

SAMPLING INSTRUCTIONS

I. Definitions

1. Sample: A sample is a known volume of wastewater representing the true characteristics of the effluent which is discharged from industrial wastewater processes and collected for a specific duration of time.
2. Types of Samples: The two most common types of samples are grab samples and 24-hour composite samples, both of which may be obtained either manually or automatically. The type of sample required for each parameter and waste stream type is detailed in Table 1.
 - a. A grab sample is a given volume of discharge which is collected at a single point in time.
 - b. A 24-hour composite sample is a mixture of individual grab samples which are collected at regular intervals. 24-hour composite samples consist of individual representative samples collected every 15 minutes. It is recommended that an automatic sampler be used, but if an automatic sampler is not available, manual grab samples may be taken every 15 minutes. A composite sample may then be prepared from the set of preserved grab samples. Equal volumes of the individual samples must be used unless flow monitoring allows for flow proportioning of the composite sample. Unless flow proportioning is being conducted, each grab sample must be at least 50 ml.
3. Manual Sampling: Manual sampling is the manual collection of a sample using an appropriate container (see Table 1).
4. Automatic Sampling: Automatic sampling is the collection of grab samples at regular intervals using a mechanical device.

II. Sample Collection and Sample Preservation

1. Metals

Collect self-monitoring samples for metals analysis at the point of discharge from the process stream downstream of any pretreatment system but prior to any dilution streams.

Immediately after collection, samples must be measured for pH and preserved by adding nitric acid until a pH <2 is attained. Please record the time and date of sample collection, pH, and the name of the person(s) collecting/preserving the

samples. Submit the composite sample as soon as collected to a laboratory approved by the California Department of Health Services for such analysis.

2. Cyanide

Collect self-monitoring samples for cyanide analysis at the point of discharge of the cyanide bearing wastestream downstream of any pretreatment system but prior to any dilution streams.

Each cyanide sample shall be collected as a grab sample and immediately preserved by adding sodium hydroxide until a pH >12 is attained. If chlorine destruction of cyanide has been used, check the sample for chlorine residual and dechlorinate the sample with 0.6 g. ascorbic acid per liter of sample before adjusting pH with sodium hydroxide. Cyanide samples shall be kept in the dark and refrigerated at 4 degrees centigrade. Please record the time and date of sample collection, pH, and the name of the person(s) collecting/preserving the samples. Submit the samples to a laboratory approved by the California Department of Health Services for such analysis.

3. Fluoride

Collect self-monitoring samples for fluoride analysis at the point of discharge of the fluoride bearing wastestream downstream of any pretreatment system but prior to any dilution stream.

Both grab and composite sample containers should be supplied to you by your analytical laboratory. Plastic containers, not glass, are appropriate for fluoride samples.

Immediately after collection, samples must be measured for pH. Please record the time and date of sample collection, pH, and the name of the person(s) collecting the samples. Submit the composite sample within one week of collection to a laboratory approved by the California Department of Health Services for such analysis.

All records must be retained and made available to City personnel upon demand. Results must be transcribed onto self-monitoring logs and submitted along with the original laboratory reports.

4. TTO

Collect self-monitoring samples for TTO analysis at the point of discharge from the process streams downstream of any pretreatment system but prior to any dilution streams.

TTO samples shall be collected as grab samples. For maximum reliability, it is suggested that at least two duplicates of each sample be taken. Only glass containers are appropriate for TTO samples and should be supplied to you by your analytical laboratory. Due to their volatile nature, a special sampling technique shall be used to collect samples for TTO analysis. A 40-ml glass sample bottle (or vial) should be filled in such a manner that no air bubbles pass through the sample as the bottle is being filled. The bottle or vial shall then be carefully sealed so that no air bubbles are entrapped in it. This hermetic seal must be maintained until the sample is analyzed

Hold samples at 4 degrees C, hermetically sealed, and analyze within the acceptable holding time for the analysis. Preserve the replicate sample(s) for verification analysis if needed. A similar protocol may be followed for other types of volatile organics samples using other container types and sizes.

The method of analysis shall be capable of detecting at least 0.005 mg/l of each of the organic constituents in the discharge.

5. COD, NH₃ and SS

The COD, NH₃ and SS samples shall be 24-hour composite samples collected every 15 minutes from the designated sampling point. If an automatic sampler is used, the sampler must be equipped with ice to prevent the biological degradation of the sample during the sample collection period.

Immediately after collection, the COD and NH₃ samples must be measured for pH and preserved by adding sulfuric acid until a pH<2 is attained. The suspended solids sample must be kept refrigerated until delivery to the laboratory and does not need chemical preservation.

III. Sample Chain of Custody and Analysis

The time and date 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 the sample chain of custody form. The chain of custody form must be retained for a minimum of three years and be made available to City personnel upon demand. Samples shall be analyzed at the discharger's expense by a laboratory accredited by the California Department of Health Services for such analysis unless otherwise specified in the Industrial Waste Permit.

Table 1
SUMMARY OF SAMPLE HANDLING REQUIREMENTS

DETERMINATIONS	CONTAINER	PRESERVATION	MAXIMUM STORAGE RECOMMENDED/REGULATORY *
Ammonia	P, G	Analyze as soon as possible or add H ₂ SO ₄ to pH<2	7 days/28 days
COD	P, G	Analyze immediately or add H ₂ SO ₄ to pH<2	7 days/28 days
Cyanide (total)	P, G	Add NaOH to pH>12 Refrigerate in dark	24 hours/14 days (24 hours if sulfide present)
Fluoride	P	None required	28 days/28 days
Metals	P, G	Add HNO ₃ to pH<2	180 days/180 days
Suspended Solids	P, G	Refrigerate	2 days/7 days
TTO	G, TFE-lined cap	Refrigerate	7 days/7 days until extraction

G: glass
H₂SO₄: sulfuric acid

HNO₃: nitric acid
TFE: teflon

P: plastic
NaOH: sodium hydroxide

- Environmental Protection Agency, Rules and Regulations, Federal Register 49: No. 209, October 26, 1984. See this citation for possible differences regarding container and preservation requirements.

