical methods used.

3. EQUIPMENT AND INSTRUMENTS

Maintenance

Instrument and equipment performance must be monitored continuously. Any indication of improper functioning should be corrected immediately and noted in a designated logbook. Major repairs and adjustments to equipment and instruments must be performed to manufacturer's specifications by qualified personnel.

General analytical equipment must be maintained as specified by the manufacturer and on an as-needed basis. Compositing samplers should be included in a preventative maintenance program. Data regarding this maintenance should be entered into a designated logbook.

Essential operating parts and components are to be kept in stock (use manufacturer's recommended list) and immediately available for repairs and service when needed.

Calibration

pH meters must be standardized using proper calibration procedures at a frequency specified by the City of Stockton or as recommended by the manufacturer, whichever is more frequent. The values, date, time and operator's I.D. are to be recorded in a designated logbook. pH buffers are to be purchased pre-prepared and traceable to the National Bureau of Standards.

Flow meters are to be calibrated by certified personnel a minimum of two times per year, or more frequently if recommended by the manufacturer.

Records

Performance, maintenance and calibration records are to be kept for all monitoring equipment. All printed data generated by an instrument (e.g. pH meters and flow meters) will be dated and annotated to clearly identify samples. These records, charts and print-outs are to be retained as a permanent record for a minimum of three years.

4. SELF-MONITORING REPORTS

At a minimum, self-monitoring reports submitted to the City of Stockton must include the following:

1. Sample source (including any QC designation).
2. Date and time sample was collected.
3. Sample type: composite or grab.
4. Start and stop times of composite samples.
5. Tests performed and corresponding method numbers (EPA, Standard Methods, AOAC, ASTM or USGS).
6. Results of analyses.

5. PERSONNEL AND TRAINING

Personnel must be trained and be competent in:

1. Sample handling (including collection, preservation and custody).
2. Operation of treatment and monitoring equipment.
3. Maintenance of treatment and monitoring equipment.

Training records for each employee must be kept on file. These records will be furnished by the discharger during the annual pretreatment inspection to verify employee training.

6. QUALITY ASSURANCE PROGRAM REVIEW AND EVALUATION

It is expected that the appropriate industrial representative of the discharger will regularly review the performance of the pretreatment system and sampling procedures to ensure that the requirements of the QA Program are being met.

At the time of the annual pretreatment inspection, QA records will be provided to the City's inspector. An evaluation of the program will be accomplished by review of:

1. Training records
2. Custody records

3. Self-Monitoring and QC sample results
4. Logbooks
5. Samples taken independently by the City of Stockton

A decision regarding the future monitoring requirements of a discharger will be based on compliance with effluent limitations and the results of the QA Program evaluation.

Since the QA program is an integral part of the Wastewater Discharge Permit Self-Monitoring Program, inadequate program implementation or documentation will be a violation of permit conditions, and will be handled according to City of Stockton enforcement procedures.

7. pH METER CALIBRATION PROCEDURES

Note: The following are typical calibration procedures for a field hand-held pH meter. Follow the manufacturer's instructions for your particular meter.

1. Calibrate the pH meter at least once per day (before use), twice if possible. You will need:
   - Squirt bottle with distilled or reverse osmosis water
   - pH 7 buffer
   - pH 4 buffer
   - pH 10 buffer
   - Kim wipes or clean paper towels
   - Bound notebook for recording pH readings

2. Rinse the probe with distilled or reverse osmosis water. Gently wipe any excess liquid from the probe.

3. Place probe in pH 7 buffer. Let sit for about 2 minutes.

4. Record pH. Adjust meter to pH 7 with the calibration mechanism.

5. Rinse the probe again with the squirt bottle, blot dry. Place the probe in pH 4 buffer.

6. Let sit for about 2 minutes. Record the pH. Adjust the slope/calibrate/sensitivity mechanism to pH 4

7. Rinse and dry the probe again. Place the probe in pH 10 buffer.

8. Let it sit for about 2 minutes. Record the pH. (as verification, do not adjust the meter)

9. Rinse and dry the probe again and replace in the solution to be analyzed.

Note: Use small bottles of buffer for everyday calibration. The buffer in these small bottles should be replaced once or twice every month. Buffer that is used every day will get cloudy and contaminated. When this happens, change the buffer.

8. 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 E. coli	PA, G	Cool, <10°C, 0.0008% $Na_2S_2O_3$[5]	6 hours.[22,23]
6. Fecal streptococci	PA, G	Cool, <10°C, 0.0008% $Na_2S_2O_3$[5]	6 hours.[22]
7. Enterococci	PA, G	Cool, <10°C, 0.0008% $Na_2S_2O_3$[5]	6 hours.[22]
8. Salmonella	PA, G	Cool, <10°C, 0.0008% $Na_2S_2O_3$[5]	6 hours.[22]
Table IA—Aquatic Toxicity Tests:			
9–11. Toxicity, acute and chronic	P, FP, G	Cool, ≤6°C[16]	36 hours.
Table IB—Inorganic Tests:			
1. Acidity	P, FP, G	Cool, ≤6°C[18]	14 days.
2. Alkalinity	P, FP, G	Cool, ≤6°C[18]	14 days.
4. Ammonia	P, FP, G	Cool, ≤6°C[18], H_2SO_4 to pH<2	28 days.
9. Biochemical oxygen demand	P, FP, G	Cool, ≤6°C[18]	48 hours.
10. Boron	P, FP, or Quartz	HNO_3 to pH<2	6 months.
11. Bromide	P, FP, G	None required	28 days.
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_2SO_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.
21. Color	P, FP, G	Cool, ≤6°C[18]	48 hours.
23–24. Cyanide, total or available (or CATC)	P, FP, G	Cool, ≤6°C[18], NaOH to pH>12[9], reducing agent[5]	14 days.
25. Fluoride	P	None required	28 days.
27. Hardness	P, FP, G	HNO_3 or H_2SO_4 to pH<2	6 months.
28. Hydrogen ion (pH)	P, FP, G	None required	Analyze within 15 minutes.
31, 43. Kjeldahl and organic N	P, FP, G	Cool, ≤6°C[18], H_2SO_4 to pH<2	28 days.
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	P, FP, G	HNO_3 to pH<2, or at least 24 hours prior to analysis[19]	6 months.
Metals, except boron, chromium VI, and mercury			

38. Nitrate	P, FP, G	Cool, ≤6°C[18]	48 hours.
39. Nitrate-nitrite	P, FP, G	Cool, ≤6°C[18], H2SO4 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 H2SO4 to pH<2	28 days.
42. Organic Carbon	P, FP, G	Cool to ≤6°C[18], HCl, H2SO4, or H3PO4 to pH<2	28 days.
44. Orthophosphate	P, FP, G	Cool, ≤6°C[18]	Filter within 15 minutes; Analyze within 48 hours.
46. Oxygen, Dissolved Probe	G, Bottle and top	None required	Analyze within 15 minutes.
47. Winkler	G, Bottle and top	Fix on site and store in dark	8 hours.
48. Phenols	G	Cool, ≤6°C[18], H2SO4 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], H2SO4 to pH<2	28 days.
53. Residue, total	P, FP, G	Cool, ≤6°C[18]	7 days.
54. Residue, Filterable	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.
61. Silica	P or Quartz	Cool, ≤6°C[18]	28 days.
64. Specific conductance	P, FP, G	Cool, ≤6°C[18]	28 days.
65. Sulfate	P, FP, G	Cool, ≤6°C[18]	28 days.
66. Sulfide	P, FP, G	Cool, ≤6°C[18], add zinc acetate plus sodium hydroxide to pH>9	7 days.
67. Sulfite	P, FP, G	None required	Analyze within 15 minutes.
68. Surfactants	P, FP, G	Cool, ≤6°C[18]	48 hours.
69. Temperature	P, FP, G	None required	Analyze.
73. Turbidity	P, FP, G	Cool, ≤6°C[18]	48 hours.
Table IC—Organic Tests[8]			
13, 18–20, 22, 24–28, 34–37, 39–43, 45–47, 56, 76, 104, 105, 108–111, 113. Purgeable Halocarbons	G, FP-lined septum	Cool, ≤6°C[18], 0.008% Na2S2O3[5]	14 days.
6, 57, 106. Purgeable aromatic hydrocarbons	G, FP-lined septum	Cool, ≤6°C[18], 0.008% Na2S2O3[5], HCl to pH 2[9]	14 days.[9]
3, 4. Acrolein and acrylonitrile	G, FP-lined septum	Cool, ≤6°C[18], 0.008% Na2S2O3[5], pH to 4–5[10]	14 days.[10]
23, 30, 44, 49, 53, 77, 80, 81, 98, 100, 112. Phenols[11]	G, FP-lined cap	Cool, ≤6°C[18], 0.008% Na2S2O3[5]	7 days until extraction, 40 days after extraction.
7, 38. Benzidines[11,12]	G, FP-lined cap	Cool, ≤6°C[18], 0.008% Na2S2O3[5]	7 days until extraction.[13]
14, 17, 48, 50–52. Phthalate esters[11]	G, FP-lined cap	Cool, ≤6°C[18]	7 days until extraction, 40 days after extraction.

82–84. Nitrosamines[11,14]	G, FP-lined cap	Cool, ≤6°C[18], store in dark, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.
88–94. PCBs[11]	G, FP-lined cap	Cool, ≤6°C[18]	1 year until extraction, 1 year after extraction.
54, 55, 75, 79. Nitroaromatics and isophorone[11]	G, FP-lined cap	Cool, ≤6°C[18], store in dark, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.
1, 2, 5, 8–12, 32, 33, 58, 59, 74, 78, 99, 101. Polynuclear aromatic hydrocarbons[11]	G, FP-lined cap	Cool, ≤6°C[18], store in dark, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.
15, 16, 21, 31, 87. Haloethers[11]	G, FP-lined cap	Cool, ≤6°C[18], 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction.
29, 35–37, 63–65, 107. Chlorinated hydrocarbons[11]	G, FP-lined cap	Cool, ≤6°C[18]	7 days until extraction, 40 days after extraction.
60–62, 66–72, 85, 86, 95–97, 102, 103. CDDs/CDFs[11]			
Aqueous Samples: Field and Lab Preservation	G	Cool, ≤6°C[18], 0.008% $Na_2S_2O_3$[5], pH<9	1 year.
Solids and Mixed-Phase Samples: Field Preservation	G	Cool, ≤6°C[18]	7 days.
Tissue Samples: Field Preservation	G	Cool, ≤6°C[18]	24 hours.
Solids, Mixed-Phase, and Tissue Samples: Lab Preservation	G	Freeze, ≤−10°C	1 year.
Table ID—Pesticides Tests:			
1–70. Pesticides[11]	G, FP-lined cap	Cool, ≤6°C[18], pH 5–9[15]	7 days until extraction, 40 days after extraction.
Table IE—Radiological Tests:			
1–5. Alpha, beta, and radium	P, FP, G	HNO_3 to pH<2	6 months.
Table IH—Bacterial Tests:			
1. E. coli	PA, G	Cool, <10°C, 0.0008% $Na_2S_2O_3$[5]	6 hours.[22]
2. Enterococci	PA, G	Cool, <10°C, 0.0008% $Na_2S_2O_3$[5]	6 hours.[22]
Table IH—Protozoan Tests:			
8. Cryptosporidium	LDPE; field filtration	0–8°C	96 hours.[21]
9. Giardia	LDPE; field filtration	0–8°C	96 hours.[21]

[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 (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 0.080% 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 ($Na_2S_2O_3$), ascorbic acid, sodium arsenite ($NaAsO_2$), or sodium borohydride ($NaBH_4$). 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 $NaBH_4$ or $NaAsO_2$ is used, 25 mg/L $NaBH_4$ or 100 mg/L $NaAsO_2$ 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.

(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.

(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.

(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.

(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.

(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) 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 "≤ °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.

9. CHAIN OF CUSTODY FORM (example)

CITY OF STOCKTON
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Custody Transfer Record
Lab Analyses Request

Date _____ Page ____ of ____

Section:	Sampler ID:
Account #:	Report to:

Lab ID	Sample Location / Description / I.D	P	G/C	Sample			Container		Pres.	ANALYSES REQUESTED							
				Date	Time Collected	Type	Type	Vol.									

Special Instructions:

Evidence Tape: Present on samples? Y or N
Unbroken on samples? Y or N

Samples were received in good condition? Y or N

Released by	Date	Time	Received by	Date	Time
Released by	Date	Time	Received by	Date	Time

Priority: 1 = 5 working days; 2 = 10 days; 3 = 15 days
G/C: G = Grab; C = Composite (24 hr unless noted)
Sample Type: D = Drinking Water; S = Sludge/Soil; W = Water (other than drinking water)
Container Type: P = Plastic; G = Glass; A = Amber
Container Volume: B = Bact; G = Gallon; L = Liter
Preservation: C = Cooled; R = Refrigerated; S = Sulfuric Acid; T = Sodium Thiosulfate (bact); N = No Preservation

Misc: NR = Not Recorded

WHITE - File CANARY - Lab 1 PINK - Lab 2 GOLDENROD – Sampler