CITY OF BOULDER

PUBLIC WORKS/UTILITIES

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Industrial Pretreatment Sampling Guidelines

A. Definitions:

1) Sample - A sample is a known volume of wastewater representing the true characteristics in both volume and nature of the monitored discharge and collected for a specific duration of time at a specific location.

2) Types of samples - The most common types of samples are grab samples and composite samples. These may be obtained either manually or automatically.

   a) Grab sample - a single 'dip and take' sample taken from a waste stream on a one-time basis with no regard to the flow in the waste stream and without consideration of time.

   b) Composite sample - a representative flow proportioned or time-proportioned sample collected within a twenty-four hour period composed of a minimum of four individual grab samples collected at equally spaced intervals and combined according to flow or in equal volumes.

B. Sample Collection and Preservation:

General Guidelines

- All sampling shall be performed in accordance with the techniques prescribed in 40 CFR Part 136 or, if 40 CFR Part 136 does not contain sampling or analytical techniques for the pollutant in question, in accordance with procedures approved by the EPA and the City.
- Self-monitoring at federal categorical sampling locations is to take place after treatment, if any, and prior to mixing with other wastestreams. (Unless alternative discharge limits have been calculated per EPA requirements.)
- Self-monitoring at local limits sampling locations is to take place prior to entering the City sewer system.
- For all samples the time and date of sample collection, pH and the name of the person(s) collecting/preserving the samples and preservation methods must be recorded.
- All samples should be collected, stored and transported at ≤ 6° C

Summary of Required Techniques

- pH – Immediately after collection of a grab sample measure for pH with a recently calibrated pH probe. Continuous pH monitoring with instantaneous data logging is also acceptable.

- Metals - Immediately after collection/compositing, samples must be measured for pH and preserved by adding nitric acid until a pH<2 is attained.
- Cyanide - The sample is to be collected at the point of discharge of cyanide bearing wastestreams and downstream of any pretreatment system but prior to mixing with any other streams. Each cyanide sample shall be collected as a grab and immediately preserved by adding sodium hydroxide until a pH>12 is attained. If chlorine is present, the sample must be dechlorinated with a reducing agent per 40 CFR 136 and in consultation with your analytical lab prior to adjusting the pH with sodium hydroxide. If sulfide is present the sample can either be preserved or analyzed within 24 hours.
- BOD, COD, NH_3 and TSS - Individual grab samples collected manually or automatically and used to make up the composite must be kept cool to ≤ 6° C to prevent biological degradation of the sample during the collection period. Immediately after collection the COD and NH_3 sample must be preserved by adding sulfuric acid until a pH<2 is attained. The BOD and TSS samples do not need chemical preservation. Samples must be kept cool to ≤ 6° C.

Summary Of Required Containers, Preservation Techniques And Holding Times from 40 CFR Part 136, Table II

Parameter No./name	Container[1]	Preservation[2,3]	Maximum holding time[4]
Table lB—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], H2SO4 to pH<2	28 days.
9. Biochemical oxygen demand	P, FP, G	Cool, ≤6 °C[18]	48 hours.
10. Boron	P, FP, or Quartz	HNO3 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], H2SO4 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[6], reducing agent[5]	14 days.
25. Fluoride	P	None required	28 days.
27. Hardness	P, FP, G	HNO3 or H2SO4 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], H2SO4 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	HNO3 to pH<2	28 days.
35. Mercury (CVAFS)	FP, G; and FP-	5 mL/L 12N HCl or 5 mL/L	90 days.[17]

Parameter No./name	Container[1]	Preservation[2,3]	Maximum holding time[4]
	lined cap[17]	BrCl[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	HNO3 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

Parameter No./name	Container[1]	Preservation[2,3]	Maximum holding time[4]
			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% Na2S2O3[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% Na2S2O3[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% Na2S2O3[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% Na2S2O3[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% Na2S2O3[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 lD—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.

This table is an except from 40 CFR Part 136 Table II and is not considered to be complete. Analytes that are not typically requested by the City of Boulder's Industrial Pretreatment Program have been removed. For information regarding the footnotes, the reader must access the full version at 40 CFR 136.

C. Sample Chain of Custody and Analysis

- The time, date, and location of sample collection, pH (if applicable) and the name of the person(s) collecting, preserving, and delivering the sample to the laboratory must be recorded on a sample chain of custody form.
- The analysis must comply with the approved methods found in 40 CFR 136.
- The chain of custody form and analytical results must be maintained a minimum of three years and made available to City personnel upon demand.

D. Quality Assurance

- Good quality assurance is based on a set of operating procedures which are

adhered to during sample collection and analysis thus ensuring that the data produced is of known and defensible quality.

- A standard operating procedure must be developed, which describes the sample control and documentation procedures during sample collection.
- The laboratory's quality control program must comply with 40 CFR 136 and should include at least seven elements: certification of operator competence, recovery of known additions, analysis of externally supplied standards, analysis of reagent blanks, calibration with standards, and analysis of duplicates and control charts.

E. Data Submittal to Control Authority

When submitting concentration data, the actual flow during the time of the sampling event must also be submitted. This enables the pretreatment program the ability to accurately calculate mass. For example, if the sample is a grab sample of a batch tank what is the volume of the tank during **that** sampling event.

Reports shall be signed by an authorized representative or his or her designate and shall include the following statement:

> "I hereby certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gathered and evaluated the information submitted. Based on my examination of the person or persons who managed the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fines and imprisonment for knowing violations."