Model of a Quality Assurance Manual for a Small Wastewater Treatment Plant Laboratory

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Model of a Quality Assurance Manual for a Small Wastewater Treatment Plant Laboratory

by

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Introduction

Purpose of This Document

This document is a guide for designing and documenting the Quality Assurance (QA) program at small wastewater treatment plant laboratories. Included in this document is a model (example) of a QA Manual for these labs. This model is referred to as the "Cascade Wastewater Treatment Plant (CWWTP)".

Following Standard Methods

As required by EPA, analyses in the lab MUST be done with standardized methods approved under 40CFR 136.3 (e.g., EPA methods, Standard Methods, ASTM methods).

Wherever CWWTP did something one way, you'll want to ask: "Is this the way I want to do it and, if not, is the way I do it allowed for wastewater monitoring?" (See 40cfr 136.6 for allowed modifications of approved methods.) If the answer is "yes" and there is no need to change, you should write your QA Manual reflecting how your lab is currently doing the work.

In places where you want to consider other ways of doing things, there are guidance notes footnoted at the bottom of the page. These notes are not intended to be part of your lab's finished manual.

Using Control Charts

When using this CWWTP model to help prepare your lab for accreditation, keep in mind that to be accredited, your lab must meet certain quality objectives as specified in the approved methods. One helpful tool is control charts, especially for standards for BOD and TSS mentioned in the model. Control charts take some effort to set up, but they are easy to use.

Control chart templates and instructions are available on the Lab Accreditation webpage, and Ecology's Laboratory Accreditation Unit can help you set up and use control charts. (See page 2 of this document.)

Additional one-time quality control (QC) is required for 4500 series Standard Methods (for example, tests for Chorine Residual, Ammonia, Nitrate, and Phosphorus), including IDC and MDL studies, as specified in Standard Method 4020 B.1.

If Questions

If you have questions about the manual or QA in general, call your lab's lead auditor at 360-871-8840. If a lead auditor hasn't been appointed for your lab, or you aren't sure who it is, talk with anyone at that number.

Model: City of Cascade Wastewater Treatment Plant Quality Assurance Manual

June 14, 2016

1. Organization/Responsibilities

The Cascade Wastewater Treatment Plant (CWWTP) is operated by a senior operator and two assistant operators. The senior operator is responsible for establishing quality assurance and quality control (QA/QC) policies and ensuring those policies are followed. The senior operator is also the primary laboratory analyst and is responsible for performing analyses on wastewater and QC samples and recording results. In the absence of, or under the direct supervision of, the senior operator, the assistant operators may also perform analyses on wastewater and QC samples and record results. The senior operator will verify such results. The senior operator is also the sample custodian.

2. Policy for Quality Assurance/Quality Control

a) The principal objective for operating the CWWTP laboratory is to consistently produce complete analytical data which accurately represent the waste stream from which samples are taken.

b) All analytical procedures will be completed according to approved methods (specified in paragraph 4 of this manual) and will include all QA/QC measures required by those methods. The initial data quality objective (DQO) is to achieve better precision and accuracy levels than those cited for each method in "Standard Methods". For example, when control charts have been established for BOD and TSS (see paragraph 5g(3) below), the statistics used for the chart (i.e., the mean and standard deviation) become the DQOs for those tests, provided they are better than the initial DQOs.

c) No sample data will be recorded without including results for the analyses of QC samples associated with the data. Data will be entered in indelible ink on printed bench sheets and kept in binders. Data will be kept for at least three years. All data is reviewed and validated prior to release of the data from the CWWTP laboratory.

d) Initial training for new operators on analytical methods and QA/QC requirements and procedures will be conducted on a priority basis. Additional training is to be conducted periodically (not less frequently than twice per year) as required to maintain competence in analytical skills. Records of all training are kept in each trainee's personnel folder.

e) Located in the lab are copies of the CWWTP discharge permit, "Standard Methods," applicable EPA methods, this QA Manual, and, in a readily available binder, safety data sheets for all potentially hazardous chemicals used in the lab.

3. Sample Management

a) Samples are taken according to the schedule in Table 1 (at the end of this section of the manual) which includes preservation techniques and maximum holding times.[1] Daily samples, including collection of composited samples, are taken between 9:00 and 10:00 a.m., and weekly samples on Wednesday mornings (same time) unless conditions (e.g., weather, plant operations, and personnel availability) do not permit sampling at that time. In such cases, samples are taken as soon as possible and a note made in the plant log justifying the delay.[2]

b) The senior operator, as sample custodian assures: (1) samples are stored properly and handled by a minimum number of people; (2) the lab is secured at all times when not in use; (3) only authorized personnel are allowed in the lab; (4) samples are logged on permanent lab record, and; (5) someone is designated to analyze the sample.

4. Methods

Methods used in a WWTP lab are those prescribed in the 22nd Edition of "Standard Methods for the Examination of Water and Wastewater". Method numbers are indicated in Table 1. Appendix D is a brief description of the methods used in the CWWTP lab.[3]

5. Calibration and Quality Control Procedures

a) Lab Facility. The lab is kept clean and orderly at all times. Specific facility tasks are addressed in the checklist in Appendix C.

b) Instrument Calibration. Instruments are calibrated on a daily basis just before use and every two hours during prolonged periods of use on any given day. Those requiring calibration are the pH meter/probe, and the DO meter/probe. The DO meter is calibrated against water-saturated air. Records of calibration are maintained on log sheets for each piece of equipment. Equipment calibration requirements are indicated in Table 2 (at the end of this section of the manual).

c) Equipment Maintenance. All lab equipment is maintained so as to keep it in proper working order at all times. Simple repairs may be made by lab personnel; qualified service representatives will perform more extensive repairs. Breakdowns and repair procedures are noted in the log on each piece of equipment. Checks of the drying oven, water bath, and/or incubator temperatures are performed and recorded. Balances are professionally cleaned and calibrated annually. They are also checked each day of use. The DO membrane is replaced every four weeks or more often if

[1] This model manual contains QC information for plant operations (i.e., process control) as well as lab operations. The Lab Accreditation Program is interested primarily in lab QC, and the QA manual could cover only lab QC. But it is probably more convenient for the plant, given the close relationship between lab operations and process control, to also include process control QC in this manual.
[2] The lab should insert its own time schedule.
[3] Methods cited in this manual are for example only. If other approved methods are used, the manual must specify what they are. If "Standard Methods" is used, follow the required 40 CFR 136.3 approved method revision year.

readings become erratic. A backup probe is kept on hand in case of probe failure. Records of all routine maintenance and repairs are kept in equipment logs. The sample refrigerator is maintained at a temperature between 0 and 6.0°C. Thermometers are checked each day of use and checked against a NIST reference thermometer annually; records are kept on file.

d) Analytical Reagents.[4] Only analytical grade reagents are used. Labels on all chemical reagents are initialed and marked with date received, date opened, and, when known, date of expiration. Chemicals are stored out of direct sunlight. Those requiring cold storage are kept in the refrigerator, separate from sample storage. Acids and bases are stored separately in specially designated areas. Care is taken to prevent cross contamination of reagents and samples. Contaminated reagents and outdated chemical solutions are disposed of in accordance with regulations and accepted practices. http://www.hazwastehelp.org/publications/publications_detail.aspx?DocID=o5fpDUrc%2f%2bc%3d . For reagents mixed in the lab, shelf life recommendations provided in the analytical method are followed and bottles are marked with date prepared and the initials of the analyst. Distilled water, produced in the lab, is stored in glass carboys (water may be purchased when necessary). Care is taken not to contaminate distilled water, and water suspected of being contaminated is discarded. Standard solutions are stored separately and safeguarded to preclude inadvertent contamination.

e) Labware Cleaning.[5] After each use, glassware is washed with phosphate-free (environmentally friendly) laboratory detergent, rinsed several times with tap water, rinsed with distilled water, allowed to dry, and stored in a cabinet. When siphon tubes are used for BOD dilution water, they are cleaned weekly with a bleach solution (25 mL of household bleach per liter of water) and rinsed thoroughly (additionally, they are flushed just prior to use with dilution water). Sample bottles and equipment for microbiological evaluations are sterilized in accordance with the current approved Standard Methods.

f) Quality Control Analyses. QC measurements are made for all analyses related to "plant performance" samples (as indicated by "PP" in Table 1). **It is critical that these tests be performed exactly as written in published methods**. Routine analyses of blanks, duplicates, and standard solutions are performed at a minimum according to the frequency shown in Table 2. Results of blank analyses are treated in the manner specified by the method. Data from results of duplicate analyses are compared to DQOs stated in the following subparagraphs. Records of analyses of standard solutions (i.e., the glucose/glutamic acid test for BOD, the cellulose standard for TSS, and a second source buffer solution for pH) are kept on daily bench sheets and in control charts (see Appendix B). They are also recorded on the plant sample bench sheets. QC considerations for specific tests follow.

[4] Distilled and/or buffered dilution/rinse water may be purchased if it is of sufficient quality to meet lab needs.

[5] The purpose of using phosphate-free detergent is to protect the environment and has nothing to do with QA/QC in the lab.

(1) *BOD*. The DO probe is air calibrated each day during which analyses are normally run or once every two hours during prolonged runs. Samples are incubated at 20±1°C as measured by a certified thermometer (i.e., one which has been checked against a National Institute of Standards and Technology – NIST thermometer). The initial DO must be measured when the sample is at 20±1°C, so initial and final DO are measured at the same temperature. Dilution water is kept in the incubator to make sure it is at 20±1°C. If necessary, samples are warmed or cooled to bring them to the same temperature. A freshly prepared check standard consisting of 150 milligrams each of glucose and glutamic acid dissolved in one liter[6] of distilled water is analyzed (using a settled primary effluent seed) at a rate of one daily. If the BOD of the check standard is outside the action range on the control chart, the source of the problem is sought and corrected. Multiple dilutions are run **with each batch** on final effluent samples. Duplicate results should give a relative percent difference (RPD - see Appendix A of this QA Manual for a definition) of 20% or less. A blank is run on unseeded dilution water with each set of samples.

Depletion (i.e., the DO drop) on the blank must not exceed 0.2 mg/l, and DO drop for samples must be at least 2 mg/L with a residual DO of at least 1 mg/L. If these targets are not met, corrective action is taken (e.g., calibration, dilution water, and the nutrient solution are checked, and problems corrected). A Proficiency Testing (PT) sample is analyzed at least annually as part of a Water Pollution (WP) Study. If results are not within acceptable limits, a QC sample is analyzed after identifying and correcting probable causes of error. PT samples are analyzed as in 5f above.

(2) *Total Suspended Solids (TSS)*. The principal calibration in the TSS determination is on the analytical balance which is checked by lab personnel monthly using class 1 weights and by a service representative annually. A check standard prepared in the lab using micropulverized (20 micron) cellulose is analyzed once per month.[7] A blank is run on deionized water each test. If the TSS value for the blank is more than 2.5 mg (the method-specified minimum residue for samples), the cause is sought and, if necessary, corrective action is initiated.[8] Duplicates are run monthly on effluent samples. The duplicate values should give an RPD of 30% or less. PT samples are analyzed as in 5f above.

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[6] Prepared standards can be purchased from Hach, North Central Laboratories, and others. Contact Ecology's Lab Accreditation Unit if you have questions on how to purchase or use the standards.

[7] The standard suspension for the TSS test can be made from finely pulverized cellulose (available from, for example, Sigma - Aldrich as cellulose powder, 20 micron). The control suspension is made in a concentration of approximately 30 mg/L which is typical of the waste samples analyzed in some WWTP labs. Five liters are made at a time by slowly adding 150 milligrams to 100 mL of warm water (35-55°C) while stirring on a hot plate/magnetic stirrer. After the cellulose is thoroughly wetted and the mixture is homogeneous, it is allowed to cool to room temperature and diluted to a final volume of 5.0 liters. The suspension is kept in a polyethylene (or Nalgene) container and agitated immediately before use just as actual samples are. The container should be emptied and cleaned when about two-thirds empty.

[8] The frequency of the TSS standard test (as well as residual chlorine) is up to the lab to determine, although it must be at least monthly so the lab can monitor its performance and know when it is out of control. The BOD standard test (glucose/glutamic acid) must be run every batch in accordance with the method.

(3) *pH*. The manufacturer's instructions are followed for storage and preparation for use of the pH meter. Two buffer solutions are used to calibrate the meter, one at approximately 2 pH units from the expected sample pH, and the other bracketing the pH expected for most samples and within 3 pH units of the first (e.g., at pH 4 and 7 for slightly acidic samples, and pH 7 and 10 for slightly basic samples). Calibration is checked just prior to use and once every two hours during prolonged runs, with two of the buffer solutions. A check standard, prepared as a buffer solution but separately from the buffer solutions prepared for meter calibration, is analyzed each day of use. Duplicates are run monthly on effluent samples. Duplicate values should not vary by more than 0.1 pH unit. PT samples are analyzed as in 5f above.

(4) *Chlorine Residual*. There are no instruments requiring a calibration curve for chlorine residual determinations (the instrument is zeroed but not calibrated with known standards). A check standard, obtained from a commercial source, is analyzed once per month. PT samples are analyzed as in 5f above.

(5) *Fecal Coliforms.* The routine method for fecal coliform testing in this lab is by membrane filtration (MF) using MFC media with rosolic acid. Using this method, there are no instruments requiring calibration for fecal coliforms determinations or requirements for analyzing check standards. A blank is run at the beginning and end of each sample filtration series. The filter in the blank determination is rinsed with MF rinse buffer solution to make sure the buffer and filtration funnel are not contaminated. Rather than doing duplicates, this lab analyzes multiple volumes of each sample in an attempt to hit the ideal count of 20-60 colonies per plate and to evaluate precision and accuracy. Although not required, the lab splits a sample annually with a lab performing the most probable number (MPN) method. The MF result should be at least 80% or more of the MPN count. Twice a year the lab exchanges samples with a nearby WWTP lab as an inter-lab accuracy check. Results should be within ± 20%. If either QC test falls outside of expected results, investigation and corrective action is implemented.

g) Evaluating Accuracy. The ability of the lab to perform accurate analyses is evaluated by analyzing QC samples.

(1) Check standards (samples of concentration known to the analyst) are used primarily to check on bias and precision. Check standards are analyzed monthly for TSS residual chlorine and daily for pH and BOD (see Table 2 for frequency). There is no check standard for fecal coliforms. By preparing a control chart using the results of several analyses of the same standard, the lab monitors overall accuracy by comparing the mean or average value[9] of all results to the true or expected value. The lab also monitors precision by plotting individual results on the control chart.

(2) PT samples (samples of concentration unknown to anyone in the WWTP lab, but known to the supplier of the sample) are used as a check on overall accuracy. PT

[9] Control charts are strongly recommended by Ecology because they are a very practical mechanism for assuring that an analytical procedure is in control. The chart used as an example in this model QA manual is based on standard deviation. Control charts should be used by any lab interested in the quality of its work.

samples for all WWTP performance parameters listed in Table 1 are analyzed annually as part of the WP studies.

(3) To evaluate precision of analysis for BOD and TSS, control charts are maintained for appropriate determinations. If problems are encountered in pH tests, control charts may also be used for pH. The control charts are based on analysis of the standard solution for BOD and the standard suspension for TSS. After a minimum of ten (but preferably 20) replicates of the standard solution for a given parameter have been completed, the standard deviation for the analysis is calculated using the control chart spreadsheet. Appendix B has an example of a control chart generated from the spreadsheet. Where the chart indicates UAL (Upper Action Limit), for example, the chart indicates the mean (average) value of the standard solution concentration plus three times the calculated standard deviation. Likewise, LAL (Lower Action Limit) indicates the standard solution concentration minus three standard deviations. The warning limits (UWL and LWL) are at ±2 standard deviations from the mean. Based on these statistics, it is expected that one point out of every 20 points will be in the warning area, but a point outside of or beyond an action limit indicates the test is out of control.

Once the control chart has been constructed, all subsequent determinations of the same standard are plotted on the control chart. As long as the values are within the action limits, values for samples analyzed in conjunction with the standard may be reported. If a value exceeds either action limit, if more than three consecutive values exceed one warning limit, or if more than seven consecutive values are on one side or the other of the central line (mean), the lab is out of control for that test. Therefore, testing for that parameter must cease until the situation is investigated, the cause found, and corrective actions taken. If the "out-of-control" sample can be re-tested after making corrections, it should be, and the new result reported. If it cannot be re-tested (e.g., for BOD), the "out-of-control" results should be reported with a qualification in the "comments" section of the report. Whenever there is a significant change in procedure (e.g., a new analyst takes over the test), a new control chart is constructed based on standard analyses for the past 20 results. If there is a change for the better (e.g., precision is improving, or the average value for recent tests is closer to the true value), new statistics should be computed and used to make a new chart. Otherwise, the old statistics are used for an unlimited period. The points on the sample control chart in Appendix B represent analyses of the standard solution taken after constructing the chart.

6. Data Management

All records mentioned in the preceding and subsequent paragraphs and required in standard methods are retained at the CWWTP office in file cabinets for at least three years. Before any result is reported, all raw data and calculations are reviewed for accuracy and signed by the senior operator acting as the QA officer. If data contained on any record is transcribed to facilitate brevity or neatness, the original record is also kept. All data is recorded in ink, and corrections are initialed. A list of initials identifying the person to whom they belong is maintained as a permanent lab record.

7. Audits

Two types of audits are used to determine status of the CWWTP lab operations. A system audit is used to assess personnel, equipment, facilities, and analytical procedures. The system audit is conducted periodically by the Department of Ecology and at least every six months by the senior operator. Performance audits (PTs) are conducted at least annually for each plant performance parameter as part of a Water Pollution (WP) PT Study.

8. Reports

A QA/QC report is prepared quarterly and given to the senior operator. The senior operator may provide the report in writing (verbatim or in summary) or verbally to the City Engineer. The checklist in Appendix C is used to assist in drafting these reports and in assessing lab capability and performance.

Tables (see following pages)

Appendices (see following pages)

A - Glossary of Common QA Terms
B - Control Charting Standards
C - Laboratory Quality Assurance Checklist
D - Summary of Analytical Methods

APPROVED: _____ _____
Patty O'Rourke, Senior Operator, CWWTP Date

Tables

Table 1. Plant Performance Parameters.

Sampling Location	Sample				Standard Methods*	Preservation	Holding Times	Container Requirements
	Analysis	Use	Freq	Type				
PRIMARY TREATMENT								
Primary influent	BOD	PP	D	C	5210B	Cool, <6°C	6 hours	P, G
	TSS	PP	D	C	2540D	Cool, <6°C	7 days	P, G
	pH	PC	W	G	4500-H	None required	Stat	P, G
Primary effluent	BOD	PP	W	C	5210B	Cool, <6°C	6 hours	P, G
	TSS	PP	W	C	2540D	Cool, <6°C	7 days	P, G
	F Col	PP	D	G	9222D	Cool, <8°C 0.008% $Na_2S_2O_3$	2 hours	P, G
	pH	PP	D	G	4500-H	None required	Stat	P, G
ACTIVATED SLUDGE								
Primary effluent	BOD	PP	D	C	5210B	Cool, <6°C	6 hours	P, G
	TSS	PP	D	C	2540D	Cool, <6°C	7 days	P, G
	pH	PC	D	G	4500-H	None required	Stat	P, G
Mixed liquor	DO	PC	D	G	4500-O	None required	Stat	P, G
	Temp	PC	D	G	2550	None required	Stat	P, G
	TSS	PC	D	C	2540D	Cool, <6°C	7 days	P, G
	NO_3	PC	D	G	EPA 353.2	Cool, <6°C	48 hours	P, G
Return sludge	TSS	PP	W	C	2540D	Cool, <6°C	7 days	P, G
Final effluent	BOD	PP	D	C	5210B	Cool, <6°C	6 hours	P, G
	TSS	PP	D	C	2540D	Cool, <6°C	7 days	P, G
	F Col	PP	D	G	9222D	Cool, <8°C 0.008% $Na_2S_2O_3$	2 hours	P, G
	Cl Res	PP	D	G	4500-Cl	None required	Stat	P, G
	pH	PP	D	G	4500-H	None required	Stat	P, G

* 22nd Edition unless otherwise indicated.

Cl Res = Chlorine residual
TSS = Total Suspended Solids
D = Once per day
F Col = Fecal coliforms
VS = Volatile solids
W = Once per week
NO3 = Nitrate nitrogen
PP = Plant performance
G = Grab
Temp = Temperature
PC = Process control
C = Composite
TS = Total solids
VSS = Volatile suspended solids
P,G = Plastic or glass
Stat = 15 minutes

Table 2. Minimum quality control procedures frequency.

Parameter	Calibration	Check Standards	Blanks	Duplicates
BOD	Air calibrate DO probe each day	Each day	Each day [1]	More than 1 dilution of final effluent each day
TSS	Balance check each month & each year by a service rep	1 per month	Each day [1]	10% of effluent samples
pH	Each day	At end of each set of samples	N/A	1 per month on final effluent
Chlorine residual	N/A	1 per month	Each day [1]	1 per month
Fecal coliforms	N/A	Positive control (diluted influent) for each media lot	Beginning and end of each filtration series	More than 1 dilution of final effluent each day

[1] "Each day" above means each day that analyses are normally run.

Appendices

Appendix A. Glossary of Quality Assurance/ Quality Control Terms

Accuracy

Degree of agreement of an analytical result with the true value. Accuracy is affected by both random and systematic errors, but is sometimes used (improperly) to denote only systematic error. (See *Bias* below.)

Action Limit

A type of control limit on a control chart, which, if exceeded, requires corrective action to be taken. Action limits are usually placed at ±3 standard deviations from the expected or mean value.

Batch

A set of consecutive determinations (analyses) made without interruption: a "run". Results are usually calculated from the same calibration curve or factor.

Bias

That part of inaccuracy of analytical results caused by systematic error.

Blank

An analysis made by the same procedure as a sample, but intended not to contain the determinand (analyte). (In water analyses, pure water would be analyzed to determine the blank.)

Check Standard

A solution of known concentration that is used to check the precision of analyses (and bias due to calibration). When used in conjunction with a control chart, it becomes a *control standard*. Check standards are prepared from different sources than standards used for calibration.

Data Quality Objectives (DQOs)

Qualitative and quantitative statements of the quality of data needed to support specific decisions or regulatory actions. Quantitative statements address accuracy, completeness, representativeness, and defensibility as a minimum, and quantitative statements should address bias and precision.

Precision

A qualitative term used to denote the scatter of results. Precision is said to improve as the scatter among results becomes smaller. Also referred to as imprecision. Precision is usually measured as standard deviation or relative percent difference (RPD).

Quality Assurance (QA)

The total integrated program for ensuring the reliability of monitoring and measurement data.

Quality Control (QC)

The routine application of statistically based procedures to evaluate and control the accuracy of results from analytical measurements.

Random Errors

Errors occurring when repeated analyses of identical portions of a homogeneous sample do not give a series of identical results. The results differ among themselves and are more or less scattered about some value. They are termed random because the sign and magnitude of the error of any particular result vary at random and cannot be predicted exactly.

Relative Percent Difference (RPD)

The difference between duplicate results for analyses of a sample, relative to the mean (average) value of those results, and expressed as a percent.

$$\text{RPD} = \frac{100(R_1 - R_2)}{(R_1 + R_2)/2}$$

$$= \frac{200(R_1 - R_2)}{(R_1 + R_2)}$$

where "R_1" is the result of the first analysis, and "R_2" the second.

Relative Standard Deviation (RSD)

The standard deviation relative to the mean (also called coefficient of variation). It is calculated as either:

$$s / \bar{x} \quad \text{or} \quad 100s / \bar{x}$$

where $\bar{x}$ is the mean result and s is the standard deviation (see *Standard Deviation* below). $100s / \bar{x}$ is sometimes referred to as the percent relative standard deviation or %RSD.

Standard

A solution of known concentration, either a "check" or "control" standard, or a calibration standard that is used to prepare a calibration curve.

Standard Deviation

A constant that describes the spread of results. An actual standard deviation is denoted by "σ", whereas an estimate of the standard deviation is denoted by "s". For a sample of "n" replicate

results taken from a population of sample analyses of known concentration, the estimate of the standard deviation is:

$$s = \sqrt{\frac{\sum x_i^2 - \left[\left(\sum x_i\right)^2 / n\right]}{n-1}}$$

$$= \sqrt{\frac{\sum x_i^2 - n\left(\bar{x}\right)^2}{n-1}}$$

$$= \sqrt{\frac{\sum\left(x_i - \bar{x}\right)^2}{n-1}}$$

where x_i is a result and $\bar{x}$ is the mean of "n" results.

For duplicate analyses of "m" pairs of unknown samples, the estimate of standard deviation of the difference (d) for the two samples in each pair is:

$$s = \sqrt{\left(\sum d_i^2\right) / 2m}$$

Standard Operating Procedure (SOP)

A detailed written description of a procedure designed to systematize performance of the procedure.

Systematic Errors

Errors that are indicated by a tendency of results to consistently be greater or smaller than the true value. Usually, bias can be consider to be equivalent to systematic error.

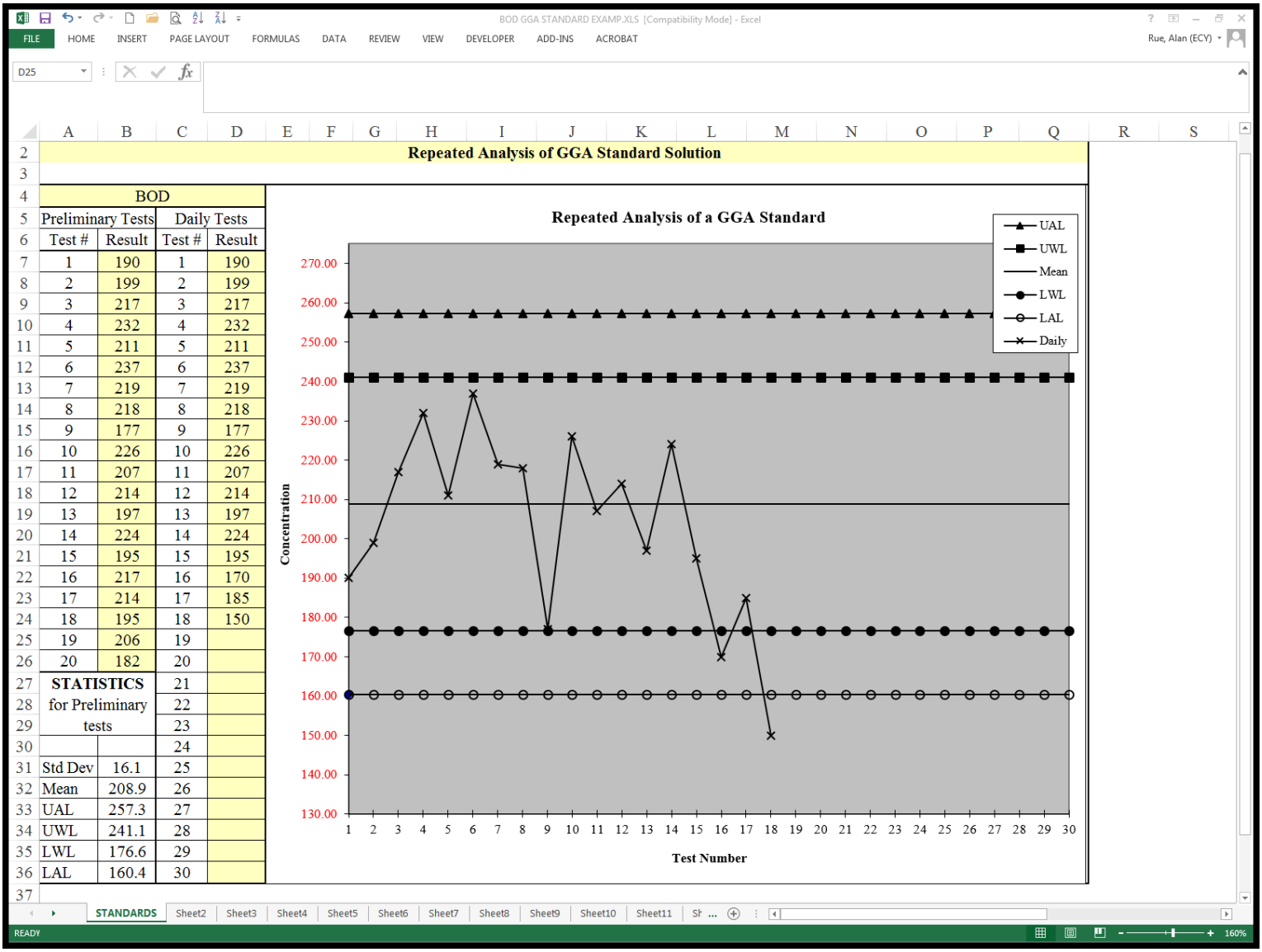
Warning Limit

A type of control limit that is specified by a value on a control chart, usually ±2 standard deviations distant from the expected or mean value. Action is required when results fall outside the warning limits too frequently. A single value outside a warning limit does not require action, but should alert one to a possible problem. Three consecutive results outside a warning limit should be cause for action.

Appendix B. Control Chart Example

After calculating a standard deviation, the control chart shown below was constructed. Subsequent analyses of the standard solution were then plotted on the chart. The chart shows the procedure was in control on analyses #1-15 but exceeded the warning limits on #16. At that point, the analyst might have investigated possible causes and taken corrective actions, but is not required to do so. By #18, the procedure was out of control (beyond the action limit on the low side). The analyst must cease doing BODs at that point until the problem has been corrected.

Control chart templates and instructions are available on the Lab Accreditation webpage (see page 2 of this document).



Repeated Analysis of GGA Standard Solution

BOD			
Preliminary Tests		Daily Tests	
Test #	Result	Test #	Result
1	190	1	190
2	199	2	199
3	217	3	217
4	232	4	232
5	211	5	211
6	237	6	237
7	219	7	219
8	218	8	218
9	177	9	177
10	226	10	226
11	207	11	207
12	214	12	214
13	197	13	197
14	224	14	224
15	195	15	195
16	217	16	170
17	214	17	185
18	195	18	150
19	206	19	
20	182	20	
STATISTICS		21	
for Preliminary		22	
tests		23	
		24	
Std Dev	16.1	25	
Mean	208.9	26	
UAL	257.3	27	
UWL	241.1	28	
LWL	176.6	29	
LAL	160.4	30	

Appendix C. CWWTP Laboratory Quality Assurance Checklist

Cascade WWTP Laboratory Quality Assurance Checklist				
General		**Yes**	**No**	**Comments**
1	Is the Quality Assurance (QA) Manual up-to-date and available to all lab personnel?			
Laboratory Procedures		**Yes**	**No**	**Comments**
1	Are EPA approved methods (e.g. Standard Methods) used and readily available to, and used by, all lab personnel?			
2	Are calibration and maintenance of instruments/equipment satisfactory?			
3	Does a written schedule for required equipment maintenance exist?			
4	Are quality control (QC) procedures in the QA Manual used consistently?			
5	Are QC records adequate to determine if lab is in control?			
Laboratory Facilities and Equipment		**Yes**	**No**	**Comments**
1	Is distilled or deionized water available (as required by the method)?			
2	Is dry, uncontaminated, compressed air available (if needed)?			
3	Is the fume hood air-flow measured periodically and is it adequate?			
4	Is the laboratory sufficiently lighted?			
5	Are adequate electrical sources available in the lab?			
6	Are instruments appropriate for the method and in good condition?			
7	Are trouble shooting procedures and written requirements for daily operation of instruments available to each instrument operator?			
8	Are standards available to perform required QC checks?			

9	Is proper volumetric glassware used?			
10	Is glassware cleaned?			
11	Are solvents and standard reagents properly stored?			
12	Are calibration and check standards frequently cross-checked?			
13	Are standards discarded after recommended shelf-life has expired?			
14	Are reagent bottles marked with date received, date opened, and when known, the expiration date?			
15	Are blanks run each day for appropriate analyses (e.g. BOD, TSS)?			
16	Are sufficient SOPs on hand for lab operations (e.g. clean-up, hazard response)?			
17	Are gas cylinders replaced at 100-200 psi?			
18	Are the thermometers used in incubators (e.g. BOD, fecal coliform incubators) traceable to a NIST-certified thermometer?			
Laboratory's Precision, Accuracy, and Control Procedures		**Yes**	**No**	**Comments**
1	Are duplicates analyzed for all analyses and are the results recorded?			
2	Are control samples required by the QA Manual introduced into the train of actual samples to ensure valid data are being generated?			
3	Are control charts maintained and used routinely?			
4	Is the lab within control (i.e. is precision good)?			
Data Handling and Reporting		**Yes**	**No**	**Comments**
1	Are round-off rules documented and uniformly applied?			
2	Are significant figures established for each analytical procedure?			
3	Are results checked by at least one person other than the analyst?			

4	Are correct formulas used to calculate final results?			
5	Do report forms exist to provide complete data documentation and permanent records and to facilitate data processing?			
6	Are data reported in proper form and units?			
7	Are lab records maintained for three years?			
8	Is all data recorded in indelible ink with corrections initialed?			
9	Is a list of initials, identifying to whom they belong, filed in the lab?			
10	Are lab notebooks and pre-printed data forms bound permanently to provide good and defensible documentation?			
11	Does an efficient filing system exist?			
Laboratory Personnel		**Yes**	**No**	**Comments**
1	Are enough analysts present to perform necessary analyses?			
2	Do analysts have on-hand necessary references for procedures being used?			
3	Are analysts trained in procedures performed?			

Appendix D. Summary of Analytical Methods

1. pH (SM #4500-H B)

pH is a numerical expression of the intensity of value of the acidity or basicity of the tested solution.[10] At 25°C, a value of 7.0 indicates the solution is neutral. Values less than 7.0 are acidic; greater than 7.0 are basic. Sudden changes in pH values may be the result of illegal discharges of acid or base into the wastewater system. Extreme shifts in pH may cause damage to the treatment facility and/or the biological treatment process.

This lab uses the electrometric method for pH measurements. The manufacturer's instructions are followed closely on use of the pH meter and on storage and preparation for use of the electrodes. Electrodes are kept wet by returning them to the storage solution recommended by the electrode manufacturer whenever the pH meter is not being used. To prepare the electrodes for use, remove them from the storage solution, rinse with distilled water, and gently blot them dry with soft tissue. Bring both the sample and buffer solutions to room temperature, record the temperature, and adjust the temperature dial on the pH meter to this temperature.

Calibrate the pH meter by (1) immersing the electrodes in a buffer solution which is within 2 pH units of the expected sample pH, and (2) setting the meter to read the pH of the buffer solution. Remove the electrodes, rinse and blot dry, and immerse in a second buffer which is approximately 3 pH units from the first buffer and which brackets the expected sample pH. If the meter reads more than 0.1 pH units from the value expected for the second buffer, look for trouble with the electrodes or potentiometer. Repeat this calibration procedure for every batch of pH analyses. Because samples normally analyzed in the CWWTP lab are slightly basic, buffers normally maintained are phosphate (1:1 mixture of 0.025M potassium dihydrogen phosphate and 0.025M disodium hydrogen phosphate) which ranges from pH 6.85 to pH 6.95, and borax (0.01M) ranging from 9.14 to 9.39 at normal lab temperatures.

When reading pH of the sample, establish equilibrium between the electrodes and the sample by stirring the sample to ensure homogeneity. Values are reported to the nearest 0.1 pH units. Typical intra-laboratory tests result in standard deviations of $\pm$0.1 to $\pm$0.2 pH units over the pH range.

2. Chlorine Residual (SM #4500-Cl G)

Chlorine is added to water to destroy or deactivate disease-producing microorganisms. Residual chlorine may be present in waters reaching the wastewater treatment plant. Since chlorine is not stable in water solutions, its concentration in samples decreases rapidly. Exposure to sunlight or other strong light, or agitation, reduces the quantity of chlorine in solutions. Samples to be analyzed for chlorine residual must be analyzed immediately after sampling.

Chlorine (hypochlorite ion, hypochlorous acid) and chloramines liberate iodine from potassium iodide at approximately pH 4 which is the basis for the residual chlorine test. The liberated iodine is measured with a colorimeter according to instructions published by the instrument

[10] The lab should document the exact procedures used for each test performed in the lab to make sure they are done the same way time after time. These documents may be in the form of SOPs (standard operating procedures), or be part of the QA Manual such as the summary used in this model.

manufacturer. In a study involving 25 laboratories analyzing a 0.66 mg/L sample, the percent relative standard deviation * was 27.6% and the relative error was 15.6%.

3. Total Suspended Solids (SM #2540 D)

The measurement of suspended solids, or suspended matter, in wastewater at various stages in the treatment gives a good indication of the efficiency of treatment. Total suspended solids may be determined by filtering a sample through a glass fiber filter and drying the residue to constant weight at 103-105°C.

This lab uses a Gooch filter apparatus attached to a water aspirator. Other apparatus used in the determination include a drying oven, an analytical balance, and a desiccator. The funnel and glass fiber disk are first dried at 103-5°C for an hour, cooled in a desiccator to room temperature, and weighed. The sample (100, 50, or 25 milliliters, depending on expected suspended matter content, which should yield between 2.5 and 200 milligrams of TSS) is filtered through the glass fiber disk, and the funnel and disk are again dried, desiccated, and weighed. The cycle of drying, cooling, desiccating, and weighing is repeated until a constant weight is obtained or until the weight loss is less than 4% of the previous weight or 0.5 mg, whichever is less. Difference in the two weights is the amount of suspended solids in the sample.

From a standpoint of quality control, the analytical balance is the most important instrument, although care must be taken to assure the drying oven is actually operating at 103-105°C, and that the desiccator is free from moisture (i.e., silica gel is replaced as required). This is a relatively imprecise procedure with the percent relative standard deviation reaching 33% for some concentrations.

4. **Biological Oxygen Demand (SM #5210 B)**

This test measures the amount of organic material in a sample by measuring the oxygen consumed by microorganisms in biodegrading organic constituents in the sample. BOD is an important measure of the quality of discharged water, as high BOD can result in undesirable effects (oxygen depletion) on receiving waters. The test is part biological and part chemical. The biological part cannot be calibrated, but the chemical part, which consists of measuring dissolved oxygen (DO) before and after an incubation period, can. DO is normally measured with a DO meter which is periodically checked using an iodometric titration (i.e., Winkler) procedure.

Samples analyzed in this lab generally are in the 6.5 to 7.5 pH range, normally have not been chlorinated or oxidized by ozone, have not been biologically treated, are not extremely hot or cold, do not contain toxics, and do not contain supersaturated DO. Therefore, CWWTP samples normally do not require any special pretreatment as described in Standard Methods. When residual chlorine is present, as it sometimes is, the dechlorination procedure in Standard Methods is done prior to BOD analysis. Past experience has shown that samples often contain materials which are not degraded at normal rates by the microorganisms in settled sewage at the CWWTP. It is therefore necessary to seed BOD samples taken in the final settling tank effluent (as in Standard Methods,). To standardize BOD procedures in the lab, <u>all</u> BOD samples are seeded. The source of the seed is settled effluent from the primary treatment process.

If oxygen demand is expected to be greater than 8 mg/L (and it generally is in the wastewater treatment plant served by this lab), the sample must be diluted. The amount of sample added to a 300-mL bottle is determined from Table D-1 below. Care must be taken in adding dilution water to avoid air bubbles which would contribute to the DO determination. Dilution water is aerated

by agitation and stored overnight in the incubator to ensure it is at approximately 20°C when used. Buffers are added the morning of the test by gentle agitation with care not to introduce air bubbles into the dilution water.

Each test includes a DO determination on a bottle containing only dilution water (i.e., a blank to ensure reagent grade water used in the lab does not contain BOD). DO is measured at the beginning of the test and after a 5-day incubation period. Incubation is in the dark at 20 ± 1°C (as measured with a certified thermometer). During periods when BOD may vary widely, an additional set of diluted bottles is prepared. The second set contains double the amount of sample as determined from the dilution chart (Table D-1). This is to assure there is some DO to measure at the end of the incubation period.

In typical intra-laboratory tests of natural water samples plus an exact increment of biodegradable organic compounds, mean values of 2.1 and 175 mg/L BOD, with respective standard deviations, were ± 0.7 and ± 26 mg/L (relative standard deviation of 33% and 15%).

Table D-1. BOD Dilutions.

Sample Added to 300 mL BOD Bottle	Expected BOD Range	
	Minimum (mg/L)	Maximum (mg/L)
3	210	560
6	105	280
9	70	187
12	53	140
15	42	112
18	35	94
21	30	80
24	26	70
27	24	62
30	21	56
45	14	37
60	11	28
75	8	22
150	4	12

5. Fecal Coliforms (SM #9222 D)

Fecal coliforms (FCs) are found in the gut and feces of warm-blooded animals. Determination of FCs in wastewater is a principal indicator of sanitary quality of the water and the effectiveness of the treatment process. The CWWTP lab takes special care in following standard methods pertaining to condition of laboratory apparatus, washing and sterilization, preparation of media, materials, distilled water, media specifications, and sampling.

Samples for FC tests must be taken in sterile bottles. The bottles should be wide-mouthed, made of borosilicate glass or plastic, and of at least 120 ml capacity. Bottles and all other glassware are cleansed thoroughly with lab detergent/hot water, rinsed with hot water, rinsed with distilled water, and autoclave sterilized. Sterilization indicator tape (e.g., Scientific Products Autoclave Indicator Tape) is used on all autoclaved labware. Sodium thiosulfate is added to each bottle if

the bottles are to be used for sampling chlorinated wastewaters. Samples should be analyzed immediately after collection, but may be stored at <8°C and analyzed within two hours of the time the sample was taken.

The CWWTP lab uses Whatman Type HC 0.7µm pore size filters which are specially designed to enhance recovery of FCs stressed by chlorine. If HC type filters cannot be obtained, then 0.45µm pore size filters are used. This lab uses disposable plastic culture dishes, commercially-prepared M-FC broth with rosolic acid inhibitor as a culture media, and incubation conditions of 24 ± 2 hours at 44.5 ± 0.2°C. A heat sink dry incubator is used preferentially; a water bath providing a uniform 44.5°C is available if needed. Plates must be put in the incubator within 30 minutes of sample filtration.

When incubation is complete, FC cultures are removed from the incubator or water bath and counted within 20 minutes, with the aid of a dissecting microscope as necessary. All partially or totally blue colonies are counted. Grey-to-cream colonies indicate non-FCs and are not counted.