Proper Sampling and Preservative Techniques for Wastewater Analysis

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Guidelines for Consideration during Sample Collection

- NPDES Permit Requirements
- Type of Sample required by Permit
- Tools and/or Equipment Required

Importance of Proper Sampling and Preservative Techniques

- Analysis dependent upon quality of sampling procedure
- Eliminate contamination
- Poor sampling can hinder plant improvements or upgrades

Sampling Definitions

- Grab Samples
- Composite Samples
- Preservatives
- Chain of Custody
- Clean sampling Techniques (Low Level Mercury Analysis)

EPA Method 1631 Low Limit Mercury

- Clean Sample Techniques (18 min. video)
- Method 1669 Sample Collection
- Clean Hands/Dirty Hands Technique
- Field Blanks

What does your Permit Require?

Guidelines for Consideration During Sample Collection

- Types of Parameters
- Samples to be Grab or Composite?
- 24-Hour Composite or 48-Hour Composite?

Tools or Equipment needed to Fulfill Requirements

- Correct Sampling Container
- Sampling “Dipper”
- Sludge Judge
- Composite Sampler (complete or neat)
- Refrigerator

Importance of Proper Sampling and Preservative Techniques

- Analysis dependent upon quality of sampling
- Sample only as representative as sampling techniques
- Avoid contamination which leads to high or low results

- Poor sampling has been know to hinder plant improvements. Engineers use data presented for calculations in upgrades. If inaccurate sample collection data is used, municipality may invest in something that may not work.

SAMPLING DEFINITIONS

GRAB SAMPLE

- Single sample collected at a specific spot over a short period of time. These samples represent a “snapshot” of space and time of a sampling area.
- D.O., pH, temperature, residual chlorine

COMPOSITE SAMPLE

- Sample made up of several grab samples over an allotted time, normally in timed intervals or flow proportional. BOD-5, TSS and NH3(N) are normally collected in this manner and are excellent in determining loadings from municipal and industrial plants.

PRESERVATIVE

- Chemical or physical technique of "holding" a sample. Enables accuracy to be continued over extended period of time.
- E.g. Cool to 4°C, H_2SO_4, HCl, NaOH

CHAIN OF CUSTODY

- Relative to sample handling and submission. This form documents a sample's history from collection to analysis. This document should contain sample date, time, who collected the sample and anyone who handled the sample from collection to analysis.

CONTAINERS, PRESERVATIVES AND HOLDING TIMES

CBOD5/BOD5

CONTAINER	PRESERVATIVE	HOLDING TIME
P,G	COOL 4°C	48 HOURS

TOTAL SUSPENDED SOLIDS

CONTAINER	PRESERVATIVE	HOLDING TIME
P,G	do	7 days

AMMONIA

CONTAINER	PRESERVATIVE	HOLDING TIME
P,G	COOL 4°C	24 HOURS
	pH<2.0 S.U.@ 4°C	28 DAYS

PHOSPHOROUS

CONTAINER	PRESERVATIVE	HOLDING TIME
P,G RINSED W/ HCl	pH<2.0 H_2SO_4, & COOL 4°C	28 DAYS

OIL & GREASE

CONTAINER	PRESERVATIVE	HOLDING TIME
GLASS ONLY PTFE CAP	pH<2.0 (H_2SO_4,HCL) & COOL 4°C	28 DAYS

METALS (Cd, Cr, Cu, Ni, Pb, Zn)
Total or Total Recoverable

CONTAINER	PRESERVATIVE	HOLDING TIME
P,G	do	6 MONTHS

Cyanide, Free or Total

CONTAINER	PRESERVATIVE	HOLDING TIME
P, G	NaOH, pH 11.0	14 days

MERCURY* Method 245.1

CONTAINER	PRESERVATIVE	HOLDING TIME
P,G	pH<2.0 (HNO_3)	28 DAYS

*LOW LEVEL MERCURY Method 1631

- Container and preservatives to be provided by analytical laboratory
- Sample must be accompanied by field blank, which is laboratory mercury free water and transferred to sample container at site of sample collection

CHROMIUM - 6

CONTAINER	PRESERVATIVE	HOLDING TIME
P,G	COOL 4°C	24 HOURS

FECAL COLIFORM / E. coli

CONTAINER	PRESERVATIVE	HOLDING TIME
P,G (STERILE)	COOL 4°C, $Na_2S_2O_3$ (if chlorinated effluent)	6 HOURS

CLEAN SAMPLING TECHNIQUES FOR METALS

- Method 1669 - sampling method of choice for low level mercury method 1631.
- Method 245.1 - Method detection level of 200ppt (0.2 ug/l)
- Method 1631 - Method detection level of 0.2-0.5 ppt

We have seen sampling techniques, weather conditions and other items interfere with low level mercury analysis.

Items that interfere with low level mercury sampling

- Dental work and fillings can contaminate samples
- Car exhaust, industrial pollution and trains can cause contamination
- Rain and wind events should be considered
- Cigar / Cigarette smoke
- Rubber items like boots, gloves must be powder free nitrile

BREAK!

20 minute USEPA video on low level mercury sample collection in ambient waters

Mercury Collection and Analysis in Ambient and Effluent Waters using EPA Method 1631

Sampling Equipment

EPA Office of Water

Sampling Equipment Requirements

- Must be **non-metallic** and free from materials that contains metals, as described in **Method 1669**
- All sampling equipment and sample containers must be **precleaned** in a laboratory or cleaning facility, as described in **Method 1631**
- Gloves, storage bags, plastic wrap may be used new without cleaning unless **equipment blank** results pinpoint any of these materials as a contamination source
  - If so, then supplies must also be precleaned or obtained from different supplier

Protective Clothing

- Protective Coveralls, Smocks or Coats (where necessary)
  - Disposable Tyvek, or equivalent
  - Constructed of synthetic material to prevent possible contamination of samples by mercury adsorbed onto cotton or other clothing fibers
  - Cost: $5 to $10 each
- Gloves
  - Clean, disposable, powder-free latex, vinyl or polyethylene
  - Sleeve protectors or shoulder-length gloves may be used by "clean hands" person
  - Cost: $15 to $20 per 100

Sample Collection Bottles

- Fluoropolymer (FEP, PFA) or Borosilicate Glass
  - 125ml to 1L
  - Fluoropolymer or fluoropolymer-lined screw cap
  - New bottles cleaned prior to use
  - Some vendors provide certified, precleaned glass bottles with various levels of cleanliness
  - Recommend analysis of **bottle blanks** on a portion of bottle lot to verify cleanliness ***prior*** to sampling
- Used fluoropolymer bottles can be cleaned and reused

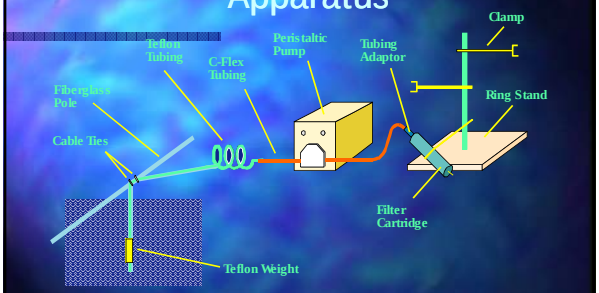
Sample Collection Bottles (cont.)

- Store cleaned sample bottles with 0.1% HCl
  - May empty weak acid solution and refill sample bottle with reagent water immediately prior to transport to the field
- Cost: 125ml to 1L
  - Fluoropolymer: $40 to $120 each
  - Glass: $2 to $5 each

Sample Storage and Transport

- Storage Bags
  - Clean, zip-lock, nonvented, colorless polyethylene
- Storage Cooler
  - Clean, non-metallic, white interior
- Ice or refrigerant packs

Continuous-Flow Sampling Apparatus



Continuous-Flow Sampling Apparatus (cont.)

- Used for **effluent** and **ambient water** sampling
- Peristaltic pump
  - AC, 12VDC or internal battery, variable speed, single pump head
  - Cole-Parmer, portable, Masterflex L/S with Easy Load pump head, or equivalent
  - Cost: $800 to $1500 per pump system

Continuous-Flow Sampling Apparatus (cont.)

- Tubing
  - Fluoroplomer (FEP)
    - 1/4" OD x 3/16" ID, in lengths as required to reach sampling point
    - Cost: $1 to $2 per ft
  - C-Flex, made w/ styrene-ethylene-butylene-silicone (SEBS) resin for use in peristaltic pump head
    - Size 25, 5/16" OD x 3/16" ID, 1ft
    - Cost: $1 to $2 per ft

Continuous-Flow Sampling Apparatus (cont.)

- Support Stand w/ Clamp
  - Used to support end of outlet tubing
  - Polyethylene, fiberglass or plastic-coated
  - Cost: $80 to $120
- Filter (dissolved metals)
  - 0.45 um, 15 mm diameter or larger, tortuous-path capsule filter
  - Gelman Supor # 12175, or equivalent
  - Cost: $20 to $25 each

Boat Sampling

- Metal-free (e.g. fiberglass) boat, along with wooden or fiberglass oars should be used
  - For most situations, use of existing, available boat is acceptable
  - Flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping
  - Gasoline- or diesel-fueled boat motors should be avoided because exhaust can be source of contamination

Boat Sampling (cont.)

- Before first use, boat should be cleaned and stored in area that minimizes exposure to dust and atmospheric particles
  - Immediately before use, boat should be washed with water at sampling site away from any sampling points to remove any dust or dirt accumulation
- Samples should be collected upstream & downwind of boat movement

Vendors

- Brand names, suppliers and part numbers in Method 1669 are for illustration only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified in Method 1631.

Vendors - cont.

- Some vendor sources include:
  - Cole-Parmer Sciences
  - Fisher Scientific Supply
  - Nalgene Labware Products
  - VWR Scientific Products
  - I-Chem
  - Gelman
  - Lab Safety
  - Bel-Art Scienceware
  - Associated Bag Co.
  - Eagle Picher