

ATTACHMENT 3

GROUNDWATER SAMPLING INSTRUCTIONS

I. Introduction

Sampling is required from all dischargers to the Regional Water Quality Control Plant (RWQCP). Sampling ensures that discharges meet effluent limitations which protect the plant, employees, collection system, and Bay from hazards and toxicities associated with pollutants. Samples must be collected, preserved, stored and analyzed according to the most current EPA requirements published in the 40 CFR part 136. All analysis must be analyzed by a laboratory certified by the California Department of Health Services.

Since the concentration of the pollutants in ground water remains fairly stable within a 24 hour period, a single grab sample from an extraction well, batch tank or treatment system is sufficient to determine compliance.

II. Definitions

1. Sample: A sample is a known volume of wastewater representing the true characteristics of the effluent which is discharged from a groundwater well or treatment system 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 and may be obtained either manually or using an automated sampler. Grab samples may be collected for all groundwater sampling requirements unless otherwise required.
 - 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. For discharges lasting less than 24 hours samples may be collected over the actual discharge event. Equal volumes of the individual samples shall be used unless flow monitoring allows for flow proportioning of the composite sample. Unless flow proportioning is being conducted, each grab sample shall be at least 50 ml. Composite samples for TTO and other organics shall consist of individual grab samples collected every two hours and composited by the laboratory immediately before analysis.
3. Manual Sampling: Manual sampling is the manual collection of a sample using an appropriate container. (See Table 1 on last page).
4. Automatic Sampling: Automatic sampling is the collection of grab samples at regular intervals using a mechanical device.

III. Sample Collection and Sample Preservation

1. Metals

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

Immediately after collection the pH must be measured and the sample preserved by adding nitric acid until a pH <2 is attained. The time and date of sample collection, flow, pH, and the name of the person(s) collecting/preserving the samples must be recorded. Submit the sample as soon as possible after collection.

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 residual chlorine and dechlorinate the sample with ascorbic acid per liter of sample before adjusting pH with sodium hydroxide. An addition of 0.6 g. of ascorbic acid per liter of sample is usually sufficient. Cyanide samples shall be kept in the dark and refrigerated at 4 degrees centigrade.

3. TTO, BTXE, and TPH

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

For maximum reliability, it is suggested that at least three duplicates of each grab sample be taken. Only glass containers are appropriate for TTO, BTXE, and TPH 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 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.

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

IV. 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 made available to the 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 Groundwater Discharge 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, BTXE and TPH	G, TFE-lined cap	Refrigerate	7 days/7 days until extraction

G: glass
NaOH: sodium hydroxide

HNO₃: nitric acid
H₂SO₄: sulfuric acid

P: plastic
TFE: teflon

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