Vermont Department of Environmental Conservation
Quality Assurance Guidelines for
Wastewater Treatment Facility Laboratories

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Prepared by:

Andrew Fish, C.E.T.
Wastewater Laboratory Specialist
for the VT Dept. of Environmental Conservation

PREFACE

These guidelines have been developed to assist operators and technicians at Vermont Wastewater Treatment Facilities to prepare acceptable Quality Control Manuals specific to their facilities. It is further hoped that the guidelines will encourage the implementation of these procedures. The quality control procedures outlined in this manual represent the minimum requirements considered acceptable by the Vermont Department of Environmental Conservation for facilities regulated under the NPDES program.

The laboratory quality control manual described in this guidance document is an integral part of the "appropriate" quality assurance procedures required of all NPDES regulated facilities pursuant to Title 40 of the Code of Federal Regulations, Part 122.41 (e) any commercial laboratory performing analyses for an NPDES regulated facility must certainly meet these minimum requirements.

It is absolutely essential that all laboratories analyzing wastewater compliance samples follow defined quality assurance procedures. Those procedures must be documented in a laboratory quality control manual.

To satisfy minimum NPDES requirements a quality control manual must address the following items. (Each of which will be discussed in detail in the following pages.)

I. Quality Assurance Program Plan Elements
II. Staff Organization and Responsibilities
III. Quality Assurance Objectives and Activities
IV. Sample Collection Procedures
V. Sample Handling and Documentation Procedures
VI. Laboratory Water Quality
VII. Standard Operating Procedure for Each Analytical Method
VIII. Reagent/Standard Quality Preparation and Traceability
IX. Calibration Procedures and Frequencies
X. Data Handling - Reduction, Validation and Reporting
XI. Preventive Maintenance, Procedures and Schedules
XII. Corrective Action Contingencies
XIII. Quality Control Procedures (General)

In order to produce a truly useful QA/QC manual a table of contents should be included. You may also wish to include things such as laboratory utilities information, electrical supply, compressed air source, etc. or anything that might effect the function of the laboratory.

I. Quality Assurance Project Plan Elements

This section of the manual simply lists the topics which will be included in your quality assurance plan. It is basically a table of contents without the page numbers. It should be the first step in preparing the manual as it will help you to organize your thoughts and establish distinct sections.

II. Staff Organization and Responsibilities

Laboratory analytical centers can obviously vary considerably in size, number, complexity of analyses performed, and in the number of people employed.

This section of the manual should identify all persons responsible for laboratory activities from sampling to preparation and signing of the Discharge Monitoring Report. It should describe the responsibilities of each of the individuals in certain terms; identifying each individual using that person's name (not just the position - i.e. Andy Fish, QA coordinator not QA coordinator).

A typical municipal wastewater facility's staff organization and responsibilities section might include:

1). The town manager as the person responsible for signing the WR-43.
2) The chief operator as the preparer of the WR-43.
3). Assistant operator as responsible for sample collection.
4) Lab tech - responsible for performing analyses maintaining bench sheets,

assisting in data review etc.

Each individuals responsibilities and limitations should be spelled out in this section.

As an example of limitations, an analysts responsibilities might include informing the chief operator if accuracy values are beyond established warning and control limits.

----This clearly shows that the analysts responsibility ends with informing his supervisor of a problem. It is presumably the chief operators responsibility to determine the action taken from that point.

An organization chart is very useful in identifying positions (where they fit into the scheme of things).

III. Quality Assurance Objectives

This section, besides being useful to inspectors and certification officials can be very helpful to the person preparing the manual to figure out "just what am I trying to demonstrate in this manual?" "What am I really after here?"

Here is an example of typical Quality Assurance Objectives.

1. To ensure data produced by the laboratory is accurate and defensible.
2. To ensure samples collected are representative of preferred universe.
3. To ensure that all laboratory procedures are EPA approved.
4. To ensure that all equipment is properly calibrated and meets EPA specifications.
5. To ensure that proper corrective actions are initiated when necessary.

III. Quality Assurance Objectives (continued)

6. To ensure that each sample is tracked from collection time until the report is finalized - with records maintained for the required intervals. Of course in addition to simply listing the objectives you might summarize referencing specific sections of the manual, how these objectives will be met.

IV. Sample Collection Procedures

Careful and precise documentation of sampling procedures is absolutely imperative to ensure that good representative samples are consistently collected. Untold time and dollars are wasted on analysis of samples that are collected at an improper location, time or in an unacceptable container. An exact sampling procedure should be written for each parameter required at your facility. It is smart to include detailed photographs and or diagrams along with sampling location descriptions.

The sampling procedures section of your QA manual should include:

1) Description of container - glass, plastic, etc.
2) Container cleaning requirements -- acid washed, DI rinsed, etc.
3) Sample preservation techniques .
4) Sample holding times.
5) Exact sampling location description.
6) Exact sampling time for most representative sample.
7) Collection method/technique - grab, composite (time-flow, auto sampler) etc.
8) Volume of sample required for analysis.

V. Sample Handling and Documentation Procedures

This section must include:

A written description of exactly how the samples are handled after collection. The methods for documentation must be clearly stated. The following items must be included in this section.

1) Documentation of exact time, date and location sample was collected.
2) Labeling of sample bottles.
3) Chain of Custody Procedures (if analysis is performed by an independent laboratory).

    a) Sample custody forms, labels, seals.
    b) Sample transportation and delivery procedure.

V. Laboratory Water Quality

As many of us are painfully aware, the quality of the water we use in rinsing glassware, preparing reagents and standards, sample dilution, and blank preparations can be the determining factory between accurate and inaccurate analytical results.

There are rather strict monitoring requirements for laboratories analyzing drinking water. These requirements are listed in EPA/570/9-90/008 document Manual for the Certification of Laboratories Analyzing Drinking Water, and include:

V. **Laboratory Water Quality** (continued)

1) General Lab Water

Parameter	Limit	Monitoring Frequency
Conductivity	<2 umhos/cm @ 25ºC	Monthly

2) Water for Microbiological Analyses

Tests	Limit	Monitoring Frequency
Conductivity	<2 umhos/cm @ 25ºC	Monthly
Total Residual Chlorine	<detection limit	Monthly
Heavy Metals, Single[4] (Cd, Cr, Cu, Ni, Pb, Zn)	<0.05 mg/L	Annually
Heterotrophic Plate Count	<500 CFU/ml	Monthly
Water Quality Test[5] (Biosuitability)	0.8 - 3.0 ratio	Annually

In wastewater analysis our main concerns regarding laboratory water quality are conductivity, chlorine and metals that might interfere with certain analyses (i.e. high copper level can affect results in the BOD analysis).

Generally accepted monitoring frequencies and limits for those parameters are listed below.

V. **Laboratory Water Quality** (continued)

2) Water for Microbiological Analyses (continued)

Parameter	Limit	Monitoring Frequency
Conductivity	<2 umhos/cm @ 25ºC	Monthly
Total Residual Chlorine	0.0 or <detectable limit	Monthly
Copper	< .05 mg/L	Semi-Annually
Other Metals (Cd, Cr, Ni, Pb, Zn)	< .05 mg/L	Annually

* Reality Check: The Vermont Department of Environmental Conservation does not expect a small wastewater treatment facility required to perform pH analyses only to have their own laboratory water analyzed for all the parameters listed above. Such a facility should consider purchasing commercially available distilled water, where concentrations of these parameters are often listed on the label. Larger facilities, performing BOD's and more sophisticated analyses would be expected to verify conductivity, chlorine and copper limits. Commercial laboratories performing numerous parameters more frequently than the average treatment facility would be expected to perform more frequent laboratory water analyses.

VII. **Standard Operating Procedures - For Each Analytical Method**

This section of the manual should include a simple step - by step procedure which details the exact method in which the analysis is performed. It should NOT simply be a copy of an analytical method from Standard Methods but instead a practical "What you really do to perform this analysis," type of description in an easy to read format.

VII. Standard Operating Procedures - For Each Analytical Method (continued)

Include specific items such as "Turn the blender to setting 6 and blend for 5 minutes to get a good homogenous sample" or "Use only Class A volumetric glassware from drawer #2.

Items that must be included in this section are:

1) Reference Method, number and Title
2) Description of instrumentation
3) Specific glassware and equipment cleaning procedures
4) Reagent and Standard Preparation
5) Step by Step Procedures (SOPs)
6) Calibration and Standardization procedures - specific to the analysis
7) Equations and Calculations

You may reference an SOP manual to satisfy #5 if you have a separate and complete manual.

VIII. Reagent/Standard Quality, Preparation and Traceability

This section of the manual should describe the general procedures for preparation of reagents and standards. The types of questions that should be addressed include:

1) Grade of materials used i.e. ASC or Analytical Reagent grade chemicals primary standards, etc.
2) Measuring methods i.e. calibrated analytical balance, class A volumetric glassware etc.
3) Reagent labeling: Must Include

VIII. Reagent/Standard Quality, Preparation and Traceability (continued)

A. Reagent name

B. Concentration

C. Preparation and Expiration dates and/or received the dates a chemical is received as well as the date it is opened.

IX. Calibrations Procedures and Frequencies

Documentation of all instrument or equipment calibration is essential to any good quality assurance plan.

This section should detail the procedures, frequencies and type of calibration as well as whether it was routine or professionally performed and finally who performed the calibration.

Written documentation must include at a minimum:

1) Established frequency of routine calibration for each piece of equipment i.e. daily, weekly, monthly.
2) Established frequency of professional calibrations for each piece of equipment.
3) Calibration procedures - Standards used, etc.
4) Dates and times calibrations are performed.
5) The name (* not just initials of the person who calibrated the instrument.)

X Data Handling - Reduction Validation and Reporting

Reduction of Data

Data reduction is the process of transforming raw data into final results that are reported in standard units to some authority. An efficient method of data reduction must exist to reduce transcription and calculation errors. That methodology, whatever it may entail, should be described in this section.

Validation of Data

Data validation starts with the analyst. It is usually the analyst's responsibility to ensure that instruments have been properly calibrated and are operating properly. He or she then records the results on a bench sheet. Generally someone then transfers the data to another form after, perhaps performing some calculations.

At this point there should be some mechanism in place to ensure that the data has been accurately transferred and that any calculations were performed properly.

At least one other person beside the analyst should look over and double check the bench sheet data vs. final results. One or both of these individuals must understand the concept of significant figures and units of measures.

* More than one technical violation could have been avoided had this knowledge been applied.

This section should describe the procedure by which data is checked. Specific responsibilities should be spelled out here.

X Data Handling - Reduction Validation and Reporting (continued)

Reduction of Data (continued)

Each WR-43 report form contains a certification signed by the permittee's authorized agent which states "I certify under penalty of law that I have personally examined and am familiar with the information submitted herein."

It would seem reasonable then to involve this person in the data validation process.

It is important to include in this section.

Examples on description of

1) 8Bench sheets, lab books
2) A description of the check system used to avoid transcription and calculation errors.
3) A procedure of how invalid data is handled on bench sheets and on the WR-43 report form (i.e. BOD results not meeting the R1 D2) requirement - How is this handled?
4) Rules for consistent rounding off of numerical results.

XI. Preventive Maintenance, Procedures and Schedules

Preventive maintenance is very important in order to minimize instrument "Down Time" and ensure the continued accuracy of analytical results.

XI. Preventive Maintenance, Procedures and Schedules (continued)

The old excuse "I couldn't report pH results for the month of April because my pH probe was broken," just isn't acceptable as a defense.

Proper preventative maintenance and contingency plans are essential for uninterrupted analyses.

This section must describe procedures for routine and scheduled contract services. Include:

1) Comprehensive routine maintenance schedule - list of instruments.
2) Professional service/maintenance schedule - list of instruments.
3) A list of employees responsible for performing maintenance.
4) A check list to ensure duties have been completed.

XI. Corrective Action

This section of the manual will outline the steps taken when any portion of the quality assurance process become questionable or invalid.

These steps should include:

1) Identifying and defining the problem i.e. QC is outside control limits, what caused unacceptable results.
2) A list defining need for corrective actions - i.e. (Poor blank or standards results)
3) Actions to eliminate the problem.
4) Actions to prevent recurrence . You may include a copy of the checklist(s)

XI. Corrective Action (4) (continued)

in the manual and include a reference describing where the actual list(s) is/are located if you desire.

5) Procedure for informing superiors of other authorities (if applicable).

6) Protocol for resampling and retesting.

XIII. Quality Control Procedures:

Quality control is defined in the 18th edition of ***Standard Methods for the Examination of Water and Wastewater, 1992***.

As "as set of measures within a sample analysis methodology to assure that the process is in control." This section of the manual is dedicated to describing those measures taken to ensure process control. In it you should define terms and describe general procedures which can be referenced in the QC portion of each analytical method.

Quality control consists of analyzing and reporting the results of quality control standards, sample duplicates and replicates, spikes and blanks.

EPA recommends that a frequency of 10% to 20% be applied for quality control measures. That is, for every 5 to 10 samples analyzed there should be one quality control sample analyzed for each parameter being tested.

For commercial laboratories analyzing multiple samples, a quality control standard or spike, a sample duplicate or replicate and a blank is expected to be run with each batch of samples analyzed.

XIII. Quality Control Procedures: (continued)

The minimum frequency for quality control analyses in laboratories performing one sample at a time would be one-in every 10 samples. *Note: Certain analyses are required by the Vermont Department of Environmental Conservation to be run in duplicate 100%. (T.S.S. and E. Coli).

The Vermont Department of Environmental Conservation has the following minimum requirements regarding QC for the common parameters listed in the Table below:

Parameter	Calibration/ Standardization	QC Standards	Duplicates/ Replicates	Spikes	Blanks
Ammonia	As per method	1/10 Tests	1/10 Tests	1/Yr	1/each
BOD	Meter before each use	1/10 Tests IGGA/Each if seeded	1/10 Tests	1/Yr	1/each
Chlorine Residual Meter	Check standard curve daily standard for each use	1/month	1/10 Tests	1/Yr	1/each
Titrimetric	FAS stand 1/month	1/month	1/10 Tests	1/Yr	1/each
COD	as per method	1/10 Tests	1/10 Tests	1/Yr	1/each
Cyanide	as per method	1/each	1/each	1/each	1/each
E. Coli	Additional QC required for E. Coli includes equipment sterility checks (indicator tape, "Kilit" ampules) each tests and pH check of dilution water (7>1 ± .2) each tests	2/Yr /POS control/each test	1/each	N/A	1/each
Metals	as per method	1/each	1/each	1/each	1/each
Nitrate Nitrogen	as per method	1/10 Tests	1/10 Tests	1/Yr	1/each
Oil & Grease	as per method	1/each	1/each	1/Yr	1/each
pH	Minimum 2 point calibration each use	*(3rd buffer)* 1/each	1/10 Tests	N/A	N/A
Phosphorus	5 Standards/each	1/10 Tests	1/10 Tests	1/Yr	1/each
Settleable Solids	N/A	N/A	1/10 Tests	N/A	N/A
Total Suspended Solids	constant weights before and after filtering sample	1/10 Tests	1/each	N/A	1/each

XIII. Quality Control Procedures: (continued)

XIII. 1B. Spikes

Spikes are prepared by adding a predetermined quantity of a known standard to a sample. By analyzing an unspiked sample and a spiked sample it is possible to determine if there is a substance in the sample that interferes with test results.

From the results of analysis of a spike and unspiked sample, percent recovery can be calculated using the equation:

$$\% \ Recovery \ ' 100\% \ x \ \frac{S \& U}{Csa}$$

Where	S	=	Measured concentration in spiked aliquot
	U	=	Measured concentration in unspiked aliquot
	Csa	=	Actual concentration of spike added

If the Percent Recovery is outside the range of 80% to 100% the contents of the sample may be interfering with the method of measurement for that analysis.

In this event the cause of the interference must be determined and corrective actions must be initiated (i.e. change methods, etc.)

* One spike or Quality Control Standard should be run with one of every 10 samples run.

* For laboratories performing sample analysis in “batches” one spike or quality control standard should be run with each “batch.”

XIII. Quality Control Procedures: (continued)

XIII. 2B. Quality Control Standards

Quality control standards are substances of known concentration. They are used to verify the accuracy of your analysis.

Quality control standards:

1) Must be prepared from a source different than what was used to calibrate the instrument or prepare the standard curve.

2) The quality control standard must be specific for the parameter being analyzed.

3) The quality control standard must approximate the concentration of the sample and must have a value between that of the highest and lowest calibration standards used.

For Example: If a sample is expected to have a pH of approximately 6, calibration standards of pH 4 and 7 might be used along with a quality control standard with a pH value of 6.

4) Remember: Quality control standards are not used to adjust the instrument as are calibration standards. The resulted quality control standards are simply recorded an compared to the actual "known" value.

XIII. Quality Control Procedures: (continued)

XIII. 2B. Quality Control Standards (continued)

5) Unless control charts are used to determine the acceptable quality control standard range. Results of the quality control standard must fall within a range of ± 20% of the known value. That is the Percent Error must be from 80% to 120% of the actual standard

$$Percent\ Error\ ' \frac{Observed\ Value\ \&\ Known\ Value}{Known\ Value}\ x\ 100$$

6) If results of a quality control standard do not fall within the acceptable range the cause must be determined and recorded on bench sheets or other appropriate record books. A not should be placed in the comments section of the WR-43 report form. Corrective actions must be implemented.

III. Duplicates/Replicates

1) Duplicate samples are samples which are collected in two separate containers at the same time and place.

2) Replicate samples are samples that are collected in a single container and are poured off into a second container for separate analyses of the same parameter(s).

3) An absolute minimum of one duplicate or replicate per 10 samples is required.

4) The result of duplicate/replicate samples should not vary by more than 20% from the original sample.

XIII. 2B. Quality Control Standards (continued)

III. Duplicates/Replicates (continued)

5) Do not average original and duplicate/replicate results. Record the result of the original sample. Then record on bench sheets or other appropriate record book the Percent error for the duplicate/replicate.

Percent error is determined by applying the following equation.

$$Percent\ Error = \frac{Observed\ Value - Known\ Value}{Known\ Value} \times 100$$

If the duplicate/replicate results fall outside the acceptable (± 20%) range of the original sample a note should be made in the comments section of the WR-43 report form and on the bench sheet. Corrective action should be implemented.

IV. Blanks

1) A blank consists of either laboratory water or parameter specific dilution water. Blanks provide a check of the laboratory water quality as well as a check of the analysts analytical technique.

2) Blank must be analyzed with each analysis where applicable.

XIII. 2B. Quality Control Standards (continued)

IV. Blanks (continued)

3) Acceptable blank values are included with each analytical method.

For example:

BOD = # 0.2 mg/L
E. Coli = 0 colonies/100 mls

If blank limit values are exceeded a note must be included in the comment section of the WR-43 report form, and on the bench sheet. In some instances such as in the E. Coli analysis, this invalidates the sample data. (Check the method info) In any blank exceedance corrective action contingencies must be implemented.

The following pages contain an

Example QC Manual

Hopefully this example will help you in preparing your own manual.

Remember: The manual must be specific to your own facility and will remain a work in progress requiring periodic updating and revisions.

Table of Contents

A.	Title Page		Page 17A
B.	Introduction		Page 18
1.	Quality Assurance Project Plan Elements		Page 19
2.	Laboratory Staff Organization and Responsibilities		Page 20
	2.1.	Town Manager	Page 21
	2.2	Chief Operator	Page 21
	2.3	Lab Supervisor	Page 21
	2.4	Operators	Page 22
.	2.5	Skills and Training	Page 22
3.0	Quality Assurance Objectives and Activities		Page 23
4.0	Sample Collection Procedures		Page 23
	4.1	General Guidelines	Page 23
	4.2	Sample Type and Holding Times	Page 24
	4.3	Sample Preservation	Page 25
5.0	Sample Handling and Documentation Procedures		Pages 27 & 28
6.0	Laboratory Water Quality		Page 28
	6.1	Deionized Water	Pages 28 & 29
7.0	Standard Operating Procedure for Each Analytical Method		Pages 30
	7.1	pH	Pages 30 to 32
	7.2	Total Residual Chlorine	Pages 32 to 35
	7.3	Settleable Solids	Pages 35 to 36
	7.4	Total Suspended Solids	Pages 36 to 40
8.0	Reagent/Standard Quality, Preparation and Traceability		Pages 40 to 41
9.0	Calibration Procedures and Frequencies		Page 41
	9.1	Instrument Calibration Procedures	Pages 41 to 43
10.0	Data Handling-Reduction, Validation and Reporting		Page 43
	10.1	Data Reduction	Pages 43 to 44
	10.2	Data Validation	Page 44
10.3	Reporting		Pages 45 to 46
11.0	Preventive Maintenance, Procedures and Schedules		Page 47
12.0	Corrective Action Contingencies		Pages 48 to 49
13.0	Quality Control Procedures (General)		Pages 50 to 55

INTRODUCTION

This Quality Control/Assurance Manual is written specifically for the WWW Wastewater Facility in an attempt to assure the continued high quality and accuracy of analytical results. This will be accomplished by monitoring the accuracy and precision of these results, by providing clear, concise Standard Operating Procedures defining sampling and analytical procedures specific to the WWW facility and by clearly defining the responsibilities of all personnel regarding required performance and documentation.

The WWW facility performs analyses required by the NPDES permit for discharge to the WWW River, in-house progress control analyses, and occasionally pH and chlorine analyses for the Water Supply Department.

Analytical results generated for NPDES permit are submitted to the State of Vermont on a monthly basis. Results of process control analyses are recorded on bench sheets and maintained in-house files for a period of three years.

I. Quality Assurance Project Plan Elements

The fourteen Quality Assurance Project Plan Elements addressed in this manual are:

Title Page

Introduction

Staff Organization and Responsibilities

Quality Assurance Objectives and Activities

Sample Collection Procedures

Sample Handling and Documentation Procedures

Laboratory Water Quality

Standard Operating Procedure for Each Analytical Method

Reagent/Standard Quality Preparation and Traceability

Calibration Procedures and Frequencies

Data Handling - Reduction, Validation and Reporting

Preventive Maintenance, Procedures and Schedules

Corrective Action Contingencies

Quality Control Procedures (General)

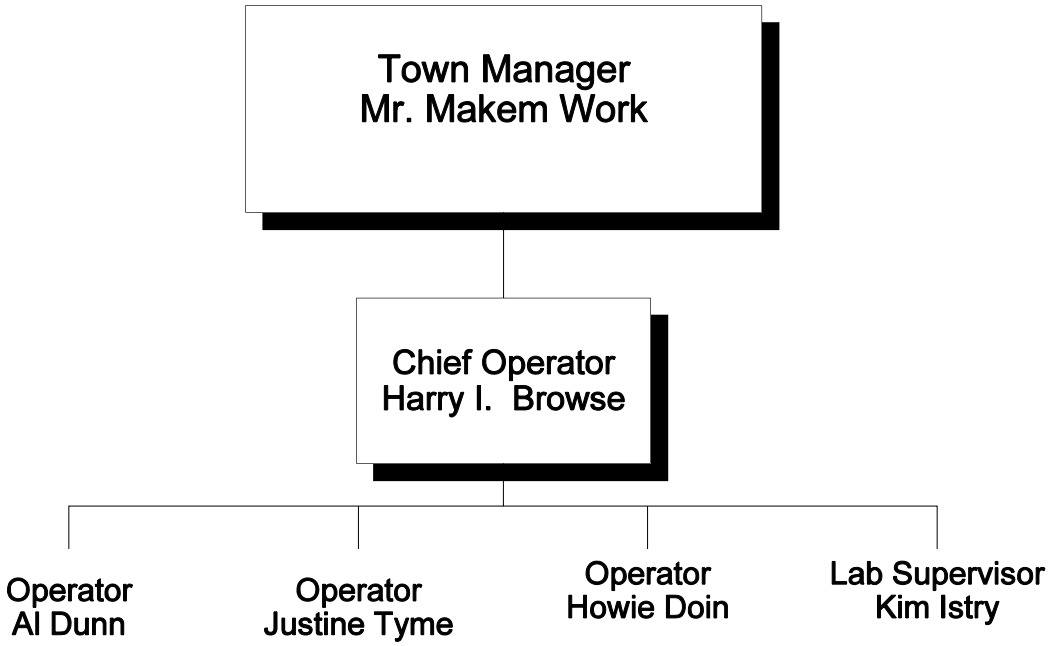
2.0 Laboratory Staff Organization and Responsibilities

The Fuzzyville Wastewater Treatment facility has 5 permanent full-time employees. At some time, all employees are responsible for collection of samples either on a daily basis or on a rotating weekend schedule.

One employee is dedicated to laboratory work only, while all 5 might perform daily analyses including pH, Cl_2 and settleable solids.

The organizational structure is summarized in Table I below.

Table I



2.1 Town Manager

The town manager is responsible for signing the WR-43 report form.

Before signing he/she questions the chief operator or to the report's accuracy and any special comments.

Reviews all data.

Compares WR-43 results to bench sheet results.

Provides final data check.

Sends report to the proper state authority.

Makes final decision on equipment purchases after conferring with chief operator.

Reviews and is familiar with the laboratory QC manual.

2.2 Chief Operator

The chief operator is responsible for signing the WR-43 report form as the "preparer."

Transfer all results from bench sheets to the WR-43 report form.

Compares final WR-43 results to bench sheets to guard against transcription errors etc.

Reviews an is familiar with the laboratory QC manual.

Schedule special sampling and analytical projects.

Reviews bench sheet data to ensure proper WC was practiced.

Is responsible for purchasing laboratory equipment.

Occasionally collect and analyzes effluent samples for pH.

On occasion when pH is analyzed he/she properly calibrates the pH meter.

2.3 Lab Supervisor

Is responsible for overall technical quality of the work performed in the laboratory.

Ensures the use of acceptable Standard analytical methods.

Provides training to all persons responsible for sampling.

Is responsible for preparation and revisions of laboratory QC manual.

Informs chief operator of any equipment needs.

Performs all instrument calibrations and reagent preparations.

Maintains proper bench sheets and equipment maintenance logs.

Responsible for maintaining current SOPs.

Collects and composites effluent samples.

2.4 Operators

Are responsible for sampling of specific parameters.

Are properly training and responsible for analysis of pH, Total Residual Chlorine and Settleable solids when necessary.

Maintain proper bench sheets and calibration logs.

2.5 Skills and Training

EDUCATION

EXPERIENCE

Time & Type

RESPONSIBILITIES

REQUIREMENTS SPECIFIC TO A POSITION

Example:

NAME	POSITION	EDUCATION	EXPERIENCE	SKILL	RESPONSIBILITIES	SPECIAL REQUIREMENTS
Kim Istry	Lab Supervisor	B.S. Chemistry	15 yrs. as lab analyst	Phosphorus determination using auto analyzer	As described in organizational chart	None

EXAMPLE

3.0 Quality Assurance Objectives

a. To ensure data produced by the laboratory is accurate and defensible.

b. To ensure samples collected are representative of preferred universe.

c. To ensure that all laboratory procedures are E.P.A. approved.

d. To ensure that all equipment is properly calibrated and meets E.P.A. specifications.

e. To ensure that proper corrective actions are initiated when necessary.

f. To ensure that each sample is tracked from collection time until the report is finalized - with records maintained for the required intervals.

4.0 Sample Collection Procedures

4.1 General Guidelines

a. Samples are collected in a well mixed area at the center of the channel avoiding eddies, backwaters and area where settling might take place.

b. Influent samples are collected after the comminuter but above the RAS line. See Diagram.

c. Effluent samples are collected after all treatment processes just before discharge to the stream. See Diagram for specific parameters.

4.1 General Guidelines (continued)

d. Grab samples

Grab samples are collected via a Nalgene container attached to an 8 foot extendable aluminum pole. All grab samples are collected and immediately returned to the lab for analysis.

***Note* E. Coli -** *collected directly into sterilized 250 ml. Plastic bottle containing 4 drops 10% Sodium Thiosulfate solution.*

e. Composite samples

All composite samples consist of 24 disrete samples collected hourly via an Isco automatic sampler. Each disrete sample (approximately 500 mls) is distributed into properly cleaned, 1 liter Isco sample bottles. Composite samples are cooled by ice packs which are placed in the sampler wells. Samples are composited at the lab based on readings from flow charts.

SAMPLING PROCEDURES

4.2 Type of Sample and Holding Time

Parameter	Type of Sample	Holding Time	Sample Container	Location
pH	Grab	15 Minutes	Plastic Bottle	Refer to Diagram
Temperature	Grab	At Site	Plastic Bottle	Refer to Diagram
Dissolved Oxygen	Grab	15 Minutes	B.O.D. Bottle	Refer to Diagram
B.O.D.	Composite Flow Proportional	6 Hours	Composite Sampler Plastic Bottles	Refer to Diagram
Total Coliform Fecal Coliform E. Coli	Grab	1 Hour	Sterile Sample Plastic Bottle w/Sodium Thiosulfate	Refer to Diagram
Chlorine Residual	Grab	15 Minutes	Opaque B.O.D. Glass Bottle	Refer to Diagram
Total Suspended Solids	Composite Flow Proportional	6 Hours	Composite Sampler Plastic Bottles	Refer to Diagram
Specific Conductance	Grab	15 Minutes	Glass	Refer to Diagram
Metals	Grab/Comp	6 Months	Amber Glass	Refer to Diagram
TKN	Grab	1 Hour	Plastic Bottle	Refer to Diagram
Settleable Solids	Grab	30 Minutes	Plastic Bottle	Refer to Diagram

4.3 Sample Preservation

If samples are taken and not run within the time frame as in Chart 9.1 then the following chart applies.

PRESERVATION CONDITIONS

Parameter	Container	Volume	Preservation	Holding Time	Representative Sampling Time
BOD, TSS	P	1L	4° C	24 Hours	8 AM - 8 AM
TKN	P	.5L	H_2SO4 pH < 2.0 4°C	28 Days	8 AM - 8 AM
Oils & Grease	G	1L	HCl pH < 2.0	24 Hours	Between 8 AM and 12 PM
Metals	GA	.2L	HN03 pH < 2.0	6 Months	8 AM - 8 AM
Phenols	G	.5L	H3PO4 pH < 2.0 + 1t CuSO4 4°C	24 Hours	8 AM - 8 AM
Sulfides	P	.5L	2 ml Zinc Acetate 4°C	24 Hours	8 AM - 8 AM
Cyanides (T)	P	1L	NaOH pH > 12.0 4 °C	24 Hours	2 PM
VOC	V	40 ml	4°C	24 Hours	2 PM

G = Glass bottle with Teflon lined lid

GA = Amber bottle with Teflon lined lid

P = Plastic Bottle

V = Approved glass vials with Teflon and pure rubber seals

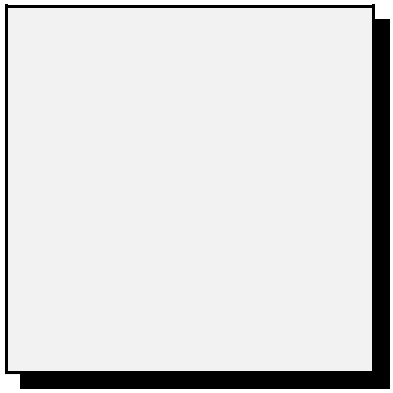
Note: All samples are refrigerated at 4°C after preservation.

4.4 Sample Collection Location

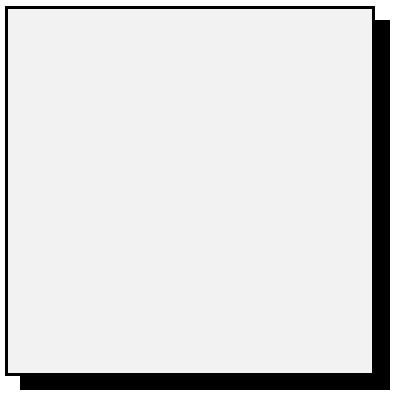
BAD EXAMPLE : Effluent sample is collected at end of chlorine contact tank.

BETTER : The effluent grab samples for pH and Total Residual Chlorine are collected at the outfall end of the chlorine contact tank at a point approximately 1 foot upstream of the v-notch weir.

BEST : The effluent grab samples for pH and Total Residual Chlorine are collected at the outfall end of the chlorine contact tank at a point approximately 1 foot upstream of the v-notch weir, in the center of the channel at a depth of approximately 1 foot. The open container attached to a 6 foot aluminum pole is lowered into the waste stream with the open end facing down stream as shown in pictures #1 and #2.



Picture #1



Picture #2

Be specific and include descriptions for each different type of sample (re: grab, composite)

5. Sample Handling Documentation Procedures

5.1 All grab samples collected for analysis of pH, Total Residual Chlorine and Settleable Solids are immediately taken to the lab. The pH and Chlorine analyses are begun immediately. The settleable solids sample is poured immediately into the Imhoff cone.

5.2 The grab sample collected for analysis of E. Coli is immediately placed into a cooler with four blue ice packs and sealed. It is immediately transported by WWW to WWW laboratory. The approximate travel time is 35 minutes.

Each bottle is properly labeled and accompanied with a chain of custody form. One copy of the COC form is maintained at the facility.

5.3 Composite samples

Immediately after the last 24 disrete sample is collected the entire sampler is brought into the laboratory where the hourly sample volumes are calculated measured and poured into a four liter jug. Aliquots are poured from the container for specific parameters (BOD, TSS etc.) After thorough shaking. Sample containers are then placed into the refrigerator at 4°C until the analysis is performed.

5. **Sample Handling Documentation Procedures** (continued)

5.4 Sample Identification/Labeling

a) All sample containers are labeled with the following information.

1) Type of sample (influent, effluent, grab, composite)

2) Parameter to be analyzed

3) Time and date collected

4) Initials of person who collected it

5) Preservation information

6) Any special instructions or remarks

b) All data from the label is transferred to bench sheets.

c) A chain of Custody form is completed. One copy accompanies the sample to the lab. One copy is retained at the wastewater facility.

Include a copy of the form in the manual

d) The sample is delivered directly to the laboratory by *"name"*, assistant operator

5. Sample Handling Documentation Procedures (continued)

5.4 Sample Identification/Labeling (continued)

e) When the sample is handed over to the commercial laboratory the recipient signs the chain of custody form indicating the time the sample was received.

f) A copy of the chain of custody form is returned to the wastewater facility along with analytical results.

6.0 Laboratory Water Quality

This example was borrowed from a QC manual (prepared by personnel of the Nashua NH Wastewater Treatment Facility *(copied here with their kind permission)*.

6.1 Deionized Water

R/O Deionized water is used in the laboratory for reagent preparation, glassware rinsing, and BOD dilution water.

System includes: Millipore R/O system followed by a Milli-Q deionization system and a 0.02 micron final filter.

TYPE: I : R/O, Deionization and 0.02 um. filter.

TYPE: II: R/O only

6.1 Deionized Water (continued)

Quality Control Tests:

	Parameter	Requirements	Frequency
(Required)	Conductivity	> 0.5 megohms resistance or < 2 microhms/cm at 25°C	Once Per Month
(Suggested)	Total Chlorine Residual	Non-detectable	Once Per Month
(Suggested)	Biosuitability of Laboratory Pure Water	Ratio of 0.8 - 3.0	Semi-annually (April & Oct.)
(Suggested)	Metals	Lead, Nickel, Zinc, Copper, Cadmium, Chromium, Iron, Silver	Semi-Annually (April & Oct.)
(Suggested)	Total Plate Count	< 200 colonies/100 ml.	Once Per Month

* All QC data generated is recorded in the bound QC Manual.

Other Quality Control Measures

R/O system is back flushed daily for one half of an hour. Water for BOD dilution water and reagent dilution is made fresh after morning flush cycle.
Tubing and associated hardware (if in contact with the water) are replaced as needed.

6.2 Distilled Water

Occasionally bottled distilled water is purchased (Poland Springs) for preparation of reagents, BOD dilution water and glassware rinsing.

6.1 Deionized Water (continued)

Other Quality Control Tests: (continued)

The quality specifications for this bottled water are included on the product label and meets all requirements for analytical use.

7. Standard Operating Procedures for Each Analytical Method

7.1 pH

7.1 A. Method Reference

Electrometric Method #4500 - HB. 18th Edition Standard Methods pages for the Examination of Water and Wastewater 4 - 65 ... 4 - 69.

7.1 B. Apparatus

pH meter (make and model)
pH temperature probe (type)
Buffer solutions Fisher, NIST certified, 4.0, 7.0, 10.0
Glass beakers (50 ml)
Magnetic stirrer and stir bars
Safety Glasses, gloves
Squeeze bottle for RO/DI water

7.1 C. Standardization

- The meter is standardized before each use with fresh pH 4.0 and 10.0 *buffer* solutions.

7.1 C. Standardization (continued)

- The pH of a fresh pH 7.0 buffer is checked and the result is recorded in the QC log.

- If the result of the "checked" buffer varies by more than ± .1 standard unit. The meter is restandardized and the problem is corrected.

- The "Fill hole" and electrode cap are removed during use and replaced after each use.

7.1 D. Interferences

- It is important, even with temperature compensation capabilities to approximate as closely as possible the sample temperature when standardizing the meter. To accomplish this , buffers are stored in the refrigerator during winter months and at room temperature during summer months.

- Sodium error is not a problem at this facility.

- Oil material, especially from influent testing can cause development of a film on the electrode causing poor response. This can be avoided by periodically washing the probe with a mild detergent followed through rinses with RO/DI water.

- pH Electrodes are replaced if proper standardization cannot be accomplished.

7. Standard Operating Procedures for Each Analytical Method (continued)

7.1 E. Sample Preparation and Preservation

A minimum 25 ml sample is collected in a glass container. The sample is taken immediately to the lab for analysis.

7.1 F. Procedure

Place pH and temperature probes into the sample. Allow meter to equilibrate. Then record the reading in pH units at temp °C.

7.1 G. Calculation

The pH meter reads directly in a pH standard units pH is reported to the nearest 0.1 unit at a given temperature.

7.1 H. Quality Control

1. All required calibrations and other preventative maintenance on instrumentation and equipment is performed regularly and recorded on bench sheets and calibration logs.

2. Buffers are NIST Traceable, are changed daily and recorded.

3. 10% Duplication and Replication.

7. Standard Operating Procedures for Each Analytical Method (continued)

7.1 H. Quality Control (continued)

4. The pH meter will be calibrated before each use, and separate standard will be processed as a control buffer to validate the calibration, pH 10 buffer will be used as a control.

5. Grab samples will be delivered immediately to the lab for analysis.

6. Glassware will be thoroughly rinsed with purified water.

7. Temperature probe will be calibrated against a NIST traceable thermometer.

8. Calibration sheet will include: date and time of calibration, buffers used and order of use, exact meter results, analyst performing calibration, buffer and sample temperature.

9. Meter range 0-14, accuracy 0.1 pH, repeatability 0.1 pH, temperature compensation and capable of 2 point calibration.

7.2. Total Residual Chlorine

7.2 A. Method Reference

Hach DR 700 method which is based on the DPD colorimetric method #4500-CL G 18th Edition Standard Methods pages 4-45 and 4-46.

7.2. **Total Residual Chlorine** (continued)

7.2 B. Apparatus

Spectro Photometer Model DR 700
DPD Total Residual Chlorine powder pillow/packets
Vials 10 ml - marked - dedicated currettes
Kimwipe Tissues
Safety glasses, gloves
Scissors or clippers

7.2 C. Standardization

The meter has an internal calibration which is automatically enabled for each use.

In addition a Hach brand Voluette ampule certified standard is used daily. Results are recorded and standard curve is plotted.

A blank consisting of the raw sample is used to zero the instrument each use.

7.2 D. Interference

Color and turbidity interferences are reduced by the use of an untreated sample as a blank to zero the device.

Organic contaminants may interfere but can usually be spotted by the strange coloration - yellowish or greenish.

7.2 D. Interference (continued)

Oxidized manganese because of its orange color can create a problem but is at least partially compensated for by use of a blank.

7.2 E. Sample Preparation and Preservation

Because of the unstable characteristics of chlorine in an aqueous solution it is important to take great care in the sample collection not to alter the sample chlorine concentration.

The sample is collected into an airtight BOD bottle which has been covered with black electrical tape. The bottle is filled well into the neck so as to overflow when the ground glass stopper is inserted. Make sure there are no bubbles in the bottle. It is then taken to the dab for immediate analysis (within 5 minutes from collection to analysis).

7.2 F. Procedure

Rinse the sample cells and caps thoroughly with RO/DI.

Pour sample into 2 sample cells to the 10 ml mark.

Empty the contents of one Total Cl_2 powder pillow or packet into one of the sample cells. Cap and invert 10 - 15 minutes to mix.

Wait 3 minutes.

7.2 F. Procedure (continued)

Using the up and down arrows set the device to mode 5207 (515 nanometers).

Wipe both sample cells carefully with a Kimwipe being careful to remove any fingerprints or other marks.

Place the cell containing untreated sample (Blank) into the cell compartment. Close the light shield and press the zero button. The meter should read 0.00 mg/L.

Place the cell containing treated sample into the cell compartment and push the read button.

Record the result in mg/L.

7.2 G. Calculations

The DR700 reads concentration of Total Residual Chlorine in mg/L. Results are recorded directly to bench sheets.

Standard curves are plotted in mg/L.

7.2 H. Quality Control

1. All reagents are NIST traceable and preparation and expiration dates are recorded.

7.2 H. Quality Control (continued)

2. The Hach DR700 colorimeter is maintained by QC Services with regularly scheduled service every 6 months.

3. Glassware is thoroughly washed with a 2% solution of Micro brand detergent, and rinsed with RO deionized water. Separate cells for duplicate total chlorine determinations.

4. Hach Volette Ampule Certified Standards are used daily, and are recorded as a standard curve for a control chart.

5. Duplicate samples are analyzed once per week.

6. Grab samples are recorded at the exact time of sampling and are analyzed immediately after entering the laboratory. The time of analysis and date are recorded.

NO HOLD TIME

Calculation for Voluette Ampule Standards:

$$\frac{ml\ of\ standard\ addition}{ml\ of\ standard\ additional\ \%\ ml\ of\ sample}\ x\ Chlorine\ conc.\ of\ Vol.\ Ampule$$

= Concentration of chlorine added to the sample.

7.3. Settleable Solids

7.3 A. Method Reference

Volumetric Method #2540 F 18th Edition Standard Methods for the Examination of Water and Wastewater pages 2-57.

7.3 B. Apparatus

1 Liter Imhoff Cones

7.3 C. Standardization N/A

7.3 D. Interferences N/A

7.3 E. Sample Preparation and Preservation

Mix the sample thoroughly before pouring off.

7.3 F. Procedure

Place one liter of well mixed sample into a clean Imhoff cone.

Allow the sample to settle for 45 minutes.

Rotate the cone to dislodge solids on the side of the cone.

Allow to settle for an additional 15 minutes.

7.3 F. Procedure (continued)

After a total of elapsed time of 60 minutes from the time the sample was poured. The settled solids are read in ml/liter and recorded.

7.3 G. Calculations

Results are recorded as ml/L.

7.3 H. Quality Control

Duplicate samples are collected and analyzed weekly.

7.4 Total Suspended Solids

7.4 A. Method Reference

Total Suspended Solids Dried at 103 - 105°C Method #2540 D.

18th Edition Standard Methods for the Examination of Waste and Wastewater pages 2-56.

7.4 B. Apparatus

Drying Oven 104° C (± 1°C)

Filter Paper, glass fiber 934AH

Buchner Funnel

7.4 B. Apparatus (continued)

Rubber stopper (to fit Buchner funnel to 1 liter side arm flask)

(2) 1 foot sections of rubber hose (one to connect side arm to filtration flask to safety trap) One to connect trap to vacuum pump.

(2) 1 liter side arm flasks - 1 filtration 1 safety vacuum pump.

Graduated Cylinders

Desiccator - fresh desiccant

Forceps

Safety glasses and gloves

Aluminum weighing tray

(4) Place analytical balance squeeze bottle for RO/DI water.

7.4. C. Standardization (or more accurately pre-test preparation)

The balance must be checked to be sure it is level and then properly zeroed after brushing any debris off the pan.

7.4. C. Standardization (or more accurately pre-test preparation) (continued)

Filters must be rinsed with RO/DI water dried at 104°C for approximately 15 minutes, weighed and then redried, redesiccated and reweighed to establish constant weight (± 0.5 mg) before the analysis is performed.

- Make sure the drying oven is maintained at a constant temperature of 104°C ± 1°.

7.4. D. Interferences

Water with every high mineral content might need to be dried longer, desiccated and weighed quickly as moisture will be quickly absorbed from the atmosphere. This affect can be reduced by placing desiccant in a container inside the balance chamber.

Don't include large floating particles in the sample unless they are truly representative of the actual sample conditions.

7.4 E. Sample Preparation and Preservation

Collect a sample volume of at least 2 liters.

Keep samples refrigerated at 4°C up until the time of analysis to reduce the microbiological decomposition of solids.

7.4 E. Sample Preparation and Preservation (continued)

Try to perform the analysis within 24 hours (7 days absolute maximum)

Bring the sample to room temperature before beginning analysis.

7.4 F. Procedure

1. Prepare the funnel and vacuum apparatus. Make sure the vacuum is not excessive so as to rip the filter.

2. Put the pre-weighed filters into the funnel wrinkled side

3. Seat the filter by rinsing the funnel and filter with about 25 mls of RO/DI water. Turn on the vacuum pump until DI water is drawn through the filter.

4. Shake sample thoroughly, then pour off 1 liter of effluent (100 ml influent) into the graduated cylinder.

5. Pour the sample slowly into the center of the filter with the vacuum on.

    - Rinse the graduated cylinder with at least 3 successive 20 ml DI water rinses turn the graduated cylinder while pouring rinsewater into funnel to insure that all solids are rinsed out.

7.4 F. Procedure (continued)

- Wash down the sides of the funnel into the filter.

- Remove the filter from the funnel with the forceps.

- Place the filter into an aluminum weighing pan and place onto the center rack of the drying oven at 104°C for 2 - 3 hours (preferably overnight).

- Cool to room temperature by putting the filter into the desiccator for 15 to 30 minutes.

- Weigh (if the aluminum pan was included in the initial weighing it must certainly be included in all weighings.)

- Redry at 104°C for at least 1 hour.

  Redesiccate for 15 to 30 minutes.

- Reweigh

- Repeat drying, desiccating and weighing if necessary until constant weight is achieved (<.5 mg difference)

7.4 G. Calculations

$$\text{TSS in mg/L} = \frac{A \ \& \ B \ x \ 100{,}000}{C}$$

7.4 G. Calculations (continued)

Where A = weight of filter and residual (in grams)

B = weight of filter (in grams)

C = volume of sample filtered (in milliliters)

7.4 H. Quality Control

1. The oven temperatures are closely monitored. Temperatures are recorded every four hours when in use.

2. The analytical balance is checked for level, auto calibrated before each use and professionally calibrated every 6 months.

3. The temperature of the sample storage refrigerator is checked and recorded every 4 hours when in use.

4. A replicate sample is analyzed each time the analysis is performed. If results are not within a specified range (determined by control chart) corrective actions are initiated.

5. One duplicate sample is analyzed for every ten TSS analyses performed. Results are recorded in QC log and are plotted on control charts.

7.4 H. Quality Control (continued)

6. A RO/DI water blank is run each time the analysis is performed. Results are plotted on a blank control chart.

7. Sufficient sample, up to one liter, is filtered to produce at least 2.5 mg residual.

8. Results are recorded in QC log and bench sheets.

7.5 5 Day BOD

7.5 A. Method Reference: 5 Day BOD Method 521 OB 18th Edition Standard Methods for Examination of Water and Wastewater pages 5-2 through 5-6.

7.5 B. Apparatus

Dissolved Oxygen Bottles
Overcaps
One Liter Graduated Cylinders
Assorted Sizes of Graduated Cylinders
Beakers, Assorted Sizes
Pipettes
Pipette Bulb
Carboy
Siphon
Propeller Mixer
DO Meter
Thermometer

7.5 B. Apparatus (continued)

Air Pump, Tubing, Filter
Stand
pH Meter
Incubator
Refrigerator
DO Bottles with Auto Pipettes
500 ml Erlenmeyer Flasks
25 ml Burette and Burette Stand
Dropping Bottles

7.5 C. Reagents:

Reagent	Recipe	Hold Time
Phosphate Buffer (Dilution water component.)	- 8.5 KH_2PO_4 - 21.75g K_2HPO_4 - 33.4g $Na_2HPO_4 \cdot 7H_2O$ - 1.7g NH_4Cl - Dilute to 1R DI water. - Autoclave 45 minutes.	- Indefinite @ 4° C - Throw out if biological growth appears.
Magnesium Sulfate	- 22.5g Mg $SO_4 \cdot 7H_2O$ in 1R DI water - Autoclave 45 minutes.	- Indefinite @ 4° C - Throw out if biological growth appears.
Calcium Chloride	- 27.5g $CaCl_2$ in 1R DI water. - Autoclave 45 minutes.	- Indefinite @ 4° C - Throwout if biological growth appears.
Ferric Chloride (Dilution water component)	- 0.25g $FeCl_3 \cdot 6H_2O$ in 1R DI water. - Autoclave 45 minutes.	- Indefinite @ 4° C - Throw out if biological growth appears.
1N Sulfuric Acid (To adjust pH sample)	- 28 ml conc. H_2SO_4 to 1R DI water.	
1N Sodium Hydroxide (To adjust pH sample)	- 40g NaOH to 1R DI water.	
GGA ampules - 300 mg/l glucose - 300 mg/l glutanic acid	Order from: Hach Company PO Box 907 Ames, Iowa	
Polyseed	Order from: Polybac Corp. 3894 Courtney Street Bethlehem, PA	1 year at 20° C
Sodium Sulfite (Dechlorination reagent)	- Prepare small vials each containing 0.79g of Na_2SO_3 - Dissolve 1 vial in 500 ml DI water prior to use.	1 - 2 hours

7.5 C. Reagents (continued)

Reagent	Recipe	Hold Time
Phosphate Buffer (For dechlorination)	- 24g Na_2HPO_4 - 46g KH_2PO_4 - 800mg disodium EDTA dihydrate into 100ml DI water. - All of above into 1R DI water. - 20mg H_2Cl_2 preservative. - Autoclave 45 minutes.	- Indefinite at 4° C - Throw out if biological growth appears.
DPD Indicator	- 1g N,N-Diethyl-p-phenylenediamine oxalate - 8ml 1 +3 H_2SO_4 - 200mg disodium EDTA dihydrate - Dissolve all of the above in 1R DI water	- Discard if pink color appears. - Store in dark bottle @ 4° C.
0.25N FAS titrant	- 49g Fe $(NH_4)_2(SO_4)_2 \cdot 6H_2O$ - 10ml H_2SO_4 - Dissolve above in 1R boiled and cooled DI water.	- 3 months @ 4° C - Must be standardized.
1 + 3 sulfuric acid	- one part H_2SO_4 to three parts distilled water.	
0.25N potassium dichromate	- 12.26g, $K_2Cr_2O_7$ to 1R DI water	Indefinite at 4° C
Potassium iodide crystals	- Prepare small vials each containing 1g KI	Indefinite

7.5 D. DO Meter Standardization

1. Turn DO meter **onto "RED LINE,"** allow to warm up for **15 minutes**.

2. Fill 1R graduated Cylinder with **DI water** and **siphon into 3 BOD bottles,** without aerating water.

7.5 D. DO Meter Standardization (continued)

3. To two of the bottles add **2 mls of DO reagent #1** and 2 mls of DO **reagent #2** below surface.

4. **Invert bottles** until uniform consistency. Let stand until floc settles to **50% bottle volume. Invert a second time** and let stand again.

5. Add **2 mls of DO #3, cap and invert** until floc is complete gone.

6. Pour contents into 50 ml wide-mouth flask and **titrate using .0375N $Na_2S_2O_3$ until pale yellow.** Add **1 ml of starch indicator** (1/2 dropper full and swirl. **Titrate slowly** until **blue becomes clear**.

7. **Add as many drops** of black titrant (potassium bi-iodate) as are necessary to bring **blue color back**. If one drop does this, **record the reading on the buret. If it takes more than 1 drop, multiply the number of drops by 0.05 mls and subtract from buret reading**.

   Reading on buret is in milliliters and is equivalent to oxygen in milligrams per liter. Report readings to nearest 0.05 ml.

8. **Average two titrations** and **record results** in record book.

9. **Place DO probe into third bottle** making sure there are no air bubbles trapped. Turn knob to "zero" and **adjust until zeroed**.

7.5 D. DO Meter Standardization (continued)

10. Turn knob to **"calibrate 1-10," turn on stirrer.**

11. Let sit 2 minutes and adjust until meter reads **average of two** Winkler titrations. If the average DO of the Winkler Titrations and the DO from the meter differ by more than .5, rerun Winkler. Run samples within 4 hours of calibration.

E. Preparation of seed - do earlier on day samples arrive.

1. Empty one capsule of **Polyseed BOD seed inoculum into 500 ml of dilution water**.

7.5 E. Interferences

Presence of copper and other metals in the sample can adversely affect results.

See Sample Preparation for Treatment of samples for other interferences.

7.5 F. Sample Preparation and Preservation

24 Hour Composite Samples -

Sample is refrigerated at 4° C from the time the first sample is collected until one hour before analysis is begun.

It is placed in a warm water bath before analysis until the sample temp reaches 20° C. The sample is thoroughly mixed just before being poured

7.5 F. Sample Preparation and Preservation (continued)

24 Hour Composite Samples - (continued)

off. Dechlorination: Samples are dechlorinated using sodium sulfite. Dechlorination is described in the Procedure section (7.5 G).

Seeding - All samples are seeded. The process is described in the Procedure section 7.5 G.

pH: The sample pH is adjusted to between 6.5 to 7.5 if necessary using sulfuric acid or sodium hydroxide (usually not necessary).

7.5 G. Procedure

A. Dilution Water Prep - **24 hours before use.**

1. **Wash 20 R carboy** and **siphon tubing** with micro and rinse very well with DI water.

2. **Fill carboy** with DI water filtered through **0.2 Fm filter.**
-10R for first sample

-3R for each sample thereafter.

ex: 7 samples would require 28R (10 for the first then 3 X 6 = 18 for rest.)

7.5 G. Procedure (continued)

3. Add **1 ml per R** for each:

$MgSO_4$

$CaCl_2$

$FeCl_3$

4. **Aerate** for about **15 minutes.**

5. Store in 20° C incubator for **at least 24 hours** and **no longer than 5 days.**

6. **Just prior to use** add **1 ml phosphate buffer per liter; aerate 15 minutes; let sit for 1 hour**, then use.

7. Be sure temp. Is **20° to 23° C**.

8. Be sure DO is between **7.5 and 8.5 mg/1**.

   a) **If >8.5 mg/l, shake closed container** vigorously, open and let sit.

   b) **If <7.5 mg/l, aerate** some more.

7.5 G. Procedure (continued)

B. Glassware prep. - **Label all** ahead of time.

	Bottles	1000 ml Graduates
Blank	3	1
GGA	3	1
Seed	9 (3/dilution)	3 (1/dilution)
Sample 1	9 (3/dilution)	3 (1/dilution)
Sample 2	9 (3/dilution)	3 (1/dilution)

C. **Dechlorination** of samples.

1. Just prior to use, prepare 0.78g Na_2SO_3 to 500 mls DI water.

2. To a 500 ml wide-mouth flask, add:

   - 100 ml sample

   - 5 mls DPD indicator

   - 5 mls PO_4 buffer

   - 1 g KI crystals (may be pre-weighed in small vials)

3. A faint **pink-red** color after 2 minutes indicates **chlorine is present. Stop here if no color.**

7.5 G. Procedure (continued)

4. Using standardized 0.00282N FAS, titrate to **clear endpoint. Ml FAS used equals mg/l Cl_2**.

5. Dechlorinate with Na_2SO_3 using in ml 5 times the amount of chlorine per liter.

   Example: Cl_2mg/l = FAS used

   2.2 mls FAS used = 2.2 mg/l Cl_2

   2R sample: 2R x 2.2 x 5 = 22 ml Na_2SO_3

   Add 22 mls Na_2SO_3 to 2R sample to dechlorinate, shake sample. _____

6. **After 15 minutes repeat steps 2 and 3**. If no pink color, then sample is

2. **Aerate** and stir for at **least 60 minutes**.

3. When pipetting be sure flakes of bran do not get into pipette.

7.5 G. Procedure (continued)

F. Seeding Chart

Expected Seed BOD mg/l	Seed Dilution (%)*	Seed (ml) to dilutions +
50 (Polyseed range)	2, 5, 10	20
75	2, 5, 10	15
100	1, 2, 5	8
125	1, 2, 5	8
150	1, 2, 5	6
175	1, 2, 5	6
200	0.51, 2,	5
225	0.5, 1, 2	5
250-400	0.5, 1,2	3

* Seed dilutions calculated for an approximate DO depletion of 3 mg/l

\+ calculated for a DO depletion of approximately 1 mg/l

2. Seed Calculation:

$$\frac{0.8\ mg/l}{Expected\ seed\ BOD\ mg/l}\ x\ 1000\ '\ \frac{ml\ seed\ used\ in\ samples\ \%\ GGA}{}$$

7.5 G. Procedure (continued)

G. Dilution Technique.

1. BOD rules:

a) Blank depletion must be <0.2 mg/l.

b) Want a dilution such that **residual** DO is at least **1.0 mg/l**.

c) Want a dilution such that **depletion** is at least **2.0 mg/l**..

2. Calculation for dilution:

$$\frac{2\ mg/l\ x\ 1000\ ml}{Expected\ sample\ BOD} = mls\ sample\ to\ dilute\ 1R$$

Example: Expected BOD is about 15 mg/l, you want 2 mg/l depletion.

$$\frac{2\ mg/l\ x\ 1000\ ml}{15\ mg/l} = 133\ ml\ to\ 1R\ or\ 13.3\%$$

3. General ranges for dilutions:

0.0 - 1.0 %	for strong industrial wastes
1 - 5%	for raw and settled wastewater
5 - 25%	for biologically treated effluent
25 - 50%	for polluted river waters

H. Actual procedure on day samples started.

7.5 G. Procedure (continued)

1. Add 10 ml **GGA ampule** to **1ℝ graduated cylinder** (gives 2% GGA).

2. **Add seed** (usually 20 ml for polyseed) to GGA and sample cylinders.

3. **Prepare dilution** of samples in graduated cylinders (be sure samples at 20° C).

4. **Set up sample sheet** to receive data (see sample data sheet).

5. **Transfer** sample dilutions, GGA, blank and seed dilutions **to BOD bottles** (3 bottles per dilution).

6. Put **plastic caps on 2 bottles** for each dilution and place in **20° incubator** for 5 days ± 3 hours.

7. **Read DO of third bottle** for each group and **record as Initial DO** (see sample data sheet).

8. **Read DO final after 5 days** ± 3 hours and record both values for each dilution.

7.5 G. Procedure (continued)

Calculations:

A. Seed factor: $\frac{BOD\ of\ seed\ x\ ml\ seed\ used}{1000\ ml}$

Example: $\frac{40\ mg/l\ x\ 15\ ml}{1000\ ml}$ ' $0.6\ mg/l$

B. DO depletion:

DO_I & $\overline{DO_F}$ ' $DO\ depletion$

$\underline{DO}_1$ ' $Initial\ DO$

DO_F ' $average\ final\ DO$

Example: 8.20 *mg/l* & 5.4 *mg/l* ' 2.8 *mg/l* (*depletion*)

C. BOD mg/l: $\frac{DO\ depletion\ \&\ Seed\ Factor}{\%\ Dilution}$

Example: $\frac{2.8\ mg/l\ \&\ 0.6\ mg/l}{.5\ (50\%\ dilution)}$ ' $4.4\ mg/l$

7.5 G. Procedure (continued)

Quality Control:

1. Blanks are run as a bottle and dilution water check. Values #0.2 mg/l are acceptable.

2. GGA should run 198 ± 30.5 mg/l.

3. A duplicate should be run in each batch.

5 Day BOD Data Sheet

Sample Locations: Sample Data Sheet

Lab ID Numbers: 96274 99385

Date & Time Sampled: 10-21-92 10:00 a.m. **Date & Time Sample arrived at Lab:** 10-12-92 1:00 pm

Date & Time BOD Setup: 10-21-92 3:00 p.m. **Date & Time Final DO Read:** 10-26-92 1:00 p.m.

Analyst:

Sample	% Dil	ml Seed	DO_I	DO_F	DO_F	Avg. DO_F	DO Depl.	Seed Factor	DO Depl.	BOD mg/l
Blank	---	---	8.80	8.75	8.65	8.70	0.10	---	---	---
GGA	2	20	8.75	4.30	4.25	4.28	4.47	0.46	4.01	200.5
S_1	2	20	8.75	8.20	8.20	8.20	0.55	---	---	<2 Depl.
S_2	5	50	8.75	7.70	7.65	7.68	1.07	---	---	<2 Depl.
S_3	10	100	8.80	6.60	6.40	6.50	2.30	---	---	23
96274 A	5	20	8.75	6.00	6.05	6.07	2.68	0.46	2.22	44.4
B	10	20	8.75	3.65	3.70	3.67	5.08	0.46	4.62	46.2
C	30	80	< 1	< 1	---	---	---	---	---	---
99385 D	5	20	8.75	6.55	6.65	6.60	2.15	0.46	1.69	<2 Depl.
E	10	20	8.75	5.10	4.95	5.03	3.72	0.46	3.26	32.6
F	30	20	8.80	< 1	< 1	---	---	---	---	

Sample	% Dil	ml Seed	DO_I	DO_F	DO_F	Avg. DO_F	DO Depl.	Seed Factor	DO Depl.	BOD mg/l

Notes and Calculations:

Seed Factor: $\frac{23\ mg/l\ x\ 20\ mg/l}{1000\ ml} = 0.46\ mg/l$

5 Day BOD Data Sheet - *Continued*

Sample	% Dil	ml Seed	DO_I	DO_F	DO_F	Avg. DO_F	DO Depl.	Seed Factor	DO Depl.	BOD mg/l

Notes and Calculations:

8.0 Reagent/Standard Quality, Preparation and Traceability

8.1 All standards and reagents are prepared from reagent grade materials, primary standards or they are purchased from reputable vendors. Reagents are stored according to manufacturers instructions and discarded upon expiration. Standards and reagents are prepared using bala nces that are calibrated daily, Class A volumetric glassware and ASTM Type II reagent water.

Once a solution is prepared it is labeled with the solution name or description, storage requirements, concentration or normality, preparation and expiration dates and initials of preparer. Expiration dates for standards and reagents are specified in methods that are adhered to unless degradation prior to this date is observed. Log books are utilized to record the preparation of standards.

Calibration standards (working standards) are dilutions or mixtures of stock standards used to calibrate an instrument. These standards are prepared or restandardized frequently as specified in Laboratory Standard Operating Procedures (SOP's). New standards are checked again old standards to insure there has not been an error in preparation.

Quality control reference samples are analyzed along with most analytes, depending upon availability to validate standards, technique and methodology. Quality control reference samples are prepared from a different source than that used in the preparation of standards for use in the standard curve and are US EPA certified, if possible.

9.0 Calibration Procedures and Frequencies

9.1 Instrument Calibration Procedures

All instruments and equipment used are routinely calibrated by laboratory personnel or by external calibration agencies or equipment manufacturers. Maintenance schedules can be found in the Preventative Maintenance Section of this manual (Section 1.0). Instrument calibration procedures, frequencies, standards and traceability are summarized in Table 9.2 To insure that instruments have performed adequately throughout the analysis, it is laboratory practice to run a standard or quality control reference sample at the end of an extended run.

9.1 Instrument Calibration Procedures (continued)

Table 9.2

Instrument/ Analytes	Calibration Frequency	Procedure	Calibration Standard (Traceability)	Quality Control Standard (Traceability)
pH/Millivolt Meter - pH	Daily	2 point calibration bracketing sample	Certified buffers (NIST traceable)	EPA Reference Sample (US EPA)
Conductance meter - conductivity	Daily	.01M Potassium Chloride	Primary Grade Reagents	Conductivity Standards (NIST)
Analytical Balances	Daily	Calibrated according to manufacturer's directions.	Calibration verified using Class -S weights	Weights NBS Traceable
Spectrophotometer - COD	Daily	3 - 5 Point Calibration	Primary Grade Reagents	EPA Reference Sample (US EPA)
Turbidity Meter - turbidity	Daily	Calibrated According to AMCO instructions	AMCO Sealed Primary Calibration Standards	AMCO Sealed Secondary Standards
Dissolved Oxygen Meter - BOD - DO	4 Hours	Winkler Titration	Primary Grade Reagents	(NIST traceable)
Cloroimeter (Fixed Photometer) - Chlorine	Each use	Internal instrument calibration and Hach Spec T Color Standard	NIST SMR 930 S/M99	EPA Reference Sample (US EPA)
COD Reactor - COD	Daily	5 Point Calibration	Primary Grade Reagents	EPA Reference Sample (US EPA)
Millivolt Meter - TKN	Daily	4 Point Calibration 2 Point Calibration Probe	Primary Grade Reagents	EPA Reference Sample (US EPA)

9.1 Instrument Calibration Procedures (continued)

Table 9.2

Instrument/ Analytes	Calibration Frequency	Procedure	Calibration Standard (Traceability)	Quality Control Standard (Traceability)
Thermometers - incubators - pH - conductivity	Annually/ Semi-Annually (bacteriology)	Accuracy checked over range to be used. Deviations recorded on thermometer.	Thermometer NIST	
Incubators - bacteriology	Twice Daily	Temperature Check	Thermometer NIST	
Autoclave - bacteriology	Weekly	Sterility Check Temperature Check	Spore Strips Maximum Thermometer NIST	
Refrigeration Units - reagent sample storage	Daily	Temperature Check	Thermometer (NBS)	

10.0 Data Handling - Reduction, Validation and Reporting

10.1 Data Reduction

Raw data is recorded directly onto bench sheets by the technician who actually performed the analysis.

If more than one analyst is involved in setting up an analysis or reading results (Ex. BOD initials DC's determined by one person and final DO's by another) both analysts initial the bench sheet. All calculations are included on bench sheets.

Only the chief operator can transfer information from the bench sheets to WR-43 report forms.

10.2 Data Validation

The analyst who generates the data has the prime responsibility for its correctness and completeness. It is the analysts responsibility to verify that the instrument was calibrated and was performing properly.

The chief operator looks over and double checks the bench sheets. He checks all calculations, looks to see that all data makes sense and that the numbers were rounded properly (section 10.5) and that proper significant numbers were recorded (section 10.4).

After transferring the data to the WR-43 report forms he checks for transcription errors.

The assistant operator performs a quick check of bench vs. WR-43 data before the report is given to the town manager for his signature.

The town manager looks at the WR-43 report form and questions the chief operator concerning any unusual or suspicious looking result before signing the report. As a rule the town manager and chief operator meet to discuss the report regardless of whether or not there are irregularities.

10.4 Significant Digits

Parameter	Significant Digits
BOD - No digit after decimal point.	28 mg/L
Chlorine Residual - Two digits after decimal point.	0.51 mg/L
Coliform - No digits after decimal point.	50/100 ml.
TKN, NH_3, NO_3 - One digit after decimal point.	17.6 mg/L
D.O. - Two digits after decimal point.	7.35 mg/L
Settleable Solids - One digit after decimal point.	5.1 ml/L
Metals - One digit after decimal point.	436.3 ppb
pH - Two digits after decimal point.	7.00 pH units
Suspended Solids - No digit after decimal point.	22 mg/L
Temperature - One digit after decimal point.	17.2°C

10.5 Rounding Policy

All digits are used in calculations, then are rounded, using the following guidelines. Numbers following decimals shall be rounded to the next higher or lower number based on this method.

For example: 3.57 is rounded to 3.6

2.41 is rounded to 2.4

7.55 is rounded to 7.6

7.44 is rounded to 7.4

11.0 Preventive Maintenance Procedures and Schedules

11.1 All laboratory equipment is serviced and professionally calibrated by QC Services on an annual basis. A service contract is maintained to include annual equipment calibration.

11.2 Routine and professional calibration/maintenance schedules are summarized in Table 11.2.

11.3 Preventive maintenance responsibilities are assigned to specific laboratory personnel. Only the lab supervisor is allowed to perform other than routine calibration or minor repair.

11.4 A maintenance log is kept in the lab for each instrument. All calibration, repairs and service visits are recorded an entitled by the responsible party.

11.0 Preventative Maintenance Procedures and Schedules Table 11.2 (Continued)

Instrument - Manufacturer - Model	Calibration Frequency	Maintenance Contractor	Preventative Maintenance Schedule
Atomic Absorption, Perkin-Elmer 3030B	Daily	Perkin-Elmer	As needed
Autoclave, Barnstead	4/year	MDT Biologic Co.	4/year
Waterbath, Precision Scientific - 83	1/year	QC Services	1/year
Waterbath, Blue M	1/year	QC Services	1/year
Air Incubator, Boekel	1/year	QC Services	1/year
pH/Millivolt Meter, Orion Model 811	Each use	QC Services	1/year
pH/Millivolt Meter, Orion Model 720A	Each use	QC Services	1/year
Ratio Turbidmeter Hach Model 18900	Daily	QC Services	1/year
Spectrophotometer, Bauch & Spectronic 100	Daily	QC Services	1/year
Dissolved Oxygen Meter, YSI Model 57	Every 4 hours	QC Services	1/year
Fluorometer, Turner Model 111	Yearly	QC Services	1/year
COD Reactor, Hach Model	Yearly	QC Services	1/year
Centrifuge, International Equipment	---	QC Services	---
Conductance Meter, YSI Model 32	Yearly	QC Services	1/year
Chlorine Meter, Hach Model DR100	Each use	QC Services	---
Balance, Mettler AE 200	Daily	QC Services	1/year
Balance, OHAUS B1500D	Daily	QC Services	1/year

12.0 Corrective Action Contingencies

12.1 Corrective actions are required as a result of less than acceptable **P**erformance **E**valuation study results, or poor comparison in split sample analyses (State lab results significantly different than facility results). The steps taken in the corrective action process include:

Identify and define the problem.

Determine who will be responsible for investigating the problem.

Find the cause of the problem.

Determine the actions needed to eliminate the problem.

Implement the corrective actions and

Establish the effectiveness of the corrective action.

Usually the lab supervisor is responsible for initiating the corrective action under these conditions. Documentation of actions taken and their effectiveness is forwarded to the lab supervisor for review and distribution.

12.2 Corrective actions might also be initiated by an analyst during or after sample analysis. These actions may be necessary because of

Unacceptable blank results (BOD blank depletion >.2 mg/L)

Suspicious positive control results (every few colonies on E Coli. positive control sample).

QC data outside the warning or control limits for precision and accuracy.

Duplicate or replicate results are inconsistent.

Under these conditions the analyst generating the data is expected to initiate and document corrective action.

12.3 Corrective Actions Required for Specific Problems are Listed in Table 12.4

Table 12.4

Problem	Corrective Action
Blank contamination is indicated	Determine cause of contamination, eliminate cause and repeat analysis.
Unexpected, unusual results occur more than once every 20 analyses	Investigate possible causes. Try to eliminate interferences. Keep a close watch on future analyses.
One or more data points falls outside the control limit.	Determine cause eliminate it an repeat analysis.
Two out of three successive data points fall outside the established warning limits.	Repeat analysis. If the next data point is less than warning limit continue the analyses. If the next point exceeds warning limits discontinue analyses and correct the problem.
4 out of 5 successive data points exceeds 1 standard deviation or are in decreasing or increasing order.	Analyze another sample. If the next data point is less than 1 standard deviation or changes the order continue analyses. If not discontinue and correct the problem.
Six successive sample results are above/below the central line on the control chart.	Analyze another sample. If the next result is on the other side of the central line continue analyses. If the next point is on the same side of the central line discontinue analyses and correct the problem.

13.0 Quality Control Procedures (General)

This section describes the method used at this laboratory to evaluate the quality of data generated.

13.1 Sampling Quality Control Checks

Sampling QC checks provide information regarding the precision and accuracy of the entire process from sample collection through analyses. Included in this category are:

13.1.1 Equipment Blanks

Equipment blanks are used to determine if contamination has been introduced through contact with sampling equipment or to verify effectiveness of equipment cleaning procedures.

Clean laboratory water is pumped through the Isco sampler. We usually place the sampler probe in a 4 liter jug of RO/DI water, pump for 10 - 15 seconds, purge for 5 seconds. This process is repeated 2 to 3 times before the equipment blank sample is collected. This sample is then taken to the lab and processed along with other samples.

13.1.2 Split Samples

Split samples are replicate samples, two aliquots taken from the same sample container. The samples are then analyzed independently by our own lab and a contract laboratory. If significant differences are noted the cause is determined and corrected.

13.0 Quality Control Procedures (General) (continued)

13.1.3 Duplicate Samples

Duplicate samples are samples collected at the same location at the same time. Collection of duplicate samples serves as a check on sampling and processing technique. Each sample is analyzed individually. Results must be within an acceptable range (10%) or the cause must be determined and corrected.

13.1.4 Replicate Samples

Replicate sample are two aliquots taken from the same sample container that are processed and analyzed separately. The results are used to measure analytical precision from sample preparation through analysis. Certain analyses are run in replicate every time the test is performed. A minimum 10% replication schedule is established for all analyses.

13.2 Procedures Used to Assess Data Quality

13.2.1 Precision

Precision is a measure of the closeness with which multiple analyses of a sample agree with each other. We calculate precision from results of replicates and duplicate analyses of quality control samples.

13.2 Procedures Used to Assess Data Quality (continued)

13.2.1 Precision (continued)

Here at the WWW Wastewater laboratory we use Relative Percent Difference (RPD) as a measure of precision. The formula used to calculate RPD is:

$$RPD = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2)/2}$$

Where: RPD = relative percent difference

C_1 = larger of the two observed values

C_2 = smaller of the two observed values

If calculated from three or more replicates, we use relative standard deviation rather than RPD:

RSD = (s/y) X 100%

where: RSD = relative standard deviation
s = standard deviation
y = mean of replicate analyses

Standard deviation is defined as follows:

$$SD = \sqrt{\frac{\sum Xi^2 - \frac{(\sum Xi)^2}{n}}{n - 1}}$$

13.2 Procedures Used to Assess Data Quality (continued)

13.2.1a Control Charts

Control charts are used to demonstrate the precision calculated from replicates and quality control sample duplicates.

The Relative Percent Difference (RPD) values for each sample are plotted on control charts and where upper and lower warning and control limits are depicted.

These control charts are used by the analysts to help make them aware of suspicious or out-of-control variability at the time of analysis. The warning and control limits are recalculated annually. An example of a control chart cal be found at the end of the section.

13.2.1b Control Limits

Control limits are defined as the mean + / - 3 standard deviations. An RPD value that falls outside the control limits is considered out-of-control and requires the analysts to repeat the analysis immediately. If the repeat value is within the control limit analysis may continue. If the repeat value exceeds the control limit analysis must stop and the problem must be corrected.

13.2.1c Warning Limits

Warning limits are narrower than control limits and are defined as the mean + / - 2 standard deviations. An RPD value that falls outside the warning limit is considered suspicious. If two out of three consecutive points exceed a warning limit the analyst must calculate the RPD on another sample. If the warning limit is exceeded analysis must stop and the problem must be corrected.

13.2 Procedures Used to Assess Data Quality (continued

13.2.2 Accuracy

Accuracy is expressed as a percent bias or percent recovery and is determined from the analysis of quality control reference samples or spikes. Method accuracy is calculated on a daily basis and summarized annually in the Laboratory Quality Assurance Plan.

Percent recovery is calculated from spike results using the following equation:

$$\%\ R = 100\% \times \frac{S \& U}{C_{sa}}$$

where: %R = percent recovery

S = measured concentration in spike aliquot

U = measured concentration in unspiked aliquot

C_{sa} = actual concentration of spike added

$$\%\ B\ '\ 100\ x\ \frac{(O \& T)}{T}$$

Where: %B = percent bias

O = measured concentration of reference material

T = actual concentration of reference material

Vermont Department of Environmental Conservation
Quality Assurance Guidelines for
Wastewater Treatment Facility Laboratories

1996

Prepared by:

Andrew Fish, C.E.T.
Wastewater Laboratory Specialist
for the VT Dept. of Environmental Conservation

PREFACE

These guidelines have been developed to assist operators and technicians at Vermont Wastewater Treatment Facilities to prepare acceptable Quality Control Manuals specific to their facilities. It is further hoped that the guidelines will encourage the implementation of these procedures. The quality control procedures outlined in this manual represent the minimum requirements considered acceptable by the Vermont Department of Environmental Conservation for facilities regulated under the NPDES program.

The laboratory quality control manual described in this guidance document is an integral part of the "appropriate" quality assurance procedures required of all NPDES regulated facilities pursuant to Title 40 of the Code of Federal Regulations, Part 122.41 (e) any commercial laboratory performing analyses for an NPDES regulated facility must certainly meet these minimum requirements.

It is absolutely essential that all laboratories analyzing wastewater compliance samples follow defined quality assurance procedures. Those procedures must be documented in a laboratory quality control manual.

To satisfy minimum NPDES requirements a quality control manual must address the following items. (Each of which will be discussed in detail in the following pages.)

I. Quality Assurance Program Plan Elements
II. Staff Organization and Responsibilities
III. Quality Assurance Objectives and Activities
IV. Sample Collection Procedures
V. Sample Handling and Documentation Procedures
VI. Laboratory Water Quality
VII. Standard Operating Procedure for Each Analytical Method
VIII. Reagent/Standard Quality Preparation and Traceability
IX. Calibration Procedures and Frequencies
X. Data Handling - Reduction, Validation and Reporting
XI. Preventive Maintenance, Procedures and Schedules
XII. Corrective Action Contingencies
XIII. Quality Control Procedures (General)

In order to produce a truly useful QA/QC manual a table of contents should be included. You may also wish to include things such as laboratory utilities information, electrical supply, compressed air source, etc. or anything that might effect the function of the laboratory.

I. Quality Assurance Project Plan Elements

This section of the manual simply lists the topics which will be included in your quality assurance plan. It is basically a table of contents without the page numbers. It should be the first step in preparing the manual as it will help you to organize your thoughts and establish distinct sections.

II. Staff Organization and Responsibilities

Laboratory analytical centers can obviously vary considerably in size, number, complexity of analyses performed, and in the number of people employed.

This section of the manual should identify all persons responsible for laboratory activities from sampling to preparation and signing of the Discharge Monitoring Report. It should describe the responsibilities of each of the individuals in certain terms; identifying each individual using that person's name (not just the position - i.e. Andy Fish, QA coordinator not QA coordinator).

A typical municipal wastewater facility's staff organization and responsibilities section might include:

1). The town manager as the person responsible for signing the WR-43.
2) The chief operator as the preparer of the WR-43.
3). Assistant operator as responsible for sample collection.
4) Lab tech - responsible for performing analyses maintaining bench sheets,

assisting in data review etc.

Each individuals responsibilities and limitations should be spelled out in this section.

As an example of limitations, an analysts responsibilities might include informing the chief operator if accuracy values are beyond established warning and control limits.

----This clearly shows that the analysts responsibility ends with informing his supervisor of a problem. It is presumably the chief operators responsibility to determine the action taken from that point.

An organization chart is very useful in identifying positions (where they fit into the scheme of things).

III. Quality Assurance Objectives

This section, besides being useful to inspectors and certification officials can be very helpful to the person preparing the manual to figure out "just what am I trying to demonstrate in this manual?" "What am I really after here?"

Here is an example of typical Quality Assurance Objectives.

1. To ensure data produced by the laboratory is accurate and defensible.
2. To ensure samples collected are representative of preferred universe.
3. To ensure that all laboratory procedures are EPA approved.
4. To ensure that all equipment is properly calibrated and meets EPA specifications.
5. To ensure that proper corrective actions are initiated when necessary.

III. Quality Assurance Objectives (continued)

6. To ensure that each sample is tracked from collection time until the report is finalized - with records maintained for the required intervals. Of course in addition to simply listing the objectives you might summarize referencing specific sections of the manual, how these objectives will be met.

IV. Sample Collection Procedures

Careful and precise documentation of sampling procedures is absolutely imperative to ensure that good representative samples are consistently collected. Untold time and dollars are wasted on analysis of samples that are collected at an improper location, time or in an unacceptable container. An exact sampling procedure should be written for each parameter required at your facility. It is smart to include detailed photographs and or diagrams along with sampling location descriptions.

The sampling procedures section of your QA manual should include:

1) Description of container - glass, plastic, etc.
2) Container cleaning requirements -- acid washed, DI rinsed, etc.
3) Sample preservation techniques .
4) Sample holding times.
5) Exact sampling location description.
6) Exact sampling time for most representative sample.
7) Collection method/technique - grab, composite (time-flow, auto sampler) etc.
8) Volume of sample required for analysis.

V. Sample Handling and Documentation Procedures

This section must include:

A written description of exactly how the samples are handled after collection. The methods for documentation must be clearly stated. The following items must be included in this section.

1) Documentation of exact time, date and location sample was collected.
2) Labeling of sample bottles.
3) Chain of Custody Procedures (if analysis is performed by an independent laboratory).

    a) Sample custody forms, labels, seals.
    b) Sample transportation and delivery procedure.

V. Laboratory Water Quality

As many of us are painfully aware, the quality of the water we use in rinsing glassware, preparing reagents and standards, sample dilution, and blank preparations can be the determining factory between accurate and inaccurate analytical results.

There are rather strict monitoring requirements for laboratories analyzing drinking water. These requirements are listed in EPA/570/9-90/008 document Manual for the Certification of Laboratories Analyzing Drinking Water, and include:

V. **Laboratory Water Quality** (continued)

1) General Lab Water

Parameter	Limit	Monitoring Frequency
Conductivity	<2 umhos/cm @ 25ºC	Monthly

2) Water for Microbiological Analyses

Tests	Limit	Monitoring Frequency
Conductivity	<2 umhos/cm @ 25ºC	Monthly
Total Residual Chlorine	<detection limit	Monthly
Heavy Metals, Single[4] (Cd, Cr, Cu, Ni, Pb, Zn)	<0.05 mg/L	Annually
Heterotrophic Plate Count	<500 CFU/ml	Monthly
Water Quality Test[5] (Biosuitability)	0.8 - 3.0 ratio	Annually

In wastewater analysis our main concerns regarding laboratory water quality are conductivity, chlorine and metals that might interfere with certain analyses (i.e. high copper level can affect results in the BOD analysis).

Generally accepted monitoring frequencies and limits for those parameters are listed below.

V. **Laboratory Water Quality** (continued)

2) Water for Microbiological Analyses (continued)

Parameter	Limit	Monitoring Frequency
Conductivity	<2 umhos/cm @ 25ºC	Monthly
Total Residual Chlorine	0.0 or <detectable limit	Monthly
Copper	< .05 mg/L	Semi-Annually
Other Metals (Cd, Cr, Ni, Pb, Zn)	< .05 mg/L	Annually

* Reality Check: The Vermont Department of Environmental Conservation does not expect a small wastewater treatment facility required to perform pH analyses only to have their own laboratory water analyzed for all the parameters listed above. Such a facility should consider purchasing commercially available distilled water, where concentrations of these parameters are often listed on the label. Larger facilities, performing BOD's and more sophisticated analyses would be expected to verify conductivity, chlorine and copper limits. Commercial laboratories performing numerous parameters more frequently than the average treatment facility would be expected to perform more frequent laboratory water analyses.

VII. **Standard Operating Procedures - For Each Analytical Method**

This section of the manual should include a simple step - by step procedure which details the exact method in which the analysis is performed. It should NOT simply be a copy of an analytical method from Standard Methods but instead a practical "What you really do to perform this analysis," type of description in an easy to read format.

VII. Standard Operating Procedures - For Each Analytical Method (continued)

Include specific items such as "Turn the blender to setting 6 and blend for 5 minutes to get a good homogenous sample" or "Use only Class A volumetric glassware from drawer #2.

Items that must be included in this section are:

1) Reference Method, number and Title
2) Description of instrumentation
3) Specific glassware and equipment cleaning procedures
4) Reagent and Standard Preparation
5) Step by Step Procedures (SOPs)
6) Calibration and Standardization procedures - specific to the analysis
7) Equations and Calculations

You may reference an SOP manual to satisfy #5 if you have a separate and complete manual.

VIII. Reagent/Standard Quality, Preparation and Traceability

This section of the manual should describe the general procedures for preparation of reagents and standards. The types of questions that should be addressed include:

1) Grade of materials used i.e. ASC or Analytical Reagent grade chemicals primary standards, etc.
2) Measuring methods i.e. calibrated analytical balance, class A volumetric glassware etc.
3) Reagent labeling: Must Include

VIII. Reagent/Standard Quality, Preparation and Traceability (continued)

A. Reagent name

B. Concentration

C. Preparation and Expiration dates and/or received the dates a chemical is received as well as the date it is opened.

IX. Calibrations Procedures and Frequencies

Documentation of all instrument or equipment calibration is essential to any good quality assurance plan.

This section should detail the procedures, frequencies and type of calibration as well as whether it was routine or professionally performed and finally who performed the calibration.

Written documentation must include at a minimum:

1) Established frequency of routine calibration for each piece of equipment i.e. daily, weekly, monthly.
2) Established frequency of professional calibrations for each piece of equipment.
3) Calibration procedures - Standards used, etc.
4) Dates and times calibrations are performed.
5) The name (* not just initials of the person who calibrated the instrument.)

X Data Handling - Reduction Validation and Reporting

Reduction of Data

Data reduction is the process of transforming raw data into final results that are reported in standard units to some authority. An efficient method of data reduction must exist to reduce transcription and calculation errors. That methodology, whatever it may entail, should be described in this section.

Validation of Data

Data validation starts with the analyst. It is usually the analyst's responsibility to ensure that instruments have been properly calibrated and are operating properly. He or she then records the results on a bench sheet. Generally someone then transfers the data to another form after, perhaps performing some calculations.

At this point there should be some mechanism in place to ensure that the data has been accurately transferred and that any calculations were performed properly.

At least one other person beside the analyst should look over and double check the bench sheet data vs. final results. One or both of these individuals must understand the concept of significant figures and units of measures.

* More than one technical violation could have been avoided had this knowledge been applied.

This section should describe the procedure by which data is checked. Specific responsibilities should be spelled out here.

X Data Handling - Reduction Validation and Reporting (continued)

Reduction of Data (continued)

Each WR-43 report form contains a certification signed by the permittee's authorized agent which states "I certify under penalty of law that I have personally examined and am familiar with the information submitted herein."

It would seem reasonable then to involve this person in the data validation process.

It is important to include in this section.

Examples on description of

1) 8Bench sheets, lab books
2) A description of the check system used to avoid transcription and calculation errors.
3) A procedure of how invalid data is handled on bench sheets and on the WR-43 report form (i.e. BOD results not meeting the R1 D2) requirement - How is this handled?
4) Rules for consistent rounding off of numerical results.

XI. Preventive Maintenance, Procedures and Schedules

Preventive maintenance is very important in order to minimize instrument "Down Time" and ensure the continued accuracy of analytical results.

XI. Preventive Maintenance, Procedures and Schedules (continued)

The old excuse "I couldn't report pH results for the month of April because my pH probe was broken," just isn't acceptable as a defense.

Proper preventative maintenance and contingency plans are essential for uninterrupted analyses.

This section must describe procedures for routine and scheduled contract services. Include:

1) Comprehensive routine maintenance schedule - list of instruments.
2) Professional service/maintenance schedule - list of instruments.
3) A list of employees responsible for performing maintenance.
4) A check list to ensure duties have been completed.

XI. Corrective Action

This section of the manual will outline the steps taken when any portion of the quality assurance process become questionable or invalid.

These steps should include:

1) Identifying and defining the problem i.e. QC is outside control limits, what caused unacceptable results.
2) A list defining need for corrective actions - i.e. (Poor blank or standards results)
3) Actions to eliminate the problem.
4) Actions to prevent recurrence . You may include a copy of the checklist(s)

XI. Corrective Action (4) (continued)

in the manual and include a reference describing where the actual list(s) is/are located if you desire.

5) Procedure for informing superiors of other authorities (if applicable).

6) Protocol for resampling and retesting.

XIII. Quality Control Procedures:

Quality control is defined in the 18th edition of ***Standard Methods for the Examination of Water and Wastewater, 1992***.

As "as set of measures within a sample analysis methodology to assure that the process is in control." This section of the manual is dedicated to describing those measures taken to ensure process control. In it you should define terms and describe general procedures which can be referenced in the QC portion of each analytical method.

Quality control consists of analyzing and reporting the results of quality control standards, sample duplicates and replicates, spikes and blanks.

EPA recommends that a frequency of 10% to 20% be applied for quality control measures. That is, for every 5 to 10 samples analyzed there should be one quality control sample analyzed for each parameter being tested.

For commercial laboratories analyzing multiple samples, a quality control standard or spike, a sample duplicate or replicate and a blank is expected to be run with each batch of samples analyzed.

XIII. Quality Control Procedures: (continued)

The minimum frequency for quality control analyses in laboratories performing one sample at a time would be one-in every 10 samples. *Note: Certain analyses are required by the Vermont Department of Environmental Conservation to be run in duplicate 100%. (T.S.S. and E. Coli).

The Vermont Department of Environmental Conservation has the following minimum requirements regarding QC for the common parameters listed in the Table below:

Parameter	Calibration/ Standardization	QC Standards	Duplicates/ Replicates	Spikes	Blanks
Ammonia	As per method	1/10 Tests	1/10 Tests	1/Yr	1/each
BOD	Meter before each use	1/10 Tests IGGA/Each if seeded	1/10 Tests	1/Yr	1/each
Chlorine Residual Meter	Check standard curve daily standard for each use	1/month	1/10 Tests	1/Yr	1/each
Titrimetric	FAS stand 1/month	1/month	1/10 Tests	1/Yr	1/each
COD	as per method	1/10 Tests	1/10 Tests	1/Yr	1/each
Cyanide	as per method	1/each	1/each	1/each	1/each
E. Coli	Additional QC required for E. Coli includes equipment sterility checks (indicator tape, "Kilit" ampules) each tests and pH check of dilution water (7>1 ± .2) each tests	2/Yr /POS control/each test	1/each	N/A	1/each
Metals	as per method	1/each	1/each	1/each	1/each
Nitrate Nitrogen	as per method	1/10 Tests	1/10 Tests	1/Yr	1/each
Oil & Grease	as per method	1/each	1/each	1/Yr	1/each
pH	Minimum 2 point calibration each use	*(3rd buffer)* 1/each	1/10 Tests	N/A	N/A
Phosphorus	5 Standards/each	1/10 Tests	1/10 Tests	1/Yr	1/each
Settleable Solids	N/A	N/A	1/10 Tests	N/A	N/A
Total Suspended Solids	constant weights before and after filtering sample	1/10 Tests	1/each	N/A	1/each

XIII. Quality Control Procedures: (continued)

XIII. 1B. Spikes

Spikes are prepared by adding a predetermined quantity of a known standard to a sample. By analyzing an unspiked sample and a spiked sample it is possible to determine if there is a substance in the sample that interferes with test results.

From the results of analysis of a spike and unspiked sample, percent recovery can be calculated using the equation:

$$\% \ Recovery \ ' 100\% \ x \ \frac{S \& U}{Csa}$$

Where	S	=	Measured concentration in spiked aliquot
	U	=	Measured concentration in unspiked aliquot
	Csa	=	Actual concentration of spike added

If the Percent Recovery is outside the range of 80% to 100% the contents of the sample may be interfering with the method of measurement for that analysis.

In this event the cause of the interference must be determined and corrective actions must be initiated (i.e. change methods, etc.)

* One spike or Quality Control Standard should be run with one of every 10 samples run.

* For laboratories performing sample analysis in “batches” one spike or quality control standard should be run with each “batch.”

XIII. Quality Control Procedures: (continued)

XIII. 2B. Quality Control Standards

Quality control standards are substances of known concentration. They are used to verify the accuracy of your analysis.

Quality control standards:

1) Must be prepared from a source different than what was used to calibrate the instrument or prepare the standard curve.

2) The quality control standard must be specific for the parameter being analyzed.

3) The quality control standard must approximate the concentration of the sample and must have a value between that of the highest and lowest calibration standards used.

For Example: If a sample is expected to have a pH of approximately 6, calibration standards of pH 4 and 7 might be used along with a quality control standard with a pH value of 6.

4) Remember: Quality control standards are not used to adjust the instrument as are calibration standards. The resulted quality control standards are simply recorded an compared to the actual "known" value.

XIII. Quality Control Procedures: (continued)

XIII. 2B. Quality Control Standards (continued)

5) Unless control charts are used to determine the acceptable quality control standard range. Results of the quality control standard must fall within a range of ± 20% of the known value. That is the Percent Error must be from 80% to 120% of the actual standard

$$Percent\ Error\ ' \frac{Observed\ Value\ \&\ Known\ Value}{Known\ Value}\ x\ 100$$

6) If results of a quality control standard do not fall within the acceptable range the cause must be determined and recorded on bench sheets or other appropriate record books. A not should be placed in the comments section of the WR-43 report form. Corrective actions must be implemented.

III. Duplicates/Replicates

1) Duplicate samples are samples which are collected in two separate containers at the same time and place.

2) Replicate samples are samples that are collected in a single container and are poured off into a second container for separate analyses of the same parameter(s).

3) An absolute minimum of one duplicate or replicate per 10 samples is required.

4) The result of duplicate/replicate samples should not vary by more than 20% from the original sample.

XIII. 2B. Quality Control Standards (continued)

III. Duplicates/Replicates (continued)

5) Do not average original and duplicate/replicate results. Record the result of the original sample. Then record on bench sheets or other appropriate record book the Percent error for the duplicate/replicate.

Percent error is determined by applying the following equation.

$$Percent\ Error = \frac{Observed\ Value - Known\ Value}{Known\ Value} \times 100$$

If the duplicate/replicate results fall outside the acceptable (± 20%) range of the original sample a note should be made in the comments section of the WR-43 report form and on the bench sheet. Corrective action should be implemented.

IV. Blanks

1) A blank consists of either laboratory water or parameter specific dilution water. Blanks provide a check of the laboratory water quality as well as a check of the analysts analytical technique.

2) Blank must be analyzed with each analysis where applicable.

XIII. 2B. Quality Control Standards (continued)

IV. Blanks (continued)

3) Acceptable blank values are included with each analytical method.

For example:

BOD = # 0.2 mg/L
E. Coli = 0 colonies/100 mls

If blank limit values are exceeded a note must be included in the comment section of the WR-43 report form, and on the bench sheet. In some instances such as in the E. Coli analysis, this invalidates the sample data. (Check the method info) In any blank exceedance corrective action contingencies must be implemented.

The following pages contain an

Example QC Manual

Hopefully this example will help you in preparing your own manual.

Remember: The manual must be specific to your own facility and will remain a work in progress requiring periodic updating and revisions.

Table of Contents

A.	Title Page		Page 17A
B.	Introduction		Page 18
1.	Quality Assurance Project Plan Elements		Page 19
2.	Laboratory Staff Organization and Responsibilities		Page 20
	2.1.	Town Manager	Page 21
	2.2	Chief Operator	Page 21
	2.3	Lab Supervisor	Page 21
	2.4	Operators	Page 22
.	2.5	Skills and Training	Page 22
3.0	Quality Assurance Objectives and Activities		Page 23
4.0	Sample Collection Procedures		Page 23
	4.1	General Guidelines	Page 23
	4.2	Sample Type and Holding Times	Page 24
	4.3	Sample Preservation	Page 25
5.0	Sample Handling and Documentation Procedures		Pages 27 & 28
6.0	Laboratory Water Quality		Page 28
	6.1	Deionized Water	Pages 28 & 29
7.0	Standard Operating Procedure for Each Analytical Method		Pages 30
	7.1	pH	Pages 30 to 32
	7.2	Total Residual Chlorine	Pages 32 to 35
	7.3	Settleable Solids	Pages 35 to 36
	7.4	Total Suspended Solids	Pages 36 to 40
8.0	Reagent/Standard Quality, Preparation and Traceability		Pages 40 to 41
9.0	Calibration Procedures and Frequencies		Page 41
	9.1	Instrument Calibration Procedures	Pages 41 to 43
10.0	Data Handling-Reduction, Validation and Reporting		Page 43
	10.1	Data Reduction	Pages 43 to 44
	10.2	Data Validation	Page 44
10.3	Reporting		Pages 45 to 46
11.0	Preventive Maintenance, Procedures and Schedules		Page 47
12.0	Corrective Action Contingencies		Pages 48 to 49
13.0	Quality Control Procedures (General)		Pages 50 to 55

INTRODUCTION

This Quality Control/Assurance Manual is written specifically for the WWW Wastewater Facility in an attempt to assure the continued high quality and accuracy of analytical results. This will be accomplished by monitoring the accuracy and precision of these results, by providing clear, concise Standard Operating Procedures defining sampling and analytical procedures specific to the WWW facility and by clearly defining the responsibilities of all personnel regarding required performance and documentation.

The WWW facility performs analyses required by the NPDES permit for discharge to the WWW River, in-house progress control analyses, and occasionally pH and chlorine analyses for the Water Supply Department.

Analytical results generated for NPDES permit are submitted to the State of Vermont on a monthly basis. Results of process control analyses are recorded on bench sheets and maintained in-house files for a period of three years.

I. Quality Assurance Project Plan Elements

The fourteen Quality Assurance Project Plan Elements addressed in this manual are:

Title Page

Introduction

Staff Organization and Responsibilities

Quality Assurance Objectives and Activities

Sample Collection Procedures

Sample Handling and Documentation Procedures

Laboratory Water Quality

Standard Operating Procedure for Each Analytical Method

Reagent/Standard Quality Preparation and Traceability

Calibration Procedures and Frequencies

Data Handling - Reduction, Validation and Reporting

Preventive Maintenance, Procedures and Schedules

Corrective Action Contingencies

Quality Control Procedures (General)

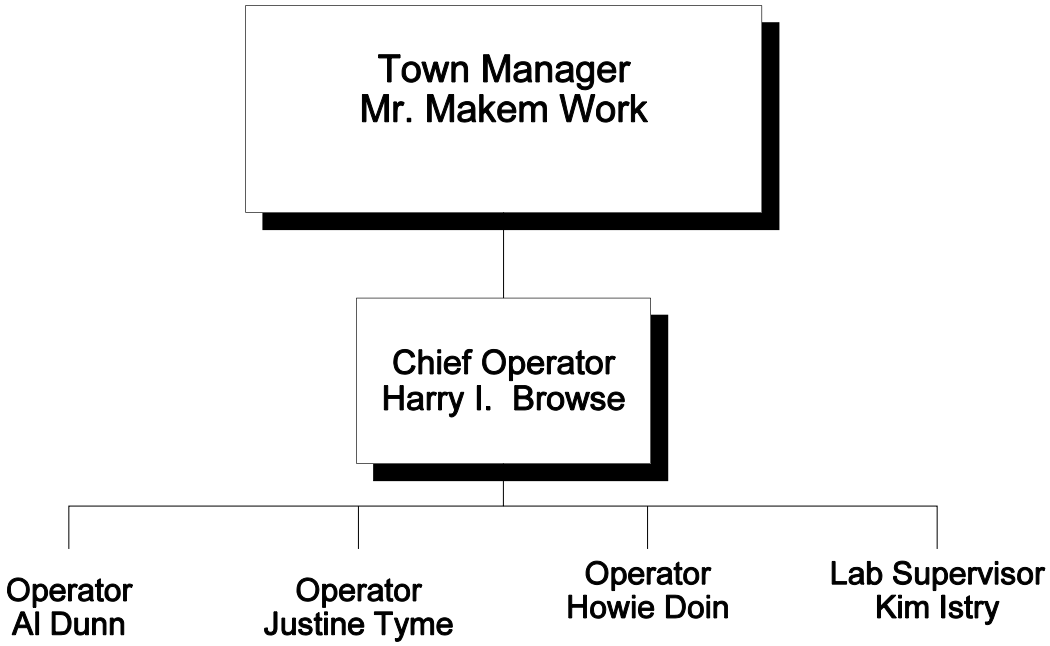
2.0 Laboratory Staff Organization and Responsibilities

The Fuzzyville Wastewater Treatment facility has 5 permanent full-time employees. At some time, all employees are responsible for collection of samples either on a daily basis or on a rotating weekend schedule.

One employee is dedicated to laboratory work only, while all 5 might perform daily analyses including pH, Cl_2 and settleable solids.

The organizational structure is summarized in Table I below.

Table I



2.1 Town Manager

The town manager is responsible for signing the WR-43 report form.

Before signing he/she questions the chief operator or to the report's accuracy and any special comments.

Reviews all data.

Compares WR-43 results to bench sheet results.

Provides final data check.

Sends report to the proper state authority.

Makes final decision on equipment purchases after conferring with chief operator.

Reviews and is familiar with the laboratory QC manual.

2.2 Chief Operator

The chief operator is responsible for signing the WR-43 report form as the "preparer."

Transfer all results from bench sheets to the WR-43 report form.

Compares final WR-43 results to bench sheets to guard against transcription errors etc.

Reviews an is familiar with the laboratory QC manual.

Schedule special sampling and analytical projects.

Reviews bench sheet data to ensure proper WC was practiced.

Is responsible for purchasing laboratory equipment.

Occasionally collect and analyzes effluent samples for pH.

On occasion when pH is analyzed he/she properly calibrates the pH meter.

2.3 Lab Supervisor

Is responsible for overall technical quality of the work performed in the laboratory.

Ensures the use of acceptable Standard analytical methods.

Provides training to all persons responsible for sampling.

Is responsible for preparation and revisions of laboratory QC manual.

Informs chief operator of any equipment needs.

Performs all instrument calibrations and reagent preparations.

Maintains proper bench sheets and equipment maintenance logs.

Responsible for maintaining current SOPs.

Collects and composites effluent samples.

2.4 Operators

Are responsible for sampling of specific parameters.

Are properly training and responsible for analysis of pH, Total Residual Chlorine and Settleable solids when necessary.

Maintain proper bench sheets and calibration logs.

2.5 Skills and Training

EDUCATION

EXPERIENCE

Time & Type

RESPONSIBILITIES

REQUIREMENTS SPECIFIC TO A POSITION

Example:

NAME	POSITION	EDUCATION	EXPERIENCE	SKILL	RESPONSIBILITIES	SPECIAL REQUIREMENTS
Kim Istry	Lab Supervisor	B.S. Chemistry	15 yrs. as lab analyst	Phosphorus determination using auto analyzer	As described in organizational chart	None

EXAMPLE

3.0 Quality Assurance Objectives

a. To ensure data produced by the laboratory is accurate and defensible.

b. To ensure samples collected are representative of preferred universe.

c. To ensure that all laboratory procedures are E.P.A. approved.

d. To ensure that all equipment is properly calibrated and meets E.P.A. specifications.

e. To ensure that proper corrective actions are initiated when necessary.

f. To ensure that each sample is tracked from collection time until the report is finalized - with records maintained for the required intervals.

4.0 Sample Collection Procedures

4.1 General Guidelines

a. Samples are collected in a well mixed area at the center of the channel avoiding eddies, backwaters and area where settling might take place.

b. Influent samples are collected after the comminuter but above the RAS line. See Diagram.

c. Effluent samples are collected after all treatment processes just before discharge to the stream. See Diagram for specific parameters.

4.1 General Guidelines (continued)

d. Grab samples

Grab samples are collected via a Nalgene container attached to an 8 foot extendable aluminum pole. All grab samples are collected and immediately returned to the lab for analysis.

***Note* E. Coli -** *collected directly into sterilized 250 ml. Plastic bottle containing 4 drops 10% Sodium Thiosulfate solution.*

e. Composite samples

All composite samples consist of 24 disrete samples collected hourly via an Isco automatic sampler. Each disrete sample (approximately 500 mls) is distributed into properly cleaned, 1 liter Isco sample bottles. Composite samples are cooled by ice packs which are placed in the sampler wells. Samples are composited at the lab based on readings from flow charts.

SAMPLING PROCEDURES

4.2 Type of Sample and Holding Time

Parameter	Type of Sample	Holding Time	Sample Container	Location
pH	Grab	15 Minutes	Plastic Bottle	Refer to Diagram
Temperature	Grab	At Site	Plastic Bottle	Refer to Diagram
Dissolved Oxygen	Grab	15 Minutes	B.O.D. Bottle	Refer to Diagram
B.O.D.	Composite Flow Proportional	6 Hours	Composite Sampler Plastic Bottles	Refer to Diagram
Total Coliform Fecal Coliform E. Coli	Grab	1 Hour	Sterile Sample Plastic Bottle w/Sodium Thiosulfate	Refer to Diagram
Chlorine Residual	Grab	15 Minutes	Opaque B.O.D. Glass Bottle	Refer to Diagram
Total Suspended Solids	Composite Flow Proportional	6 Hours	Composite Sampler Plastic Bottles	Refer to Diagram
Specific Conductance	Grab	15 Minutes	Glass	Refer to Diagram
Metals	Grab/Comp	6 Months	Amber Glass	Refer to Diagram
TKN	Grab	1 Hour	Plastic Bottle	Refer to Diagram
Settleable Solids	Grab	30 Minutes	Plastic Bottle	Refer to Diagram

4.3 Sample Preservation

If samples are taken and not run within the time frame as in Chart 9.1 then the following chart applies.

PRESERVATION CONDITIONS

Parameter	Container	Volume	Preservation	Holding Time	Representative Sampling Time
BOD, TSS	P	1L	4° C	24 Hours	8 AM - 8 AM
TKN	P	.5L	H_2SO4 pH < 2.0 4°C	28 Days	8 AM - 8 AM
Oils & Grease	G	1L	HCl pH < 2.0	24 Hours	Between 8 AM and 12 PM
Metals	GA	.2L	HN03 pH < 2.0	6 Months	8 AM - 8 AM
Phenols	G	.5L	H3PO4 pH < 2.0 + 1t CuSO4 4°C	24 Hours	8 AM - 8 AM
Sulfides	P	.5L	2 ml Zinc Acetate 4°C	24 Hours	8 AM - 8 AM
Cyanides (T)	P	1L	NaOH pH > 12.0 4 °C	24 Hours	2 PM
VOC	V	40 ml	4°C	24 Hours	2 PM

G = Glass bottle with Teflon lined lid

GA = Amber bottle with Teflon lined lid

P = Plastic Bottle

V = Approved glass vials with Teflon and pure rubber seals

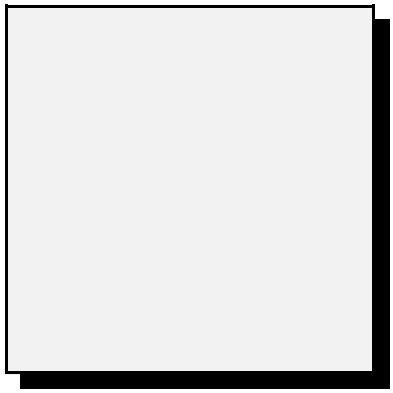
Note: All samples are refrigerated at 4°C after preservation.

4.4 Sample Collection Location

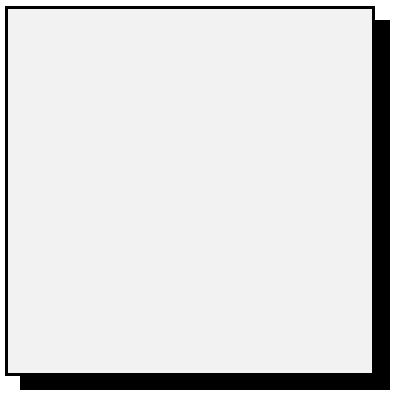
BAD EXAMPLE : Effluent sample is collected at end of chlorine contact tank.

BETTER : The effluent grab samples for pH and Total Residual Chlorine are collected at the outfall end of the chlorine contact tank at a point approximately 1 foot upstream of the v-notch weir.

BEST : The effluent grab samples for pH and Total Residual Chlorine are collected at the outfall end of the chlorine contact tank at a point approximately 1 foot upstream of the v-notch weir, in the center of the channel at a depth of approximately 1 foot. The open container attached to a 6 foot aluminum pole is lowered into the waste stream with the open end facing down stream as shown in pictures #1 and #2.



Picture #1



Picture #2

Be specific and include descriptions for each different type of sample (re: grab, composite)

5. Sample Handling Documentation Procedures

5.1 All grab samples collected for analysis of pH, Total Residual Chlorine and Settleable Solids are immediately taken to the lab. The pH and Chlorine analyses are begun immediately. The settleable solids sample is poured immediately into the Imhoff cone.

5.2 The grab sample collected for analysis of E. Coli is immediately placed into a cooler with four blue ice packs and sealed. It is immediately transported by WWW to WWW laboratory. The approximate travel time is 35 minutes.

Each bottle is properly labeled and accompanied with a chain of custody form. One copy of the COC form is maintained at the facility.

5.3 Composite samples

Immediately after the last 24 disrete sample is collected the entire sampler is brought into the laboratory where the hourly sample volumes are calculated measured and poured into a four liter jug. Aliquots are poured from the container for specific parameters (BOD, TSS etc.) After thorough shaking. Sample containers are then placed into the refrigerator at 4°C until the analysis is performed.

5. **Sample Handling Documentation Procedures** (continued)

5.4 Sample Identification/Labeling

a) All sample containers are labeled with the following information.

1) Type of sample (influent, effluent, grab, composite)

2) Parameter to be analyzed

3) Time and date collected

4) Initials of person who collected it

5) Preservation information

6) Any special instructions or remarks

b) All data from the label is transferred to bench sheets.

c) A chain of Custody form is completed. One copy accompanies the sample to the lab. One copy is retained at the wastewater facility.

Include a copy of the form in the manual

d) The sample is delivered directly to the laboratory by *"name"*, assistant operator

5. Sample Handling Documentation Procedures (continued)

5.4 Sample Identification/Labeling (continued)

e) When the sample is handed over to the commercial laboratory the recipient signs the chain of custody form indicating the time the sample was received.

f) A copy of the chain of custody form is returned to the wastewater facility along with analytical results.

6.0 Laboratory Water Quality

This example was borrowed from a QC manual (prepared by personnel of the Nashua NH Wastewater Treatment Facility *(copied here with their kind permission)*.

6.1 Deionized Water

R/O Deionized water is used in the laboratory for reagent preparation, glassware rinsing, and BOD dilution water.

System includes: Millipore R/O system followed by a Milli-Q deionization system and a 0.02 micron final filter.

TYPE: I : R/O, Deionization and 0.02 um. filter.

TYPE: II: R/O only

6.1 Deionized Water (continued)

Quality Control Tests:

	Parameter	Requirements	Frequency
(Required)	Conductivity	> 0.5 megohms resistance or < 2 microhms/cm at 25°C	Once Per Month
(Suggested)	Total Chlorine Residual	Non-detectable	Once Per Month
(Suggested)	Biosuitability of Laboratory Pure Water	Ratio of 0.8 - 3.0	Semi-annually (April & Oct.)
(Suggested)	Metals	Lead, Nickel, Zinc, Copper, Cadmium, Chromium, Iron, Silver	Semi-Annually (April & Oct.)
(Suggested)	Total Plate Count	< 200 colonies/100 ml.	Once Per Month

* All QC data generated is recorded in the bound QC Manual.

Other Quality Control Measures

R/O system is back flushed daily for one half of an hour. Water for BOD dilution water and reagent dilution is made fresh after morning flush cycle.
Tubing and associated hardware (if in contact with the water) are replaced as needed.

6.2 Distilled Water

Occasionally bottled distilled water is purchased (Poland Springs) for preparation of reagents, BOD dilution water and glassware rinsing.

6.1 Deionized Water (continued)

Other Quality Control Tests: (continued)

The quality specifications for this bottled water are included on the product label and meets all requirements for analytical use.

7. Standard Operating Procedures for Each Analytical Method

7.1 pH

7.1 A. Method Reference

Electrometric Method #4500 - HB. 18th Edition Standard Methods pages for the Examination of Water and Wastewater 4 - 65 ... 4 - 69.

7.1 B. Apparatus

pH meter (make and model)
pH temperature probe (type)
Buffer solutions Fisher, NIST certified, 4.0, 7.0, 10.0
Glass beakers (50 ml)
Magnetic stirrer and stir bars
Safety Glasses, gloves
Squeeze bottle for RO/DI water

7.1 C. Standardization

- The meter is standardized before each use with fresh pH 4.0 and 10.0 *buffer* solutions.

7.1 C. Standardization (continued)

- The pH of a fresh pH 7.0 buffer is checked and the result is recorded in the QC log.

- If the result of the "checked" buffer varies by more than ± .1 standard unit. The meter is restandardized and the problem is corrected.

- The "Fill hole" and electrode cap are removed during use and replaced after each use.

7.1 D. Interferences

- It is important, even with temperature compensation capabilities to approximate as closely as possible the sample temperature when standardizing the meter. To accomplish this , buffers are stored in the refrigerator during winter months and at room temperature during summer months.

- Sodium error is not a problem at this facility.

- Oil material, especially from influent testing can cause development of a film on the electrode causing poor response. This can be avoided by periodically washing the probe with a mild detergent followed through rinses with RO/DI water.

- pH Electrodes are replaced if proper standardization cannot be accomplished.

7. Standard Operating Procedures for Each Analytical Method (continued)

7.1 E. Sample Preparation and Preservation

A minimum 25 ml sample is collected in a glass container. The sample is taken immediately to the lab for analysis.

7.1 F. Procedure

Place pH and temperature probes into the sample. Allow meter to equilibrate. Then record the reading in pH units at temp °C.

7.1 G. Calculation

The pH meter reads directly in a pH standard units pH is reported to the nearest 0.1 unit at a given temperature.

7.1 H. Quality Control

1. All required calibrations and other preventative maintenance on instrumentation and equipment is performed regularly and recorded on bench sheets and calibration logs.

2. Buffers are NIST Traceable, are changed daily and recorded.

3. 10% Duplication and Replication.

7. Standard Operating Procedures for Each Analytical Method (continued)

7.1 H. Quality Control (continued)

4. The pH meter will be calibrated before each use, and separate standard will be processed as a control buffer to validate the calibration, pH 10 buffer will be used as a control.

5. Grab samples will be delivered immediately to the lab for analysis.

6. Glassware will be thoroughly rinsed with purified water.

7. Temperature probe will be calibrated against a NIST traceable thermometer.

8. Calibration sheet will include: date and time of calibration, buffers used and order of use, exact meter results, analyst performing calibration, buffer and sample temperature.

9. Meter range 0-14, accuracy 0.1 pH, repeatability 0.1 pH, temperature compensation and capable of 2 point calibration.

7.2. Total Residual Chlorine

7.2 A. Method Reference

Hach DR 700 method which is based on the DPD colorimetric method #4500-CL G 18th Edition Standard Methods pages 4-45 and 4-46.

7.2. **Total Residual Chlorine** (continued)

7.2 B. Apparatus

Spectro Photometer Model DR 700
DPD Total Residual Chlorine powder pillow/packets
Vials 10 ml - marked - dedicated currettes
Kimwipe Tissues
Safety glasses, gloves
Scissors or clippers

7.2 C. Standardization

The meter has an internal calibration which is automatically enabled for each use.

In addition a Hach brand Voluette ampule certified standard is used daily. Results are recorded and standard curve is plotted.

A blank consisting of the raw sample is used to zero the instrument each use.

7.2 D. Interference

Color and turbidity interferences are reduced by the use of an untreated sample as a blank to zero the device.

Organic contaminants may interfere but can usually be spotted by the strange coloration - yellowish or greenish.

7.2 D. Interference (continued)

Oxidized manganese because of its orange color can create a problem but is at least partially compensated for by use of a blank.

7.2 E. Sample Preparation and Preservation

Because of the unstable characteristics of chlorine in an aqueous solution it is important to take great care in the sample collection not to alter the sample chlorine concentration.

The sample is collected into an airtight BOD bottle which has been covered with black electrical tape. The bottle is filled well into the neck so as to overflow when the ground glass stopper is inserted. Make sure there are no bubbles in the bottle. It is then taken to the dab for immediate analysis (within 5 minutes from collection to analysis).

7.2 F. Procedure

Rinse the sample cells and caps thoroughly with RO/DI.

Pour sample into 2 sample cells to the 10 ml mark.

Empty the contents of one Total Cl_2 powder pillow or packet into one of the sample cells. Cap and invert 10 - 15 minutes to mix.

Wait 3 minutes.

7.2 F. Procedure (continued)

Using the up and down arrows set the device to mode 5207 (515 nanometers).

Wipe both sample cells carefully with a Kimwipe being careful to remove any fingerprints or other marks.

Place the cell containing untreated sample (Blank) into the cell compartment. Close the light shield and press the zero button. The meter should read 0.00 mg/L.

Place the cell containing treated sample into the cell compartment and push the read button.

Record the result in mg/L.

7.2 G. Calculations

The DR700 reads concentration of Total Residual Chlorine in mg/L. Results are recorded directly to bench sheets.

Standard curves are plotted in mg/L.

7.2 H. Quality Control

1. All reagents are NIST traceable and preparation and expiration dates are recorded.

7.2 H. Quality Control (continued)

2. The Hach DR700 colorimeter is maintained by QC Services with regularly scheduled service every 6 months.

3. Glassware is thoroughly washed with a 2% solution of Micro brand detergent, and rinsed with RO deionized water. Separate cells for duplicate total chlorine determinations.

4. Hach Volette Ampule Certified Standards are used daily, and are recorded as a standard curve for a control chart.

5. Duplicate samples are analyzed once per week.

6. Grab samples are recorded at the exact time of sampling and are analyzed immediately after entering the laboratory. The time of analysis and date are recorded.

NO HOLD TIME

Calculation for Voluette Ampule Standards:

$$\frac{ml\ of\ standard\ addition}{ml\ of\ standard\ additional\ \%\ ml\ of\ sample}\ x\ Chlorine\ conc.\ of\ Vol.\ Ampule$$

= Concentration of chlorine added to the sample.

7.3. Settleable Solids

7.3 A. Method Reference

Volumetric Method #2540 F 18th Edition Standard Methods for the Examination of Water and Wastewater pages 2-57.

7.3 B. Apparatus

1 Liter Imhoff Cones

7.3 C. Standardization N/A

7.3 D. Interferences N/A

7.3 E. Sample Preparation and Preservation

Mix the sample thoroughly before pouring off.

7.3 F. Procedure

Place one liter of well mixed sample into a clean Imhoff cone.

Allow the sample to settle for 45 minutes.

Rotate the cone to dislodge solids on the side of the cone.

Allow to settle for an additional 15 minutes.

7.3 F. Procedure (continued)

After a total of elapsed time of 60 minutes from the time the sample was poured. The settled solids are read in ml/liter and recorded.

7.3 G. Calculations

Results are recorded as ml/L.

7.3 H. Quality Control

Duplicate samples are collected and analyzed weekly.

7.4 Total Suspended Solids

7.4 A. Method Reference

Total Suspended Solids Dried at 103 - 105°C Method #2540 D.

18th Edition Standard Methods for the Examination of Waste and Wastewater pages 2-56.

7.4 B. Apparatus

Drying Oven 104° C (± 1°C)

Filter Paper, glass fiber 934AH

Buchner Funnel

7.4 B. Apparatus (continued)

Rubber stopper (to fit Buchner funnel to 1 liter side arm flask)

(2) 1 foot sections of rubber hose (one to connect side arm to filtration flask to safety trap) One to connect trap to vacuum pump.

(2) 1 liter side arm flasks - 1 filtration 1 safety vacuum pump.

Graduated Cylinders

Desiccator - fresh desiccant

Forceps

Safety glasses and gloves

Aluminum weighing tray

(4) Place analytical balance squeeze bottle for RO/DI water.

7.4. C. Standardization (or more accurately pre-test preparation)

The balance must be checked to be sure it is level and then properly zeroed after brushing any debris off the pan.

7.4. C. Standardization (or more accurately pre-test preparation) (continued)

Filters must be rinsed with RO/DI water dried at 104°C for approximately 15 minutes, weighed and then redried, redesiccated and reweighed to establish constant weight (± 0.5 mg) before the analysis is performed.

- Make sure the drying oven is maintained at a constant temperature of 104°C ± 1°.

7.4. D. Interferences

Water with every high mineral content might need to be dried longer, desiccated and weighed quickly as moisture will be quickly absorbed from the atmosphere. This affect can be reduced by placing desiccant in a container inside the balance chamber.

Don't include large floating particles in the sample unless they are truly representative of the actual sample conditions.

7.4 E. Sample Preparation and Preservation

Collect a sample volume of at least 2 liters.

Keep samples refrigerated at 4°C up until the time of analysis to reduce the microbiological decomposition of solids.

7.4 E. Sample Preparation and Preservation (continued)

Try to perform the analysis within 24 hours (7 days absolute maximum)

Bring the sample to room temperature before beginning analysis.

7.4 F. Procedure

1. Prepare the funnel and vacuum apparatus. Make sure the vacuum is not excessive so as to rip the filter.

2. Put the pre-weighed filters into the funnel wrinkled side

3. Seat the filter by rinsing the funnel and filter with about 25 mls of RO/DI water. Turn on the vacuum pump until DI water is drawn through the filter.

4. Shake sample thoroughly, then pour off 1 liter of effluent (100 ml influent) into the graduated cylinder.

5. Pour the sample slowly into the center of the filter with the vacuum on.

    - Rinse the graduated cylinder with at least 3 successive 20 ml DI water rinses turn the graduated cylinder while pouring rinsewater into funnel to insure that all solids are rinsed out.

7.4 F. Procedure (continued)

- Wash down the sides of the funnel into the filter.

- Remove the filter from the funnel with the forceps.

- Place the filter into an aluminum weighing pan and place onto the center rack of the drying oven at 104°C for 2 - 3 hours (preferably overnight).

- Cool to room temperature by putting the filter into the desiccator for 15 to 30 minutes.

- Weigh (if the aluminum pan was included in the initial weighing it must certainly be included in all weighings.)

- Redry at 104°C for at least 1 hour.

  Redesiccate for 15 to 30 minutes.

- Reweigh

- Repeat drying, desiccating and weighing if necessary until constant weight is achieved (<.5 mg difference)

7.4 G. Calculations

$$\text{TSS in mg/L} = \frac{A \ \& \ B \ x \ 100{,}000}{C}$$

7.4 G. Calculations (continued)

Where A = weight of filter and residual (in grams)

B = weight of filter (in grams)

C = volume of sample filtered (in milliliters)

7.4 H. Quality Control

1. The oven temperatures are closely monitored. Temperatures are recorded every four hours when in use.

2. The analytical balance is checked for level, auto calibrated before each use and professionally calibrated every 6 months.

3. The temperature of the sample storage refrigerator is checked and recorded every 4 hours when in use.

4. A replicate sample is analyzed each time the analysis is performed. If results are not within a specified range (determined by control chart) corrective actions are initiated.

5. One duplicate sample is analyzed for every ten TSS analyses performed. Results are recorded in QC log and are plotted on control charts.

7.4 H. Quality Control (continued)

6. A RO/DI water blank is run each time the analysis is performed. Results are plotted on a blank control chart.

7. Sufficient sample, up to one liter, is filtered to produce at least 2.5 mg residual.

8. Results are recorded in QC log and bench sheets.

7.5 5 Day BOD

7.5 A. Method Reference: 5 Day BOD Method 521 OB 18th Edition Standard Methods for Examination of Water and Wastewater pages 5-2 through 5-6.

7.5 B. Apparatus

Dissolved Oxygen Bottles
Overcaps
One Liter Graduated Cylinders
Assorted Sizes of Graduated Cylinders
Beakers, Assorted Sizes
Pipettes
Pipette Bulb
Carboy
Siphon
Propeller Mixer
DO Meter
Thermometer

7.5 B. Apparatus (continued)

Air Pump, Tubing, Filter
Stand
pH Meter
Incubator
Refrigerator
DO Bottles with Auto Pipettes
500 ml Erlenmeyer Flasks
25 ml Burette and Burette Stand
Dropping Bottles

7.5 C. Reagents:

Reagent	Recipe	Hold Time
Phosphate Buffer (Dilution water component.)	- 8.5 KH_2PO_4 - 21.75g K_2HPO_4 - 33.4g $Na_2HPO_4 \cdot 7H_2O$ - 1.7g NH_4Cl - Dilute to 1R DI water. - Autoclave 45 minutes.	- Indefinite @ 4° C - Throw out if biological growth appears.
Magnesium Sulfate	- 22.5g Mg $SO_4 \cdot 7H_2O$ in 1R DI water - Autoclave 45 minutes.	- Indefinite @ 4° C - Throw out if biological growth appears.
Calcium Chloride	- 27.5g $CaCl_2$ in 1R DI water. - Autoclave 45 minutes.	- Indefinite @ 4° C - Throwout if biological growth appears.
Ferric Chloride (Dilution water component)	- 0.25g $FeCl_3 \cdot 6H_2O$ in 1R DI water. - Autoclave 45 minutes.	- Indefinite @ 4° C - Throw out if biological growth appears.
1N Sulfuric Acid (To adjust pH sample)	- 28 ml conc. H_2SO_4 to 1R DI water.	
1N Sodium Hydroxide (To adjust pH sample)	- 40g NaOH to 1R DI water.	
GGA ampules - 300 mg/l glucose - 300 mg/l glutanic acid	Order from: Hach Company PO Box 907 Ames, Iowa	
Polyseed	Order from: Polybac Corp. 3894 Courtney Street Bethlehem, PA	1 year at 20° C
Sodium Sulfite (Dechlorination reagent)	- Prepare small vials each containing 0.79g of Na_2SO_3 - Dissolve 1 vial in 500 ml DI water prior to use.	1 - 2 hours

7.5 C. Reagents (continued)

Reagent	Recipe	Hold Time
Phosphate Buffer (For dechlorination)	- 24g Na_2HPO_4 - 46g KH_2PO_4 - 800mg disodium EDTA dihydrate into 100ml DI water. - All of above into 1R DI water. - 20mg H_2Cl_2 preservative. - Autoclave 45 minutes.	- Indefinite at 4° C - Throw out if biological growth appears.
DPD Indicator	- 1g N,N-Diethyl-p-phenylenediamine oxalate - 8ml 1 +3 H_2SO_4 - 200mg disodium EDTA dihydrate - Dissolve all of the above in 1R DI water	- Discard if pink color appears. - Store in dark bottle @ 4° C.
0.25N FAS titrant	- 49g Fe $(NH_4)_2(SO_4)_2 \cdot 6H_2O$ - 10ml H_2SO_4 - Dissolve above in 1R boiled and cooled DI water.	- 3 months @ 4° C - Must be standardized.
1 + 3 sulfuric acid	- one part H_2SO_4 to three parts distilled water.	
0.25N potassium dichromate	- 12.26g, $K_2Cr_2O_7$ to 1R DI water	Indefinite at 4° C
Potassium iodide crystals	- Prepare small vials each containing 1g KI	Indefinite

7.5 D. DO Meter Standardization

1. Turn DO meter **onto "RED LINE,"** allow to warm up for **15 minutes**.

2. Fill 1R graduated Cylinder with **DI water** and **siphon into 3 BOD bottles,** without aerating water.

7.5 D. DO Meter Standardization (continued)

3. To two of the bottles add **2 mls of DO reagent #1** and 2 mls of DO **reagent #2** below surface.

4. **Invert bottles** until uniform consistency. Let stand until floc settles to **50% bottle volume. Invert a second time** and let stand again.

5. Add **2 mls of DO #3, cap and invert** until floc is complete gone.

6. Pour contents into 50 ml wide-mouth flask and **titrate using .0375N $Na_2S_2O_3$ until pale yellow.** Add **1 ml of starch indicator** (1/2 dropper full and swirl. **Titrate slowly** until **blue becomes clear**.

7. **Add as many drops** of black titrant (potassium bi-iodate) as are necessary to bring **blue color back**. If one drop does this, **record the reading on the buret. If it takes more than 1 drop, multiply the number of drops by 0.05 mls and subtract from buret reading**.

   Reading on buret is in milliliters and is equivalent to oxygen in milligrams per liter. Report readings to nearest 0.05 ml.

8. **Average two titrations** and **record results** in record book.

9. **Place DO probe into third bottle** making sure there are no air bubbles trapped. Turn knob to "zero" and **adjust until zeroed**.

7.5 D. DO Meter Standardization (continued)

10. Turn knob to **"calibrate 1-10," turn on stirrer.**

11. Let sit 2 minutes and adjust until meter reads **average of two** Winkler titrations. If the average DO of the Winkler Titrations and the DO from the meter differ by more than .5, rerun Winkler. Run samples within 4 hours of calibration.

E. Preparation of seed - do earlier on day samples arrive.

1. Empty one capsule of **Polyseed BOD seed inoculum into 500 ml of dilution water**.

7.5 E. Interferences

Presence of copper and other metals in the sample can adversely affect results.

See Sample Preparation for Treatment of samples for other interferences.

7.5 F. Sample Preparation and Preservation

24 Hour Composite Samples -

Sample is refrigerated at 4° C from the time the first sample is collected until one hour before analysis is begun.

It is placed in a warm water bath before analysis until the sample temp reaches 20° C. The sample is thoroughly mixed just before being poured

7.5 F. Sample Preparation and Preservation (continued)

24 Hour Composite Samples - (continued)

off. Dechlorination: Samples are dechlorinated using sodium sulfite. Dechlorination is described in the Procedure section (7.5 G).

Seeding - All samples are seeded. The process is described in the Procedure section 7.5 G.

pH: The sample pH is adjusted to between 6.5 to 7.5 if necessary using sulfuric acid or sodium hydroxide (usually not necessary).

7.5 G. Procedure

A. Dilution Water Prep - **24 hours before use.**

1. **Wash 20 R carboy** and **siphon tubing** with micro and rinse very well with DI water.

2. **Fill carboy** with DI water filtered through **0.2 Fm filter.**
-10R for first sample

-3R for each sample thereafter.

ex: 7 samples would require 28R (10 for the first then 3 X 6 = 18 for rest.)

7.5 G. Procedure (continued)

3. Add **1 ml per R** for each:

$MgSO_4$

$CaCl_2$

$FeCl_3$

4. **Aerate** for about **15 minutes.**

5. Store in 20° C incubator for **at least 24 hours** and **no longer than 5 days.**

6. **Just prior to use** add **1 ml phosphate buffer per liter; aerate 15 minutes; let sit for 1 hour**, then use.

7. Be sure temp. Is **20° to 23° C**.

8. Be sure DO is between **7.5 and 8.5 mg/1**.

   a) **If >8.5 mg/l, shake closed container** vigorously, open and let sit.

   b) **If <7.5 mg/l, aerate** some more.

7.5 G. Procedure (continued)

B. Glassware prep. - **Label all** ahead of time.

	Bottles	1000 ml Graduates
Blank	3	1
GGA	3	1
Seed	9 (3/dilution)	3 (1/dilution)
Sample 1	9 (3/dilution)	3 (1/dilution)
Sample 2	9 (3/dilution)	3 (1/dilution)

C. **Dechlorination** of samples.

1. Just prior to use, prepare 0.78g Na_2SO_3 to 500 mls DI water.

2. To a 500 ml wide-mouth flask, add:

   - 100 ml sample

   - 5 mls DPD indicator

   - 5 mls PO_4 buffer

   - 1 g KI crystals (may be pre-weighed in small vials)

3. A faint **pink-red** color after 2 minutes indicates **chlorine is present. Stop here if no color.**

7.5 G. Procedure (continued)

4. Using standardized 0.00282N FAS, titrate to **clear endpoint. Ml FAS used equals mg/l Cl_2**.

5. Dechlorinate with Na_2SO_3 using in ml 5 times the amount of chlorine per liter.

   Example: Cl_2mg/l = FAS used

   2.2 mls FAS used = 2.2 mg/l Cl_2

   2R sample: 2R x 2.2 x 5 = 22 ml Na_2SO_3

   Add 22 mls Na_2SO_3 to 2R sample to dechlorinate, shake sample. _____

6. **After 15 minutes repeat steps 2 and 3**. If no pink color, then sample is

2. **Aerate** and stir for at **least 60 minutes**.

3. When pipetting be sure flakes of bran do not get into pipette.

7.5 G. Procedure (continued)

F. Seeding Chart

Expected Seed BOD mg/l	Seed Dilution (%)*	Seed (ml) to dilutions +
50 (Polyseed range)	2, 5, 10	20
75	2, 5, 10	15
100	1, 2, 5	8
125	1, 2, 5	8
150	1, 2, 5	6
175	1, 2, 5	6
200	0.51, 2,	5
225	0.5, 1, 2	5
250-400	0.5, 1,2	3

* Seed dilutions calculated for an approximate DO depletion of 3 mg/l

\+ calculated for a DO depletion of approximately 1 mg/l

2. Seed Calculation:

$$\frac{0.8\ mg/l}{Expected\ seed\ BOD\ mg/l}\ x\ 1000\ '\ \frac{ml\ seed\ used\ in\ samples\ \%\ GGA}{}$$

7.5 G. Procedure (continued)

G. Dilution Technique.

1. BOD rules:

a) Blank depletion must be <0.2 mg/l.

b) Want a dilution such that **residual** DO is at least **1.0 mg/l**.

c) Want a dilution such that **depletion** is at least **2.0 mg/l**..

2. Calculation for dilution:

$$\frac{2\ mg/l\ x\ 1000\ ml}{Expected\ sample\ BOD} = mls\ sample\ to\ dilute\ 1R$$

Example: Expected BOD is about 15 mg/l, you want 2 mg/l depletion.

$$\frac{2\ mg/l\ x\ 1000\ ml}{15\ mg/l} = 133\ ml\ to\ 1R\ or\ 13.3\%$$

3. General ranges for dilutions:

0.0 - 1.0 %	for strong industrial wastes
1 - 5%	for raw and settled wastewater
5 - 25%	for biologically treated effluent
25 - 50%	for polluted river waters

H. Actual procedure on day samples started.

7.5 G. Procedure (continued)

1. Add 10 ml **GGA ampule** to **1ℝ graduated cylinder** (gives 2% GGA).

2. **Add seed** (usually 20 ml for polyseed) to GGA and sample cylinders.

3. **Prepare dilution** of samples in graduated cylinders (be sure samples at 20° C).

4. **Set up sample sheet** to receive data (see sample data sheet).

5. **Transfer** sample dilutions, GGA, blank and seed dilutions **to BOD bottles** (3 bottles per dilution).

6. Put **plastic caps on 2 bottles** for each dilution and place in **20° incubator** for 5 days ± 3 hours.

7. **Read DO of third bottle** for each group and **record as Initial DO** (see sample data sheet).

8. **Read DO final after 5 days** ± 3 hours and record both values for each dilution.

7.5 G. Procedure (continued)

Calculations:

A. Seed factor: $\frac{BOD\ of\ seed\ x\ ml\ seed\ used}{1000\ ml}$

Example: $\frac{40\ mg/l\ x\ 15\ ml}{1000\ ml}$ ' $0.6\ mg/l$

B. DO depletion:

DO_I & $\overline{DO_F}$ ' $DO\ depletion$

$\underline{DO}_1$ ' $Initial\ DO$

DO_F ' $average\ final\ DO$

Example: 8.20 *mg/l* & 5.4 *mg/l* ' 2.8 *mg/l* (*depletion*)

C. BOD mg/l: $\frac{DO\ depletion\ \&\ Seed\ Factor}{\%\ Dilution}$

Example: $\frac{2.8\ mg/l\ \&\ 0.6\ mg/l}{.5\ (50\%\ dilution)}$ ' $4.4\ mg/l$

7.5 G. Procedure (continued)

Quality Control:

1. Blanks are run as a bottle and dilution water check. Values #0.2 mg/l are acceptable.

2. GGA should run 198 ± 30.5 mg/l.

3. A duplicate should be run in each batch.

5 Day BOD Data Sheet

Sample Locations: Sample Data Sheet

Lab ID Numbers: 96274 99385

Date & Time Sampled: 10-21-92 10:00 a.m. **Date & Time Sample arrived at Lab:** 10-12-92 1:00 pm

Date & Time BOD Setup: 10-21-92 3:00 p.m. **Date & Time Final DO Read:** 10-26-92 1:00 p.m.

Analyst:

Sample	% Dil	ml Seed	DO_I	DO_F	DO_F	Avg. DO_F	DO Depl.	Seed Factor	DO Depl.	BOD mg/l
Blank	---	---	8.80	8.75	8.65	8.70	0.10	---	---	---
GGA	2	20	8.75	4.30	4.25	4.28	4.47	0.46	4.01	200.5
S_1	2	20	8.75	8.20	8.20	8.20	0.55	---	---	<2 Depl.
S_2	5	50	8.75	7.70	7.65	7.68	1.07	---	---	<2 Depl.
S_3	10	100	8.80	6.60	6.40	6.50	2.30	---	---	23
96274 A	5	20	8.75	6.00	6.05	6.07	2.68	0.46	2.22	44.4
B	10	20	8.75	3.65	3.70	3.67	5.08	0.46	4.62	46.2
C	30	80	< 1	< 1	---	---	---	---	---	---
99385 D	5	20	8.75	6.55	6.65	6.60	2.15	0.46	1.69	<2 Depl.
E	10	20	8.75	5.10	4.95	5.03	3.72	0.46	3.26	32.6
F	30	20	8.80	< 1	< 1	---	---	---	---	

Sample	% Dil	ml Seed	DO_I	DO_F	DO_F	Avg. DO_F	DO Depl.	Seed Factor	DO Depl.	BOD mg/l

Notes and Calculations:

Seed Factor: $\frac{23\ mg/l\ x\ 20\ mg/l}{1000\ ml} = 0.46\ mg/l$

5 Day BOD Data Sheet - *Continued*

Sample	% Dil	ml Seed	DO_I	DO_F	DO_F	Avg. DO_F	DO Depl.	Seed Factor	DO Depl.	BOD mg/l

Notes and Calculations:

8.0 Reagent/Standard Quality, Preparation and Traceability

8.1 All standards and reagents are prepared from reagent grade materials, primary standards or they are purchased from reputable vendors. Reagents are stored according to manufacturers instructions and discarded upon expiration. Standards and reagents are prepared using bala nces that are calibrated daily, Class A volumetric glassware and ASTM Type II reagent water.

Once a solution is prepared it is labeled with the solution name or description, storage requirements, concentration or normality, preparation and expiration dates and initials of preparer. Expiration dates for standards and reagents are specified in methods that are adhered to unless degradation prior to this date is observed. Log books are utilized to record the preparation of standards.

Calibration standards (working standards) are dilutions or mixtures of stock standards used to calibrate an instrument. These standards are prepared or restandardized frequently as specified in Laboratory Standard Operating Procedures (SOP's). New standards are checked again old standards to insure there has not been an error in preparation.

Quality control reference samples are analyzed along with most analytes, depending upon availability to validate standards, technique and methodology. Quality control reference samples are prepared from a different source than that used in the preparation of standards for use in the standard curve and are US EPA certified, if possible.

9.0 Calibration Procedures and Frequencies

9.1 Instrument Calibration Procedures

All instruments and equipment used are routinely calibrated by laboratory personnel or by external calibration agencies or equipment manufacturers. Maintenance schedules can be found in the Preventative Maintenance Section of this manual (Section 1.0). Instrument calibration procedures, frequencies, standards and traceability are summarized in Table 9.2 To insure that instruments have performed adequately throughout the analysis, it is laboratory practice to run a standard or quality control reference sample at the end of an extended run.

9.1 Instrument Calibration Procedures (continued)

Table 9.2

Instrument/ Analytes	Calibration Frequency	Procedure	Calibration Standard (Traceability)	Quality Control Standard (Traceability)
pH/Millivolt Meter - pH	Daily	2 point calibration bracketing sample	Certified buffers (NIST traceable)	EPA Reference Sample (US EPA)
Conductance meter - conductivity	Daily	.01M Potassium Chloride	Primary Grade Reagents	Conductivity Standards (NIST)
Analytical Balances	Daily	Calibrated according to manufacturer's directions.	Calibration verified using Class -S weights	Weights NBS Traceable
Spectrophotometer - COD	Daily	3 - 5 Point Calibration	Primary Grade Reagents	EPA Reference Sample (US EPA)
Turbidity Meter - turbidity	Daily	Calibrated According to AMCO instructions	AMCO Sealed Primary Calibration Standards	AMCO Sealed Secondary Standards
Dissolved Oxygen Meter - BOD - DO	4 Hours	Winkler Titration	Primary Grade Reagents	(NIST traceable)
Cloroimeter (Fixed Photometer) - Chlorine	Each use	Internal instrument calibration and Hach Spec T Color Standard	NIST SMR 930 S/M99	EPA Reference Sample (US EPA)
COD Reactor - COD	Daily	5 Point Calibration	Primary Grade Reagents	EPA Reference Sample (US EPA)
Millivolt Meter - TKN	Daily	4 Point Calibration 2 Point Calibration Probe	Primary Grade Reagents	EPA Reference Sample (US EPA)

9.1 Instrument Calibration Procedures (continued)

Table 9.2

Instrument/ Analytes	Calibration Frequency	Procedure	Calibration Standard (Traceability)	Quality Control Standard (Traceability)
Thermometers - incubators - pH - conductivity	Annually/ Semi-Annually (bacteriology)	Accuracy checked over range to be used. Deviations recorded on thermometer.	Thermometer NIST	
Incubators - bacteriology	Twice Daily	Temperature Check	Thermometer NIST	
Autoclave - bacteriology	Weekly	Sterility Check Temperature Check	Spore Strips Maximum Thermometer NIST	
Refrigeration Units - reagent sample storage	Daily	Temperature Check	Thermometer (NBS)	

10.0 Data Handling - Reduction, Validation and Reporting

10.1 Data Reduction

Raw data is recorded directly onto bench sheets by the technician who actually performed the analysis.

If more than one analyst is involved in setting up an analysis or reading results (Ex. BOD initials DC's determined by one person and final DO's by another) both analysts initial the bench sheet. All calculations are included on bench sheets.

Only the chief operator can transfer information from the bench sheets to WR-43 report forms.

10.2 Data Validation

The analyst who generates the data has the prime responsibility for its correctness and completeness. It is the analysts responsibility to verify that the instrument was calibrated and was performing properly.

The chief operator looks over and double checks the bench sheets. He checks all calculations, looks to see that all data makes sense and that the numbers were rounded properly (section 10.5) and that proper significant numbers were recorded (section 10.4).

After transferring the data to the WR-43 report forms he checks for transcription errors.

The assistant operator performs a quick check of bench vs. WR-43 data before the report is given to the town manager for his signature.

The town manager looks at the WR-43 report form and questions the chief operator concerning any unusual or suspicious looking result before signing the report. As a rule the town manager and chief operator meet to discuss the report regardless of whether or not there are irregularities.

10.4 Significant Digits

Parameter	Significant Digits
BOD - No digit after decimal point.	28 mg/L
Chlorine Residual - Two digits after decimal point.	0.51 mg/L
Coliform - No digits after decimal point.	50/100 ml.
TKN, NH_3, NO_3 - One digit after decimal point.	17.6 mg/L
D.O. - Two digits after decimal point.	7.35 mg/L
Settleable Solids - One digit after decimal point.	5.1 ml/L
Metals - One digit after decimal point.	436.3 ppb
pH - Two digits after decimal point.	7.00 pH units
Suspended Solids - No digit after decimal point.	22 mg/L
Temperature - One digit after decimal point.	17.2°C

10.5 Rounding Policy

All digits are used in calculations, then are rounded, using the following guidelines. Numbers following decimals shall be rounded to the next higher or lower number based on this method.

For example: 3.57 is rounded to 3.6

2.41 is rounded to 2.4

7.55 is rounded to 7.6

7.44 is rounded to 7.4

11.0 Preventive Maintenance Procedures and Schedules

11.1 All laboratory equipment is serviced and professionally calibrated by QC Services on an annual basis. A service contract is maintained to include annual equipment calibration.

11.2 Routine and professional calibration/maintenance schedules are summarized in Table 11.2.

11.3 Preventive maintenance responsibilities are assigned to specific laboratory personnel. Only the lab supervisor is allowed to perform other than routine calibration or minor repair.

11.4 A maintenance log is kept in the lab for each instrument. All calibration, repairs and service visits are recorded an entitled by the responsible party.

11.0 Preventative Maintenance Procedures and Schedules Table 11.2 (Continued)

Instrument - Manufacturer - Model	Calibration Frequency	Maintenance Contractor	Preventative Maintenance Schedule
Atomic Absorption, Perkin-Elmer 3030B	Daily	Perkin-Elmer	As needed
Autoclave, Barnstead	4/year	MDT Biologic Co.	4/year
Waterbath, Precision Scientific - 83	1/year	QC Services	1/year
Waterbath, Blue M	1/year	QC Services	1/year
Air Incubator, Boekel	1/year	QC Services	1/year
pH/Millivolt Meter, Orion Model 811	Each use	QC Services	1/year
pH/Millivolt Meter, Orion Model 720A	Each use	QC Services	1/year
Ratio Turbidmeter Hach Model 18900	Daily	QC Services	1/year
Spectrophotometer, Bauch & Spectronic 100	Daily	QC Services	1/year
Dissolved Oxygen Meter, YSI Model 57	Every 4 hours	QC Services	1/year
Fluorometer, Turner Model 111	Yearly	QC Services	1/year
COD Reactor, Hach Model	Yearly	QC Services	1/year
Centrifuge, International Equipment	---	QC Services	---
Conductance Meter, YSI Model 32	Yearly	QC Services	1/year
Chlorine Meter, Hach Model DR100	Each use	QC Services	---
Balance, Mettler AE 200	Daily	QC Services	1/year
Balance, OHAUS B1500D	Daily	QC Services	1/year

12.0 Corrective Action Contingencies

12.1 Corrective actions are required as a result of less than acceptable **P**erformance **E**valuation study results, or poor comparison in split sample analyses (State lab results significantly different than facility results). The steps taken in the corrective action process include:

Identify and define the problem.

Determine who will be responsible for investigating the problem.

Find the cause of the problem.

Determine the actions needed to eliminate the problem.

Implement the corrective actions and

Establish the effectiveness of the corrective action.

Usually the lab supervisor is responsible for initiating the corrective action under these conditions. Documentation of actions taken and their effectiveness is forwarded to the lab supervisor for review and distribution.

12.2 Corrective actions might also be initiated by an analyst during or after sample analysis. These actions may be necessary because of

Unacceptable blank results (BOD blank depletion >.2 mg/L)

Suspicious positive control results (every few colonies on E Coli. positive control sample).

QC data outside the warning or control limits for precision and accuracy.

Duplicate or replicate results are inconsistent.

Under these conditions the analyst generating the data is expected to initiate and document corrective action.

12.3 Corrective Actions Required for Specific Problems are Listed in Table 12.4

Table 12.4

Problem	Corrective Action
Blank contamination is indicated	Determine cause of contamination, eliminate cause and repeat analysis.
Unexpected, unusual results occur more than once every 20 analyses	Investigate possible causes. Try to eliminate interferences. Keep a close watch on future analyses.
One or more data points falls outside the control limit.	Determine cause eliminate it an repeat analysis.
Two out of three successive data points fall outside the established warning limits.	Repeat analysis. If the next data point is less than warning limit continue the analyses. If the next point exceeds warning limits discontinue analyses and correct the problem.
4 out of 5 successive data points exceeds 1 standard deviation or are in decreasing or increasing order.	Analyze another sample. If the next data point is less than 1 standard deviation or changes the order continue analyses. If not discontinue and correct the problem.
Six successive sample results are above/below the central line on the control chart.	Analyze another sample. If the next result is on the other side of the central line continue analyses. If the next point is on the same side of the central line discontinue analyses and correct the problem.

13.0 Quality Control Procedures (General)

This section describes the method used at this laboratory to evaluate the quality of data generated.

13.1 Sampling Quality Control Checks

Sampling QC checks provide information regarding the precision and accuracy of the entire process from sample collection through analyses. Included in this category are:

13.1.1 Equipment Blanks

Equipment blanks are used to determine if contamination has been introduced through contact with sampling equipment or to verify effectiveness of equipment cleaning procedures.

Clean laboratory water is pumped through the Isco sampler. We usually place the sampler probe in a 4 liter jug of RO/DI water, pump for 10 - 15 seconds, purge for 5 seconds. This process is repeated 2 to 3 times before the equipment blank sample is collected. This sample is then taken to the lab and processed along with other samples.

13.1.2 Split Samples

Split samples are replicate samples, two aliquots taken from the same sample container. The samples are then analyzed independently by our own lab and a contract laboratory. If significant differences are noted the cause is determined and corrected.

13.0 Quality Control Procedures (General) (continued)

13.1.3 Duplicate Samples

Duplicate samples are samples collected at the same location at the same time. Collection of duplicate samples serves as a check on sampling and processing technique. Each sample is analyzed individually. Results must be within an acceptable range (10%) or the cause must be determined and corrected.

13.1.4 Replicate Samples

Replicate sample are two aliquots taken from the same sample container that are processed and analyzed separately. The results are used to measure analytical precision from sample preparation through analysis. Certain analyses are run in replicate every time the test is performed. A minimum 10% replication schedule is established for all analyses.

13.2 Procedures Used to Assess Data Quality

13.2.1 Precision

Precision is a measure of the closeness with which multiple analyses of a sample agree with each other. We calculate precision from results of replicates and duplicate analyses of quality control samples.

13.2 Procedures Used to Assess Data Quality (continued)

13.2.1 Precision (continued)

Here at the WWW Wastewater laboratory we use Relative Percent Difference (RPD) as a measure of precision. The formula used to calculate RPD is:

$$RPD = \frac{(C_1 - C_2) \times 100\%}{(C_1 + C_2)/2}$$

Where: RPD = relative percent difference

C_1 = larger of the two observed values

C_2 = smaller of the two observed values

If calculated from three or more replicates, we use relative standard deviation rather than RPD:

RSD = (s/y) X 100%

where: RSD = relative standard deviation
s = standard deviation
y = mean of replicate analyses

Standard deviation is defined as follows:

$$SD = \sqrt{\frac{\sum Xi^2 - \frac{(\sum Xi)^2}{n}}{n - 1}}$$

13.2 Procedures Used to Assess Data Quality (continued)

13.2.1a Control Charts

Control charts are used to demonstrate the precision calculated from replicates and quality control sample duplicates.

The Relative Percent Difference (RPD) values for each sample are plotted on control charts and where upper and lower warning and control limits are depicted.

These control charts are used by the analysts to help make them aware of suspicious or out-of-control variability at the time of analysis. The warning and control limits are recalculated annually. An example of a control chart cal be found at the end of the section.

13.2.1b Control Limits

Control limits are defined as the mean + / - 3 standard deviations. An RPD value that falls outside the control limits is considered out-of-control and requires the analysts to repeat the analysis immediately. If the repeat value is within the control limit analysis may continue. If the repeat value exceeds the control limit analysis must stop and the problem must be corrected.

13.2.1c Warning Limits

Warning limits are narrower than control limits and are defined as the mean + / - 2 standard deviations. An RPD value that falls outside the warning limit is considered suspicious. If two out of three consecutive points exceed a warning limit the analyst must calculate the RPD on another sample. If the warning limit is exceeded analysis must stop and the problem must be corrected.

13.2 Procedures Used to Assess Data Quality (continued

13.2.2 Accuracy

Accuracy is expressed as a percent bias or percent recovery and is determined from the analysis of quality control reference samples or spikes. Method accuracy is calculated on a daily basis and summarized annually in the Laboratory Quality Assurance Plan.

Percent recovery is calculated from spike results using the following equation:

$$\%\ R = 100\% \times \frac{S \& U}{C_{sa}}$$

where: %R = percent recovery

S = measured concentration in spike aliquot

U = measured concentration in unspiked aliquot

C_{sa} = actual concentration of spike added

$$\%\ B\ '\ 100\ x\ \frac{(O \& T)}{T}$$

Where: %B = percent bias

O = measured concentration of reference material

T = actual concentration of reference material