LABORATORY QUALITY ASSURANCE AND QUALITY CONTROL FOR SMALL WASTEWATER LABORATORY

Brett Ward, Utility Operations Consultant
December 2009

THE UNIVERSITY of TENNESSEE
MUNICIPAL TECHNICAL ADVISORY SERVICE

In cooperation with the Tennessee Municipal League

DISCLAIMER

Throughout this manual there are many references to specific companies and products in order to show the lab analyst precisely what materials should be used and where they may be purchased. Products mentioned by name were selected based on the personal experience of the author or of those who reviewed the manuscript. Whenever possible, the named companies are those with which many lab analysts are familiar or already are doing business. In most cases, an effort was made to present the names of two or more companies that supply a particular product. These references should not be construed as an endorsement of any particular product or company by the Municipal Technical Advisory Service or the University of Tennessee.

ACKNOWLEDGMENTS

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Thanks also go to several people from the Tennessee Department of Environment and Conservation (TDEC). Barbara Loudermilk of the Nashville field office helped make this a much better manual through her encouragement and multiple reviews. I also want to thank the late Jim Pilkin from the Chattanooga office, Lanny Bonds of the Knoxville office, Jere Dougan from the Jackson office and Felica Hix from the Fleming Training Center.

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Though this is a technical manual, there is also a need for publishing expertise. Thanks are due to Donna Weems of the National Environmental Training Center for Small Communities for her review and valuable comments on how to improve the quality of this manual.

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SECOND EDITION REVIEWS

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MTAS OFFICES

Knoxville (Headquarters) ..... (865) 974-0411
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MTAS provides one copy of our publications free of charge to each Tennessee municipality, county and department of state and federal government. There is a $25 charge for additional copies of "Laboratory Quality Assurance and Quality Control for Small Wastewater Laboratory."

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LABORATORY QUALITY ASSURANCE AND QUALITY CONTROL FOR SMALL WASTEWATER LABORATORY

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HOW TO USE THIS MANUAL

This manual is intended to be a guide for wastewater laboratory analysts in setting up their own quality assurance/quality control (QA/QC) programs. A laboratory QA/QC program usually is required by regulatory agencies, but there are good reasons to institute such programs voluntarily. A QA/QC program consists of procedures that ensure that test data can be reliably trusted to represent what is actually happening in the treatment plant. It is all the extra steps you take in the lab to produce truthful data and to prove that your data are truthful.

The QA/QC program includes three phases:

- Keeping careful and accurate records;
- Documenting that all the equipment and methods used in the lab and the conditions in the lab are appropriate; and
- Performing quality control (QC) tests to document the presence or absence of three types of testing error bias, precision and accuracy.

This last phase is particularly important since QC testing evaluates the laboratory analyst's abilities, techniques, tools and methods. Many laboratories are already performing individual parts of this program, but may not have organized them as a formal QA/QC program.

Most of the data generated from the wastewater laboratory tests are required by the state. This data can also be very useful to plant operators or managers. Test data is the voice of the treatment plant, telling you what is happening during the treatment process. Analyzing the data is a fascinating process that can reveal useful insights about how a plant is performing and that can be used to predict problems before they occur. Having quality data also can make troubleshooting treatment process easier.

This manual contains three main parts that will help you organize your program. Part I contains a description of a general outline for a QA/QC program. It also shows you how to develop and maintain the central quality assurance/quality control document. Part II of this manual consists of 13 chapters that describe in greater detail the steps in the general outline. You should begin by reading Part One to gain a general understanding of the QA/QC process and how to set up your system.

Quick Tips

1. Start simple.
2. Do one step at a time.
3. Each step leads you closer.
4. Ask for help if you need it.
5. Work step by step until you have a more complete system than you have now. Generally, there is no need to be in a hurry. Complete each step, become comfortable with that work, then move to advance your program with another step.

Part I: OUTLINE
Steps to Improvement

DATA AND RECORDS

Step 1

Post a copy of Part 1-A of the National Pollutant Discharge Elimination System (NPDES) permit requirements in the lab. Keep a full copy of the permit on site. (See Chapter 1.)

Step 2

Maintain a complete and accurate list of the exact locations of all sampling sites. List individuals responsible for collecting samples and performing analysis. List all contract labs used, including which tests they perform and when they are to be performed. (See Part 1-B (1) of your permit and Chapter 2.)

Step 3

Maintain a complete and accurate list of all test methods used. Refer to Table 1, A-B of 40 C.F.R. 136 to determine the specific code for the particular test method being used in your lab. Record this method code on the daily bench sheets or in the Quality Assurance Program. (See Chapter 3.)

Step 4

Refer to Part 1-B (2) of your permit, "Test Procedures." Each test should include the required information as to date and times of sampling; name of individual who collected the sample; the test method; type of preservative, if used; and the chain-of-custody report, if needed. When on-site testing is done, the information can be included easily on the bench sheet. If the testing is done by a contract lab, this information is probably already being provided to them. As tests are performed, also record the date, times, name of the analyst, and the test results. (See Chapter 4.)

Step 5

Have a qualified technician calibrate the plant's flow meters at least once a year, and maintain a log of the results. If an instantaneous check falls outside ± 10% of the flow meter reading, corrective action must be taken. (See Chapter 5.)

LABORATORY CONDITIONS

Step 6

Conditions in the laboratory should be maintained in such a way to ensure that test results will be of high quality. The equipment should be in good working order, calibrated, and checked against standards. Laboratory quality distilled water and fresh, pure reagents must be on hand. Do not overlook the temperature in the laboratory. Laboratory glassware is calibrated at 20° C or 68° F. The lab itself should be kept near this temperature. Most regulators will ask for "room temperature" or 65-75° F. Incubators, ovens and water baths must be checked daily when used. (See Chapter 6.)

QUALITY CONTROL TESTING

Step 7

Blanks are a form of quality control test. Blanks show interference or bias in the test. Ideally, the results should be zero, indicating there is no interference or bias. Most plants already perform blanks in their BOD tests to show the quality of the dilution water. For the TSS test, rinse and weigh a filter pad, then filter distilled water instead of a wastewater sample. The weight of the TSS in the distilled water should be zero. If the weight increases, the filter may not have been dried thoroughly, or there could be solids contaminating the water, the filter apparatus, or the glassware used in the test. If the weight decreases, the filter was not rinsed well enough or perhaps was allowed to absorb moisture from the air between weighings. Most labs probably are already including a blank in the fecal coliform or E.coli test. In the ammonia procedure, test distilled water instead of a sample. The target for blanks is zero. Blanks generally are

performed with each set of samples. A control chart, described later, will aid the analyst in making decisions about values that are greater than zero. More details on blanks are included in Chapter 7.

Step 8

Duplicate testing is another type of quality control test. It consists simply of performing a test a second time, or of splitting a sample and running two tests instead of one. For the biochemical oxygen demand (BOD) test, put up two bottles with the same dilution. For the TSS test, set up two filter pads for the influent or effluent. For an ammonia test, pour out two beakers of sample, run the first one, then the second. Duplicate tests can be performed on any parameter, even pH, DO, or chlorine. The general recommendation is to perform a duplicate test after 10 sets of samples or, perhaps, one per week. These tests show how precise an analyst's procedure is. Two tests performed on the same sample should yield very close results; if they don't, there could be a problem with the procedure or the equipment. The goal is to have no, or almost no, difference between the results of duplicate tests. Record the results in table form. These data can be graphed on a control chart as described in Chapter 13. For more information on duplicate testing see Chapter 8.

Step 9

The use of laboratory standards reveals test accuracy. If the tested value agrees with the true value, the test has been done accurately. Standards can be mixed on site or purchased from chemical suppliers. Perform standard tests along with the duplicate tests, or about every 10th sample. To avoid the possibility of mixing error, consider using purchased standards. For the BOD test, use glucose glutamic acid. To perform a TSS standard, you might use 3M's product called Filter Aid or Whatman's Ashless Powder. Each can be used to make a solids standard. There are several manufacturers of ammonia standard to use with their ammonia test. A chlorine standard can be purchased, or potassium permanganate can be used to mix a standard.

Step 10

Another type of quality assurance test is to test unknown laboratory standards. Many plants already perform the EPA, DMR QA studies each year. These same standards can be purchased and tested throughout the year as internal tests of lab quality. If you are unfamiliar with these standards, they will include the material to test, directions, and, in a separate envelope, the true values and range of acceptable values. Performing this type of unknown standard test will give confidence to the analyst and perhaps show deficiencies in the testing procedure.

Step 11

Laboratory standard operating procedures are becoming more common in small laboratories. Most regulators are asking that they be written, followed and kept up to date. An easy way to produce an SOP is to photocopy parts of *Standard Methods* for the specific method, then cut and past the sections into a notebook along with photos of equipment and supplies. For more information see Chapter 11.

SPIKED SAMPLES

Step 12

Spiking a wastewater sample allows the analyst to evaluate test accuracy while performing the regular test procedure. A known amount of test standard is added to the sample. The results should be equal to the sample value plus the value of the added spike. The target is to have 100 percent recovery of spike and the sample. Chapter 12 describes the use of spiked samples.

CONTROL CHARTS FOR QUALITY CONTROL DATA

Step 13

Quality control tests produce lots of test data. Chapter 13 describes how to evaluate the data using control charts. Walter Shewhart of Bell Laboratories developed a method of describing variation in

a manufacturing process. This method also works in the wastewater laboratory testing process. Shewhart's control charts and constants are used in this description.

CREATING THE MAIN DOCUMENT

QUALITY ASSURANCE

The simplest way to organize your own QA/QC program is with a set of loose-leaf notebooks. Begin with a single notebook that will serve as the main QA/QC document. It should contain 13 chapters. Notice that each chapter corresponds to one step in the general process. Refer to the General Outline and to the individual chapters for more information.

CHAPTER 1: A copy of your full NPDES permit.

CHAPTER 2: A record of exact sample locations.

CHAPTER 3: A list of all the tests you perform and the test methods you use.

CHAPTER 4: A blank copy of your bench sheets that also may show the test method. You might also include a copy of 40 C.F.R. 136, of this manual as a handy reference.

CHAPTER 5: A description of your policy regarding flow meter calibration and a log showing when this task was completed.

CHAPTER 6: A description of lab policy for each item in Chapter 6. Include log sheets and quality test results on reagent water or indicate where these results can be found.

CHAPTERS 7 through 13: QUALITY CONTROL SECTION

These chapters document the quality control section of your program. Devote one chapter to each type of quality control test you perform. Each chapter will contain a description of the laboratory testing policy, a description of the frequency with which the test is performed, sample log sheets, and a description of how and where test results are recorded.

TEST RESULT NOTEBOOKS

In addition to the primary notebook, you will need to create one or more additional loose-leaf notebooks that contain quality control data.

INDIVIDUAL QUALITY CONTROL RECORDS

Each laboratory analyst should maintain records of his or her own test results. This is important because QC testing tests the abilities and techniques of the individual analyst.

LABORATORY STANDARD OPERATING PROCEDURE MANUAL

Finally, your QA/QC program may include a Laboratory Standard Operating Procedure manual. This is a detailed description of how each test is performed at your lab. It must be written on site because of the differences between labs. Recently produced lab SOPs included photos of equipment, references to laboratory equipment literature, and photo copies of the text of *Standard Methods*. Once you have set up the main QA/QC document, use this manual to develop your QA/QC program. It should include the following parts:

- The main document notebook;
- Documents with QC results and control charts for each analyst; and
- The Laboratory Standard Operating Procedure.

Part II

CHAPTER 1

Post a copy of Part 1-A of the National Pollutant Discharge Elimination System (NPDES) permit requirements in the lab (Figures 1a and 1b.). This makes it easy for everyone to view our target. Keep a full copy of the permit on site. Plant operators should know the permit requirements and follow them. Remember that in addition to the numeric limits that are in Part 1-A, permits also contain narrative limits such as "no visible floating scum or color contrast in the receiving stream."

The NPDES permit contains a great deal of useful information for plant operators. In addition to stating discharge limits, the permit has information about monitoring procedures, reporting results, and reporting bypasses, overflows, and washouts. Part II of the permit discusses subjects such as applying for a new permit, operation and maintenance, changes in the permit, and noncompliance. Part III addresses subjects such as operator certification, industrial pretreatment, sludge or biosolids management, and biomonitoring. There also is a rationale sheet that includes the details of the plant and why the limits are set where they are.

«FACILITY_NAME»
NPDES Permit TN00«PermstatNUMBER1»
Page 1 of 32

PART I

A. EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

The (Facility name) STP is authorized to discharge treated municipal wastewater to ********** River at mile *****. Discharge 001 consists of municipal wastewater from a treatment facility with a design capacity of # MGD. Discharge 001 shall be limited and monitored by the permittee as specified below:

Effluent Characteristics	Effluent Limitations						Monitoring Requirements		
	Monthly Average Conc. (mg/l)	Monthly Average Amount (lb/day)	Weekly Average Conc. (mg/l)	Weekly Average Amount (lb/day)	Daily Maximum Conc. (mg/l)	Daily Minimum Percent Removal	Measurement Frequency	Sample Type	Sampling Point
$CBOD_5$ (May 1 - Oct. 31)	# Report	#	#	#	# Report	#	3/week 3/week	composite composite	effluent influent
$CBOD_5$ (Nov. 1 - April 30)	Report				Report		3/week 3/week	composite composite	effluent influent
Ammonia as N (May 1 - Oct. 31)	Report				Report		3/week 3/week	composite composite	effluent influent
Ammonia as N (Nov. 1 - April 30)	Report				Report		3/week 3/week	composite composite	effluent influent
Suspended Solids (May 1 - Oct. 31)	# Report	#	#	#	# Report	#	3/week 3/week	composite composite	effluent influent
Suspended Solids (Nov. 1 - April 30)	Report				Report		3/week 3/week	composite composite	effluent influent

Note: The permittee shall achieve #% removal of $CBOD_5$ and TSS as a monthly average. The permittee shall report all instances of overflow and/or bypasses. See Part 1.D.5a for reporting requirements.

Figure 1a.

«FACILITY_NAME»
NPDES Permit TN00«PermstatNUMBER1»
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Effluent Characteristics	Effluent Limitations			Monitoring Requirements		
	Monthly Average	Daily Minimum	Daily Maximum	Measurement Frequency	Sample Type	Sampling Point
Fecal Coliform	#/100 ml (see the following paragraphs)		#/100 ml	3/week	grab	effluent
Chlorine residual (Total)			# instantaneous	5/week	grab	effluent
Settleable solids			#.0 ml/l	3/week	composite	effluent
Dissolved oxygen		#.0 mg/l instantaneous		5/week	grab	effluent
pH (Standard Units)		#.0	#.0	5/week	grab	effluent
Flow (MGD)	Report Report		Report Report	7/week 7/week	continuous continuous	influent effluent
48 hr LC_{50}			%	1/quarter	composite	effluent
96 hr LC_{50}			%	1/quarter	composite	effluent
IC_{25}			%	1/quarter	composite	effluent

Note: See Part III (D) for biomonitoring test and reporting requirements. See next page for percent removal calculations.

Measurement Frequency and Sample Type may vary.

Figure 1b.

CHAPTER 2: Sample Location

Part 1, section B, of the NPDES permit describes how sampling is to be done. It tells whether grab or composite samples are to be taken and the location of these sample collection points. EPA says sample locations should be physically marked with labels or numbers. Make a list of the exact locations of the sample points in the plant and identify individuals who will be conducting the sampling for each test. In most cases, the laboratory analyst will do the sampling as well as the testing. Also, list any contract labs that are used, which tests they perform, their addresses, phone numbers, and contact names. The following example shows a listing of sample locations, who does the sampling, and the contract laboratories that are used. Some operators use placards to mark the sample locations within the facility as the following photo shows.

Effluent composite sampler and grab sample locations marked on a chlorine contact chamber.

Example: Sample Location List

XYZ SEWER PLANT
SAMPLE LOCATIONS, SAMPLE COLLECTOR, CONTRACT LABORATORIES

Sample Locations

Composite samplers are located at the influent head works and at the outfall of the secondary clarifier.

Raw grab samples are collected at the intake to the raw composite sampler by the influent flow meter.

Effluent grab samples are collected where the effluent pipe discharges into the stream.

Stream above samples are collected at the bend of the creek next to the parking lot.

Stream below samples are collected at the bridge on John Doe's farm.

Biomonitoring samples are collected with the portable composite sampler at the plant effluent pipe.

Raw sludge samples are collected from the final clarifier waste line.

Digested sludge is collected as the sludge truck is loaded.

Sample Collector

All samples are collected by the lab analyst unless noted otherwise.

Contract Labs

Analyses performed: biomonitoring, sludge metals
Mr. Lab Analyst
Acme Laboratory
123 Park Street
Labtown, TN 33333-4444
1-800-555-WXYZ

WASTEWATER TREATMENT PLANT
SAMPLE LOCATIONS, SAMPLE COLLECTOR, CONTRACT LABORATORIES

SAMPLE LOCATION

Influent Composite: _____

Effluent Composite: _____

Influent Grab: _____

Effluent Grab: _____

Stream Above: _____

Stream Below: _____

Biomonitoring: _____

Undigested Sludge: _____

Digested Biosolids: _____

SAMPLE COLLECTOR

Composite: _____

Grab: _____

Stream: _____

Biomonitoring: _____

Sludge/Biosolids: _____

CONTRACT LABORATORIES

Tests performed: _____

Name: _____

Address: _____

Phone/Fax: _____

Contact Person: _____

CHAPTER 3: Test Methods

Your NPDES permit clearly states that all required regulatory testing must be performed using an approved test method. The list of approved test methods is found in Title 40 C.F.R. (Code of Federal Regulations) Part 136.

Table 1 A-B, from 40 C.F.R. 136, is a list of the approved test methods that can be used in the wastewater lab. First, check the list for the methods you are using. Then make a list of the methods you use, as shown in Figures 2a and 2b, or show the method on your bench sheet. See the sample bench sheet in Chapter 4.

Table 1A of 136 is a list of approved biological tests. Table 1B lists the inorganic tests, which are shown alphabetically. Ammonia is number 4, BOD is number 9, CBOD is number 14, pH is number 28 under hydrogen ion, and "solids" tests are numbers 53 through 57 under residue.

Keep a copy on site of the reference book from which the method was selected. If the method from *Standard Method*s was used, then keep a copy of *Standard Methods* on hand. Please note that if you are performing tests of biosolids for land application, the 503 rule references only the 18th edition of *Standard Methods*. If you are performing 503 tests keep your 18th edition.

Review the method to make sure that this is actually the procedure that is being used in the lab. This material also can be used as a guide when writing a laboratory standard operating procedure.

Sample Test Methods for Wastewater Laboratory Test Method Used, 20th Edition, *Standard Methods*

TEST	METHOD
Dissolved Oxygen	4500-O C
Temperature	2550
pH	4500-H+B
Chlorine, Total	4500-Cl G
Residue, TSS	2540 D
Residue, settleable	2540 F
Residue, total	2540 B
Ammonia	4500-NH D
CBOD	5210 B
Fecal Coliform	9222 D
E. Coli	HACH m-Coli Blue or Colilert Quantitray IDEXX

NOTE: *Methods here are for examples only. Each lab will vary.*

Figure 2a.

Table II, 40 C.F.R. 136, lists approved containers, preservatives, and holding times. You will find the most up-to-date form of this table at the Government Printing Office Web site: http://www.epa.gov/EPA-WATER/2007/March/Day-26/w1455.pdf.

This information also is available from EPA's Web site at http://www.epa.gov/. Select the Laws and Regulations links to the Code of Federal Regulations and to 40 C.F.R. 136. This may take several mouse clicks because Part 136 is buried deep through links back to the Government Printing Office site.

At the review date of this publication the 21st edition of *Standard Methods* is the only one that is available for purchase. As is the general custom, there is a delay before the available edition is approved, and that approval is published in 40 C.F.R. 136. Several of the commonly used methods are approved. An EPA letter listing the approved 21st edition methods is at http://www.mtas.tennessee.edu/Citydept/Sewer/21st_edition_method_approval.pdf.

Wastewater Laboratory Test Methods

Reference Document: Standard Methods 20th

Test Parameter	Method
Ammonia as Nitrogen	4500-NH E
BOD/CBOD	5210 B
Chlorine Residual, Total	4500-Cl G
Dissolved Oxygen	4500-O C
E-Coli	HACH mColi Blue
Fecal Coliform	9222 D
pH	4500-H B
Setteable Solids	2540 F
Total Suspended Solids	2540 D
Total Solids	2540 B
Temperature	5540 C

Figure 2b.

WASTEWATER LABORATORY TEST METHODS

Reference Document: _____

Test Parameter	Method
Ammonia as Nitrogen	
BOD/CBOD	
Chlorine Residual, Total	
Dissolved Oxygen	
E-Coli	
Fecal Coliform	
pH	
Settleable Solids	
Total Suspended Solids	
Total Solids	
Temperature	

CHAPTER 4: Sample Data

There are many versions of laboratory bench sheets. Some are simple; others are very complex. Any version of a bench sheet can be used as long as the needed information is included. Part 1, section B, paragraph 3, of your permit describes what supporting information should be included:

A. The exact place, date and time of sampling;
B. The exact person(s) collecting samples;
C. The date and times the analyses were performed;
D. The person(s) or laboratory that performed the analyses;
E. The analytical technique or methods used; and
F. The results of all acquired analyses.

If preservatives are used, record the name of the preservative and any other pertinent data, such as pH and sample temperature. When a contract lab is used, this information probably is already included on the chain-of-custody.

To simplify bench sheets, the methods can be recorded in another paper as stated in chapter 3.

NOTE: *When calculating and recording test data, always use the correct significant figures. Do not make up your own rules. Use the correct mathematical rules for significant figures and rounding of numbers. If you are unsure about these rules or how to use them, check the math section of most wastewater training manuals or a standard math textbook. You also may consult Standard Methods, Chapter 1, Section 1050 B Significant Figures.*

LABORATORY BENCH SHEET

Date: _____ **Sampler:** _____ **Analyst:** _____

TEST and Method		**Influent**		**Effluent**		**Above**		**Below**
Sample Time								
DAILY TEST	**Test Time**	**Test Result**	**Test Time**	**Test Result**	**Test Time**	**Test Result**	**Test Time**	**Test Result**
Settleable Solids 2540-F								
Temp. 5540 C								
pH 4500-H+B								
DO Sample Time								
DO 4500-O C								
Chlorine Sample Time								
Chlorine 4500-Cl G								
Composite Test Time Begin: _____ End: _____								
Ammonia 4500-NH 3 E								
Ammonia QC Test								

E. COLI BENCH SHEET

Sampler: _____ Sample Time: _____ Analyst:_____

	MI of Sample	Time In	Time Out	Total Count	E. Coli Count	Count* 100/mLs of Sample = E. Coli Count/Sample Size
Control						
Final						
Final						
Final						
Above						
Below						
Control						
QC						

TOTAL SUSPENDED SOLIDS/VOLATILE SOLIDS
STANDARD METHOD 2540 D.E.

Date: _____

Sample: _____ **Collected by:** _____ **Sample Time:** _____

TOTAL SUSPENDED SOLIDS		
Analyst		
Analysis Time		
Final Weight		
Final Weight		
Avg. Final Wt. (A)		
Initial Weight		
Initial Weight		
Avg. Initial Wt. (B)		
Solids Wt. A-B = (C)		
TSS: C* 1,000,000 Sample Size		
Volatile Solids		
Ignition Time		
Ignition Weight		
Ignition Weight		
Avg. Ignition Wt. (D)		
Volatile Wt. A-D = E		
VSS E* 1,000,000 Sample Size		
% Volatile E/A *100		

Balance Check:

1.0000 g = _____, 2.0000 g = _____, Other _____ = _____

TSS Solids Weight should be between 0.0025 g to 0.2000 g.

BIOCHEMICAL OXYGEN DEMAND

Date: _____ Sample Time: _____ Sampler: _____ Sample Temp.: _____

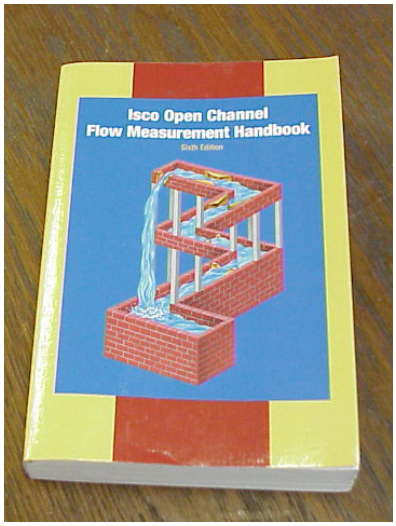
Test In Time: _____ Analyst: _____

Test Out Date: _____Time: _____ Analyst: _____

	Influent				Effluent				Seed Correction	Seed Correction
Bottle Number										
Percent Sample										
Sample Volume, mL										
Seed Volume, mL										
GGA Volume, mL										
Initial DO, mg/L										
Final DO, mg/L										
Depletion, mg/L										
Seed Correction										
Corrected Depletion										
% or Dilution Factor										
Bottle BOD										
Average of Valid Bottles										

CHAPTER 5: Flow Meter Calibration

The EPA requires that the plant flow meter or meters be checked for accuracy annually or whenever maintenance is required that involves changing parts that are part of the flow meter. Record the results of this work on a permanent log. A sample log is included. Plant operators can check their flow meters by doing drop or fill tests of plant basins. If a flume type flow meter is in place, check the flow depth by using the installed ruler on the side of the flume or by using a standard ruler and the flume chart provided by the manufacture. Using these measurements, the flow for your size flume can be determined from flume charts. If these checks vary more than 10% from the flow meters, have an equipment technician check the calibration. If a flume chart is not available, you can obtain one from the manufacture of your flume or from the Open Channel Flow Measurement Handbook from ISCO at 800-228-4373.



ISCO Open Channel Flow Measurement Handbook

FLOW METER CALIBRATION
Annually

FLOW METER IDENTIFICATION:

Type Meter _____ Manufacture _____

Model _____ Serial Number _____

Date	Influent/Effluent	Technician	Results

CHAPTER 6: Laboratory Conditions

The goal of a laboratory quality assurance program is to ensure accurate and precise test results. To achieve highly reliable results, the conditions within the laboratory must be controlled. A clean, organized, well-lighted and climate-controlled laboratory is the first step toward assuring quality analyses.

Lab Temperature

Lab temperature should be from 65-75° F.
BOD incubator should register 20° C ±1°C.
Fecal coliform incubator should be at 44.5°±0.2° C.
E. coli incubator should be at 35° C ± 0.5° C.
TSS drying oven at 103-105° C.
Muffle furnace should be at 550° ±50° C.
Autoclave: Sterilize at 121-124° C for 15 minutes; discarded cultures and contaminated materials for 30 min.

Sample logs for recording these temperatures are included in this chapter. All thermometers used in the lab should be checked for accuracy. Most labs use an outside service technician.

CLEAN GLASSWARE

Lab testing always involves the use of some kind of glassware. Use Class A or B glassware. If glassware is dirty, the test results could be wrong. Clean glassware thoroughly by rinsing after use, washing with laboratory detergent, rinsing with tap water, then distilled water. Then rinse again with fresh distilled water. BOD bottles may require different cleaning methods. Because soap has a high BOD make sure all soap is rinsed from BOD bottles. Many labs do not use soap on BOD bottles but acid rinse them with concentrated acid. Fecal coliform or E. coli test equipment must be sterile, either by using an autoclave or by purchasing sterile supplies.

EQUIPMENT CALIBRATION

Dissolved Oxygen (DO) Meter

Calibrate the dissolved oxygen (DO) meter every day. Air calibration and Winkler calibration are acceptable methods. On-site barometric pressure is the best calibration method. New DO meters have built-in barometers that speed the process. Make sure that the DO probe does not have water drops on it when calibrating. A common procedure is to turn the meter on, dry the probe, then allow the meter to warm up for 30 minutes. This also gives the air in the bottle time to stabilize after the probe has been removed and dried. Record settings before and after calibration and document the daily changes. When using the Winkler Method to verify accuracy, note that sodium thiosulfate is an unstable compound that should be standardized daily. There are suppliers that sell stabilized sodium thiosulfate, but the age of the reagent could affect calibration results.

The new LDO meters are not listed in the current 40 C.F.R. 136. Region 4 has approved ASTM method D-888-05. If you are using this type of oxygen meter, the manufacturer should supply you with this method, or you can purchase it from ASTM. This method recommends calibration verification as part of a lab quality control program. This simply is checking the reading of the meter as one would in air calibration of a membrane DO meter, with the exception that no adjustment will be made. The calibration check should be within 96 to 104% of

the theoretical DO for your temperature and pressure or attitude. Also, log the date whenever the probe or probe membrane is changed or cleaned.

pH Meter

Calibrate the pH meter before use according to the manufacturer's directions. At a minimum, this is performed with one buffer higher and one buffer lower than the expected value of the sample. If your sample pH is expected to be between 4 and 7, use these buffers. If it is expected to be between 7 and 10, calibrate with the 7 and 10 buffers. Also, record probe data such as cleaning times and slope. You may also record buffer identification such as manufacturer, expiration date, and lot number. Use fresh buffer each day.

Chlorine Test Equipment

Chlorine test equipment should be checked using a primary standard. See Chapter 9 for details on mixing and using potassium permanganate or a commercial chlorine standard.

Analytic Balances

It is recommended that analytical balances be checked for accuracy annually by the manufacturer or other service technician. EPA suggests that all plants have on hand American Society of Testing Materials (ASTM) Class 1 weights to check the calibration of their balances. As a minimum, have a 1.0 gram, 2.0 gram, and 50.0 mg weight to be able to make checks over the generally used range of the balance. This information should be recorded in a log book or on daily test worksheet prior to using the balance.

There are private service companies that will do a calibration check on the balance, pH meter, DO meter, and all lab thermometers for a modest fee. Whenever repairs or maintenance are done on lab equipment, record those activities in a log book.

ACS Reagent Grade Chemicals

It also is important to use only fresh ACS (American Chemical Society) reagent grade chemicals when doing the analyses. Regularly check your chemicals on hand for expiration dates. Mark newly arrived reagents with the date they were received and the date opened. When in doubt about the value of a chemical, call the supplier. When solutions are mixed using dry reagents, record the date in a reagent log. If standardization is required, include this information in the reagent log as well. A sample reagent log is included at the end of this chapter.

Distilled or Deionized Water

The quality of distilled or deionized water can greatly influence the quality of the test. Check for chlorine, ammonia, and total suspended solids (TSS). There should be no traces of these parameters in the water supply. The water should conform to the requirements of a Type II water as noted in *Standard Methods*. If your lab cannot perform these tests, use a commercially available laboratory water.

The total dissolved solids (TDS) of the water should be less than one milligram per liter (TDS<1.0 mg/L). Most wastewater labs can perform this test with the equipment they use for doing the total and volatile solids tests.

Store Type II water in glass containers when it is used to perform organic tests such as BOD and ammonia. Use plastic containers to store Type II water when it is used to perform metals tests. If your plant tests for metals, always check your water for their presence.

The best log sheets are customized for your plant. Log sheets like those shown on pages 18-22 are easy to make on most computer systems. Most word processing and spreadsheet software can be formatted to produce exactly the type of log sheet you need. If computer-generated sheets cannot be made, you can use the cut and paste method, along with a copy machine, to customize the bench sheets and log sheets you need.

LAB EQUIPMENT LOG

DATE	LAB TEMP	BOD INCUBATOR	DRYING OVEN	E. COLI INCUBATOR	AUTOCLAVE	INFLUENT SAMPLER	EFFLUENT SAMPLER	ANALYST

DISSOLVED OXYGEN METER

DATE	ANALYST	LAB TEMP	BEGIN DO	NEW DO	CHANGE	MEMBRANE	NOTES

pH METER CALIBRATION

DATE	ANALYST	BUFFER #4		BUFFER #7		BUFFER #10		NEW BUFFER	CLEAN NOTES
		READING	RESET	READING	RESET	READING	RESET		

REAGENT LOG – ACIDS

.02N H_2SO_4				BORIC ACID			
DATE MIXED	STANDARDIZE DATE	RESULTS	ANALYST	DATE MIXED	ANALYST	DATE MIXED	ANALYST

REAGENT LOG – BASIC SOUTIONS

6N NaOH		0.1N NaOH				SODIUM CARBONATE	
MIXING DATE	ANALYST	MIXING DATE	STANDARDIZE	RESULTS	ANALYST	MIXED	ANALYST

CHAPTER 7: Quality Control Test for Bias: Blanks, or Reagent Blanks

Blanks are a basic form of quality control test that shows interference or bias in the test. The results of a blank test should be zero. Most wastewater labs probably are already using blanks on several tests. *Standard Method*s states "At a minimum, include one reagent blank with each sample set (batch) or on a 5% basis, whichever is more frequent." Blanks show the absence or presence of a type of error called bias. For a target shooter, bias would occur if shots were low no matter what type of weapon was used. If shots from a .22, .45 auto and 12-gauge shotgun were always low, there is bias in marksmanship. In the lab, this is error that occurs in all results. Bias often can be easily corrected. Eliminate the source of error where possible. Otherwise, make a note of process bias when reporting results. Common sources of bias are:

- Poor calibration of equipment;
- Dirty glassware or equipment;
- Sampling errors;
- Sample preparation errors; warm-up, cool-down, pH adjustments;
- Balance errors;
- Contaminated lab water or reagents; and
- Software errors.

Biochemical Oxygen Demand (BOD)

For the BOD test, a blank consists of a bottle of dilution water with no sample. Generally, two blank bottles are used. They should deplete less than 0.2 mg/L. When performing a seeded BOD test, a seeded blank often is included. This bottle would contain dilution water and the seed material. The desired depletion of a seeded blank from the initial reading to the final reading is 0.6-1.0 mg of oxygen.

Fecal Coliform/E. coli

For the membrane filter tests, a blank is included before the first and following the final sample. Use 100 mL of sterile buffered dilution water. This is the same water that is used to rinse the sample through the membrane filter. Simply treat this blank as another sample. The difference would be in the results; a blank should never have bacterial growth. If the pre-sample blank has colony growth, the equipment was not properly sterilized or was contaminated after sterilization. If the post-sample blank is contaminated, this would indicate that the equipment was not cleaned well enough between samples.

An IDEXX blank would be 100 mL of distilled water with reagent added.

A positive control can be run on the fecal coliform, or E. coli test to ensure that the test process is good. A positive test should be run when very effective disinfection causes standard effluent dilutions to have results at or near zero. Plant influent is used for this test. Pour a small amount of rinse water onto the filter then add one drop of sewage. The rinse water allows the small sample to spread uniformly across the filter. For the IDEXX test, add a drop of sewage into the sample bottle filled with dilution water. These are qualitative tests that show the analyst that the procedure is correct and will grow coliforms if they are present. The colonies do not need to be counted.

Total Suspended Solids (TSS)

To perform a TSS blank, use 100 mL of distilled water instead of a sample. The filter weight should not change. If the weight decreases, more complete pretest rinsing of the filter might be necessary. If the weight increases, contamination is entering the process, or the filter may not have been dried sufficiently. For example, if a TSS blank shows a 0.5 mg loss in weight, there is a very good chance that all samples in that group have weights that are biased 0.5 mg low.

Remember that *Standard Methods* requires that more than one weight be performed on each filter. The process of drying, desecating, and weighing must be repeated until a stable weight is reached. This generally means within 0.0005 g of the other weight.

CHAPTER 8: Quality Control Test for Precision: Duplicate Testing

Duplicate testing shows the degree of precision that a laboratory analyst achieves when performing a particular test. Precision refers to the repeatability of the test result. If you test a single sample several times and get the same results each time, you have a high degree of precision. Another way of looking at precision is to think of target shooting. A tight pattern on the target would show precise shooting. A scattered pattern would be imprecise shooting. Whether you are shooting or testing wastewater, you want the procedure to be precise. You want two tests of the same wastewater sample to be exactly the same, just like you want the second shot to be very close to the first one.

Duplicate tests can be performed on all wastewater tests. If there is more than one lab analyst doing the tests, each analyst should perform his or her own duplicate tests. There is a sample log included at the end of this chapter for recording the results of duplicate tests. Data from the tests are recorded in the sample and duplicate column. The difference between the test values is called the range and is recorded in the range column. The goal is to have a range of zero.

Several sources of error could cause the range to be unacceptably high. If the samples are not mixed well, the sample and duplicate tests could yield very different values. This is especially true with BOD and solids tests. Unequal sample volumes obviously can cause different test values.

Record the test data in a table form. (Sample forms are available at the end of this chapter.) In the beginning, use only the first four columns, recording the date, test results, and the range or difference between the two results. If the range is small, good work! If the range is large, look for sources of error that would account for the difference between the values. Some common sources of error are:

- Sample size (samples must be exactly the same size);
- Insufficient mixing;
- Dirty glassware;
- Calculation errors;
- Titration (misreading the pipette or burette);
- Weighing;
- Calibration;
- Reagent water; and
- Reagents.

Standard Methods states "At a minimum, include one duplicate with each sample set (batch) or on a 5% basis, whichever is more frequent." Most regulators ask that you perform duplicate tests on 1 of every 10 samples. If tests show large ranges between duplicates, perform the tests more frequently in order to discover the source of error.

For those wanting a more sophisticated system, calculate the average of the two duplicates then divide the range by this average to calculate the relative percent difference (RPD). This number places each duplicate test, whether influent or effluent, on an equal level. This percent can then be graphed on a control chart. Control charts are discussed in Chapter 13. The relative percent data recorded in Figure 3 is charted in Graph 4 of Chapter 13.

DUPLICATE TESTS

TEST: TSS ANALYST: BNW

Date 1995	Sample	Duplicate	Range	Average	Relative Percentage Difference = Range ÷ Average
1-5	14	14	0	14	0
1-8	13	12	1	12.5	.08
1-12	11	11	0	11	0
3-2	16	17	1	16.5	.06
3-12	10	11	1	10.5	.09
3-25	10	11	1	10.5	.09
5-7	17	16	1	16.5	.06
5-12	10	12	2	11	.18
5-18	12	12	0	12	0
7-2	13	11	2	12	.17
7-7	3	4	1	3.5	.28
7-14	16	13	3	14.5	.20
7-19	18	18	0	18	0
9-8	8	8	0	8	0
9-15	13	13	0	13	0
9-18	13	10	3	11.5	.26

Figure 3.

DUPLICATE TESTS

TEST: _____ ANALYST: _____

DATE	SAMPLE	DUPLICATE	RANGE	AVERAGE	RELATIVE % DIFFERENCE = RANGE + AVERAGE

CHAPTER 9: Quality Control Tests for Accuracy: Standards Tests or Laboratory Fortified Blank

To show the accuracy of tests performed in the wastewater lab, an analyst should check his or her work by testing laboratory standards. A standard is a material that has a known or true value for a particular parameter. Accuracy is defined as agreement between the tested value and the true value. Another way of looking at accuracy is to think of the target shooter again. An accurate shot lands exactly where you aim; generally this is the bullseye. The farther the shot falls from the point of aim, the less accurate it is. The shooter wants all the shots to be in the bullseye just as the lab analyst wants all his test results to hit the true value dead center. Standard testing should be done at least once every 10 tests.

Standards are available for most laboratory tests. They can be made on site or purchased from different chemical suppliers. Purchased standards should be the preference because this should reduce the possibility of having mixing error as well as testing error.

> **NOTE:** The annual DMR QA/QC studies that are performed by major facilities and some minor facilities are a test of a laboratory standard. Many lab analysts will, in addition to the official samples, purchase additional material just for practice. These same materials can be purchased to perform regular in-house standards checks throughout the year. Be advised that the DMR QA/AC studies are regulatory evaluations. All Clean Water Act enforcement and criminal laws apply. Any form of cheating, comparing records, or falsification could bring serious consequences. If you do not understand the requirements or instructions of the DMR QA/QA studies call state or EPA personnel until your questions are answered fully. If your questions are not answered adequately, clearly document the difficulties that you are having in securing answers.

Biochemical Oxygen Demand (BOD)

The standard for BOD testing is glucose glutamic acid (GGA). A mixture of 150 mg of glucose and 150 mg of glutamic acid has a BOD of 198 mg/L. If your test of glucose glutamic acid equals 198 mg/L, you have 100 percent accuracy. GGA may be made in the lab by following instructions in *Standard Methods* and other lab manuals. It also may be purchased from various laboratory suppliers. If you add a nitrification inhibitor to the GGA test expect results to be 164 mg/L instead of 198 mg/L.

BOD acid checks must be done using seeded dilution water or with seed added to each bottle. It often takes the experience of several tests to find the right strength of seed to use. As a guide, the seed added to each bottle should add to the bottle's depletion an extra 0.6-1.0 mg/L. Some analysts add a bottle they call a seeded dilution water blank or just a seeded blank as a way of checking for this 0.6-1.0 mg depletion. The seeded blank will have dilution water and the same volume of seed that is added to the sample bottles. The seed correction (seed control depletion times volume of seed in each bottle) is the official way of to document this 0.6-1.0 mg/L depletion.

Total Suspended Solids (TSS)

For the TSS test, there are several products that can be purchased and mixed to make different levels of standards. 3M has a product called Filter Aide; Whatman sells Ashless Powder; and Sigma has cellulose products. Each of these products has a particle size that will not pass through the TSS filter. To make a standard at 100 mg/L, simply weigh exactly 100 mg of the dry material and mix in one liter of distilled water. Make standard concentrations that are approximately equal to the concentrations of your normal plant influent and effluent. If your influent averages 150 mg/L, make a TSS standard at 150 mg/L. If your effluent averages 5 mg/L, make a standard at about 5 mg/L. See Figure 3.

Figure 3.

Ammonia

Ammonia standards also can either be made in the lab or purchased. As before, mix standards in the approximate concentrations of your effluent and influent levels. The goal with standards tests is to have test results that are equal to or very close to the true value. If there is a large difference between these values, there is a problem with the test procedure. Check for sources of error, make corrections, and retest. This is the way a laboratory analyst can evaluate his own procedure, make whatever improvements are needed, then continue to improve the testing process. Another dimension can be added to the standards tests by doing duplicates of the standards test. This will show both precision and accuracy in the same procedure.

Record the data from standards tests in table form. These can be graphed and control charts constructed as the QA/QC program becomes more sophisticated.

Chlorine

Chlorine standards also can be purchased or made in the lab. A standard stock solution for chlorine can be made by mixing 891 mg of potassium permanganate in a liter of distilled water. This solution is stable for three months. It is recommended that this solution be refrigerated to minimize evaporation, which would change the concentration. A dilution chart is shown in Figure 4. Use dilutions in the range of your regular daily tests.

Calibrating the HACH pocket colorimeters with $KMnO_4$ (for Total Chlorine Residual)

1. Prepare a stock potassium permanganate ($KMnO_4$) solution as follows:
   a. Dry reagent-grade $KMnO_4$ at 105° C for one hour. Cool in desiccator.
   b. Weigh 0.891 grams of $KMnO_4$ on an analytical balance.
   c. Place in a 1000 mL class A volumetric flask, and fill to the mark with distilled or deionized water.
   d. Store this stock solution in the refrigerator. Discard if a brown precipitate forms. This solution typically is good for six months.

2. Prepare a working standard $KMnO_4$ solution by diluting 10 mL of the stock solution to 1000 mL with distilled or deionized water in a 1000 mL Class A volumetric flask. Prepare this solution once per month.

3. Prepare a series of calibration standards according to the following table. Make these standards daily.

mL of working standard dilution added to *mL of distilled of deionized water*	***Cl2 equivalent***
Distilled or deionized water	0.00 mg/L
1.0 mL (vol. pipette) to 500 mL (vol. flask)	0.02 mg/L
1 mL (vol. pipette) to 100 mL (vol. flask)	0.1 mg/L
5 mL (vol. pipette) to 100 mL (vol. flask)	0.5 mg/L
10 mL (vol. pipette) to 100 mL (vol. flask)	1.0 mg/L
20 mL (vol. pipette) to 100 mL (vol. flask)	2.0 mg/L

4. Perform a residual chlorine analysis on each of the calibration standards using the HACH reagents and the colorimeter.

5. If the colorimeter results are not within ±10%, check the batteries and the stock solution. If the colorimeter is still off by ±10%, contact HACH for instructions for data correction or possible repair.

6. You can construct a calibration slope graphing the theoretical chlorine values on the vertical axis and the actual reading of the standards on the horizontal axis of standard or logarithmic graph paper. To determine chlorine values of a sample, locate the colorimeter reading on the horizontal axis, then move vertically to the point where the slope line is intersected, and move horizontally until the true value is found on the vertical axis.

Though regulators prefer this method, the HACH company recommends that a chlorine standard be used to make various standard levels for checking the calibration of their colorimeters. They sell standards in both 2 mL and 10 mL ampules. Figure 5 shows 2 mL ampules.

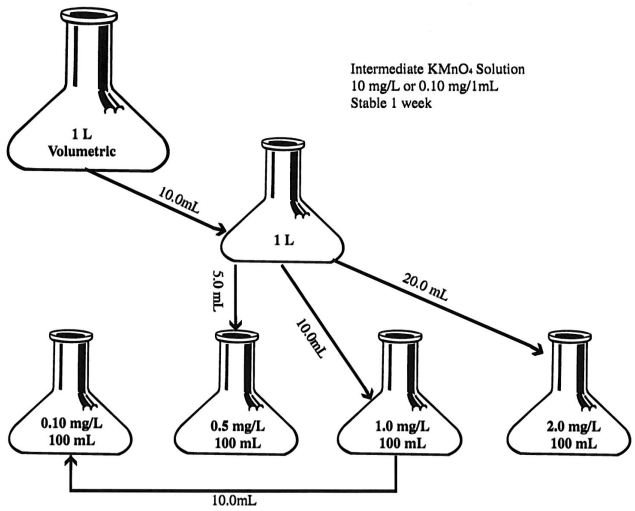


Figure 4.

Figure 5. *HACH pocket colorimeter and Chlorine standard ampules. Volumetric flasks will be used to make standards in the concentration range of the effluent limits.*

CHAPTER 10: Another Test of Laboratory Accuracy: Laboratory Unknowns and Split Samples

Another self test for laboratory accuracy is to test laboratory unknowns. There are several sources of these unknowns. North Central Labs will custom mix standards for 15 different parameters. Other suppliers, such as Environmental Resource Associates, have wastewater standards. The unknowns come in several bottles, along with directions and the approximate concentrations. Each of these companies includes the true values and acceptable ranges in separate envelopes to allow the testing to be done without any knowledge of the true value. If you are required to test EPA unknowns, testing these can be an excellent check of your procedure before you do the official test. Many labs perform unknown tests quarterly. The frequency is up to the individual laboratories. See ERA instructions on pages 31 and 32.

Some wastewater labs split influent or effluent samples with other labs. This is another way of checking the accuracy of the testing procedure. Regulators often use this quality control test to check the accuracy of a plant lab. The results can be evaluated subjectively simply by noting how close the two results are. The smaller the range between the two split samples, the more accurate we assume the tests to be. For an objective evaluation, construct a control chart using the pattern set for duplicate samples in Chapter 13.

ENVIRONMENTAL
RESOURCE ASSOCIATES
Arvada, Colorado 80002 1-800-ERA-0122

Instructions for the use of

WasteWatR™ Quality Control Standards

Caution: Read instructions carefully before opening **WasteWatR™** standards.

I. Standard Preparation

A. The MINERALS, HARDNESS and GREASE & OIL Quality Control Standards have been prepared as whole volume samples for use full strength without dilution.

B. DEMAND, NUTRIENTS, CYANIDE & PHENOL, RESIDUAL CHLORINE and TRACE METALS standards are concentrates and must be diluted by the following directions before analysis. Only the diluted concentrates are to be considered as sample, not the concentrates themselves. Approximately 11 ml of each concentrate is supplied so that two dilutions of each standard can be prepared. Approximately 2.5 ml of RESIDUAL CHLORINE concentrate is provided.

1. TRACE METALS concentrate. Volumetrically pipet (with a clean, dry pipet) 5.0 ml of concentrate into a 500 ml volumetric flask; add nitric acid to preserve and dilute to the mark with reagent water. No separate dilution is required for silver.
2. DEMAND, NUTRIENTS and CYANIDE & PHENOL concentrates. Volumetrically pipet (with a clean, dry pipet) 5.0 ml of concentrate into a 1 liter volumetric flask; dilute to the mark with reagent water. Prepare and analyze each concentrate independently of the others. If you desire other concentrations, dilute the concentrates proportionately and multiply the approximate, certified values and advisory range of values by the appropriate factor.
3. RESIDUAL CHLORINE concentrate. Volumetrically pipet 1.0 ml into a 1 liter volumetric flask; dilute to the mark with reagent water that has been verified to be free of organics. Analyze immediately upon dilution.

C. The stability and certified values are unconditionally guaranteed for one year. Due to possible sample contamination the guarantee is void after the samples are opened.

II. Standard Storage

A. MINERALS, HARDNESS and GREASE & OIL standards should be stored at or below 25°C.

B. DEMAND, NUTRIENTS, CYANIDE & PHENOL, RESIDUAL CHLORINE and TRACE METALS standards have been prepared in concentrated form to increase their stability. Concentrates should be stored at or below 25°C in the dark. However, the preservative treatment is rendered ineffective once the concentrates are opened and diluted. Therefore, the WasteWatR™ standards supplied in concentrate form must be analyzed as soon as possible after the concentrates are opened and diluted.

III. Standard Analysis

Remember... ERA WasteWatR™ standards are a tool to help you evaluate the accuracy of your wastewater data. Therefore, ERA WasteWatR™ standards should be analyzed as part of a routine sample load by your regular methods including all preparation or digestion steps. A list of "Approximate Concentrations" for ERA WasteWatR™ standards is on the reverse side to assist the analyst in choosing an appropriate aliquot for analysis.

A. MINERALS and HARDNESS standards must be well shaken for 5 seconds before removing every aliquot for analysis. Be careful to correct for pH, color and turbidity effects in each analysis. If there are any visible clumps in the samples, homogenize before analysis. The alkalinity is titrated to pH4.5. Alkalinity and pH should be analyzed immediately upon opening the MINERALS standard.

B. Transfer the whole GREASE & OIL standard to a separatory funnel. Carefully rinse the sample bottle with solvent, add the solvent washings to the funnel and extract the sample well. The certified value of GREASE & OIL is given as mg per bottle to avoid confusion due to the sample volume being less than 1 liter. Great care must be taken in the extraction, separation and drying steps to avoid determining results that are too low. Certified values are given for both gravimetric and infrared methods of analysis.

C. DEMAND standard must be seeded with a biologically active seed material when determining BOD. Be sure to determine the BOD of the seed material so that a proper seed correction can be made. See "Standard Methods for the Examination of Water and Wastewater" for complete details. Commonly, a laboratory will determine the correct values for COD and TOC but be low for BOD. If this happens, check the quality of the seed. Note that phosphorus and Kjeldahl nitrogren are analyzed out of the DEMAND standard. Both parameters are present as organic compounds which will test the adequacy of your digestion methods.

D. NUTRIENTS standard contains common interferences which will really test your methods. Be sure to check for pH before sample analysis.

E. CYANIDE & PHENOL standard is prepared using free and complex cyanide. An inadequate sample digestion will cause cyanide results to be significantly low. Check the sample pH before performing the phenol distillation, and acidify only under a fume hood.

F. TRACE METALS standard is prepared so that the analyses can be completed by ICP or atomic absorption. If low recoveries are obtained when using GFAA, ERA recommends the use of standard additions.

G. RESIDUAL CHLORINE standard must be prepared in organic-free water. If you use a "kit" for analysis, typically your results will be too low. Check your reagents or change methods.

IV. Certified Results

The ERA certified and advisory range of values are included. The advisory range is the range of values that an experienced laboratory can expect to attain using the most precise methods and equipment. In determining its advisory ranges, ERA considers both the parameter and the most commonly used method of analysis for the parameter. Whenever available the advisory range is based on EPA data collected during method or performance evaluation studies. ERA stresses that it is the responsibility of the individual laboratory to determine acceptable levels of performance for a particular analytical result depending on the intended use of the data.

V. Safety

ERA products may be hazardous and are intended for use by professional laboratory personnel trained in the competent handling of such materials. Responsibility for the safe use of these products rests entirely with the buyer and/or user. If you need a Material Safety Data Sheet for any ERA product, please call toll-free at 1-800-ERA-0122.

Approximate Concentrations of

WasteWatR™ Quality Control Standards

These concentration ranges are given to assist the analyst in choosing the appropriate sample aliquot size for analysis.

Parameter	Approximate Concentration
MINERALS	mg/l
total solids at 105°C	500-2000
dissolved solids at 180°C	500-2000
conductivity	500-2500 micromhos
alkalinity as $CaCO_3$	100-300
chloride	50-400
fluoride	1-20
sulfate	50-400
potassium	50-300
sodium	50-300
pH	6-10 units
HARDNESS	mg/l
suspended solids at 105°C	10-120
calcium	50-150
magnesium	5-50
hardness as $CaCO_3$	50-500
GREASE & OIL[1]	10-100 mg/bottle
DEMAND	mg/l
BOD	20-300
COD	40-400
TOC	10-100
total phosphorus as P	1-10
Kjeldahl nitrogen as N	1-20
NUTRIENTS	mg/l
ammonia as N	1-20
nitrate plus nitrite as N	1-20
phosphate as P	1-10
CYANIDE & PHENOL	mg/l
complex cyanide, free cyanide	0.025-0.5
total cyanide	0.05-0.5
total phenol	0.025-0.5
TRACE METALS	mg/l
antimony, arsenic, beryllium, cadmium, selenium, silver, & thallium	0.01-0.25
mercury	0.001-0.02
aluminum, barium, boron, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, strontium, vanadium & zinc	0.05-1.0
RESIDUAL CHLORINE	0.5-3.0 mg/l

[1]Method References:

a. Gravimetric: 413.1, Separatory Funnel Extraction (EPA 600/4-79-020)

b. Infrared: 413.2 (EPA 600/4-79-020)

c. The oil used in ERA Grease & Oil standards absorbs infrared light more intensely than the reference oil used in 413.2; therefore, the infrared certified values will be approximately 20% higher than those for the gravimetric method.

Chapter 11: Laboratory Standard Operating Procedures

Laboratory standard operating procedures are becoming more common in small laboratories. Many regulators are asking that they be written, followed and kept up to date. An easy way to produce an SOP is to photocopy parts of *Standard Methods* then cut and past the sections into a notebook along with photos of the equipment and supplies.

The SOP should describe the testing process in enough detail so that a competent analyst who is unfamiliar with your lab can follow the procedures to perform the test with reliability or can review your work and results. Include in the SOP sampling and preservation information, test method to be used, reagents and equipment to be used, equipment conditions and calibration details, actual testing procedures followed, quality assurance instructions, equipment maintenance, and data recording and reporting details.

Additionally, there may be instructions to the analyst regarding what actions should be taken when test values vary from the normal or approach regulatory limits.

Chapter 12: Spiked Samples, or Lab Fortified Matrix or Surrogates

Spiked samples are used to test accuracy while performing the regular test procedure. The goal is to have the total value of the spiked test equal the sum of the sample value plus the value of the added spike material. If your sample value is 100 and you add 50 in spike material, the value of the spiked sample should be 150. This is called 100 percent recovery. It is the author's opinion that spikes tell the analyst little usable information about the quality of day-to-day lab results, but they are part of *Standard Methods* under the confusing name of lab fortified matrix, and many commercial labs report these as surrogate recovery.

Biochemical Oxygen Demand (BOD) Spike

EPA does not recommend that BOD tests be spiked.

Total Suspended Solids (TSS) Spike

To spike a TSS test, set up three filter pads. One is for the sample, one is for the standard material that will be added to the sample, and the last is for the spike, which is the sample and added standard. If a 100 mL sample and a 100 mL standard sample are tested regularly, use one filter for the 100 mL sample, the second for the 100 mL standard sample, and through the third filter pour 100 mL of sample and 100 mL of standard. To calculate the percent recovery, divide the weight of the combined sample and spike minus the sample value by the spike value, then multiply by 100:

$$\left(\frac{\text{weight of combined sample and added standard - net weight of sample}}{\text{Net weight of added standard}}\right) * 100 = \%\ \text{recovery}$$

SAMPLE	NET WEIGHT
Plant effluent, background	0.1 mg/L
TSS standard, spike	0.2 mg/L
Spiked effluent value	0.35 mg/L

$$\text{Percent recovery} = \frac{0.35 - 0.1}{0.2} * 100 = 125\%$$

Ammonia Spike

When performing the ammonia test with a direct pH meter reading, a spike of ammonia standard can be added easily. When using a 100 mL sample, obtain the sample ammonia value, then add a pre-determined amount of ammonia standard directly into the sample beaker. This should result in a reading equal to the sample value plus the spike.

For example, if the sample reads 0.5 on the scale, the ammonia concentration would be 0.5 mg/L. Next, add 0.2 mL of a 1000 mg/L ammonia concentration standard. This should give a reading of 2.5 or 2.5 mg/L ammonia. The percent recovery is calculated the same way as in the other spike tests. Subtract the effluent value from the total spike value, divide that result by the spike value, then multiply by 100.

$$\frac{(\text{Sample and added standard value} - \text{sample value})}{\text{Added standard}} * 100 = \%\ \text{recovery}$$

SAMPLE	NET WEIGHT
Plant effluent, background	1.2 mg/L
TSS standard, spike	2.0 mg/L
Spiked effluent value	0.35 mg/L

$$\text{Percent recovery} = \frac{3.2 - 1.2}{2.0} * 100 = 125\%$$ recover of the added spiked

Chapter 13: Control Charts

A control chart simply is a graph of the quality control test data with some extra lines that allow the analyst to evaluate how well the testing process is going. Graphs 1-5 are examples of different types of quality control test data that have been control charted. Each graph shows a picture of the testing process. For example, a graph of the TSS (Graph 1) duplicate tests would represent the process of duplicate testing for TSS and would show graphically how precise the analyst's tests have been in the past. The graph also is a general predictor of future precision. An average line or center line is drawn through the middle of the graph. The average is commonly referred to as the location of the process. Upper, and perhaps lower, control limits are added to indicate how much variation takes place in the testing process. Where control limits are far above or below the average line there is a great deal of variation in the testing process. Where the control limits are close to the average line there is less variation. Generally, it is desirable to have less variation. Having widely spaced control limits and lots of variation does not automatically mean an analyst is doing a poor job. These control limits document variation of the testing process, which includes variation caused by the method, equipment and lab conditions, as well as the analyst. The BOD GGA test is an example of a test that can have wide limits due to the variability of the test method. Biological tests are not very precise. Control charts can be drawn on plain graph paper or preprinted forms like the example from SPC Inc., or created from spreadsheet software.

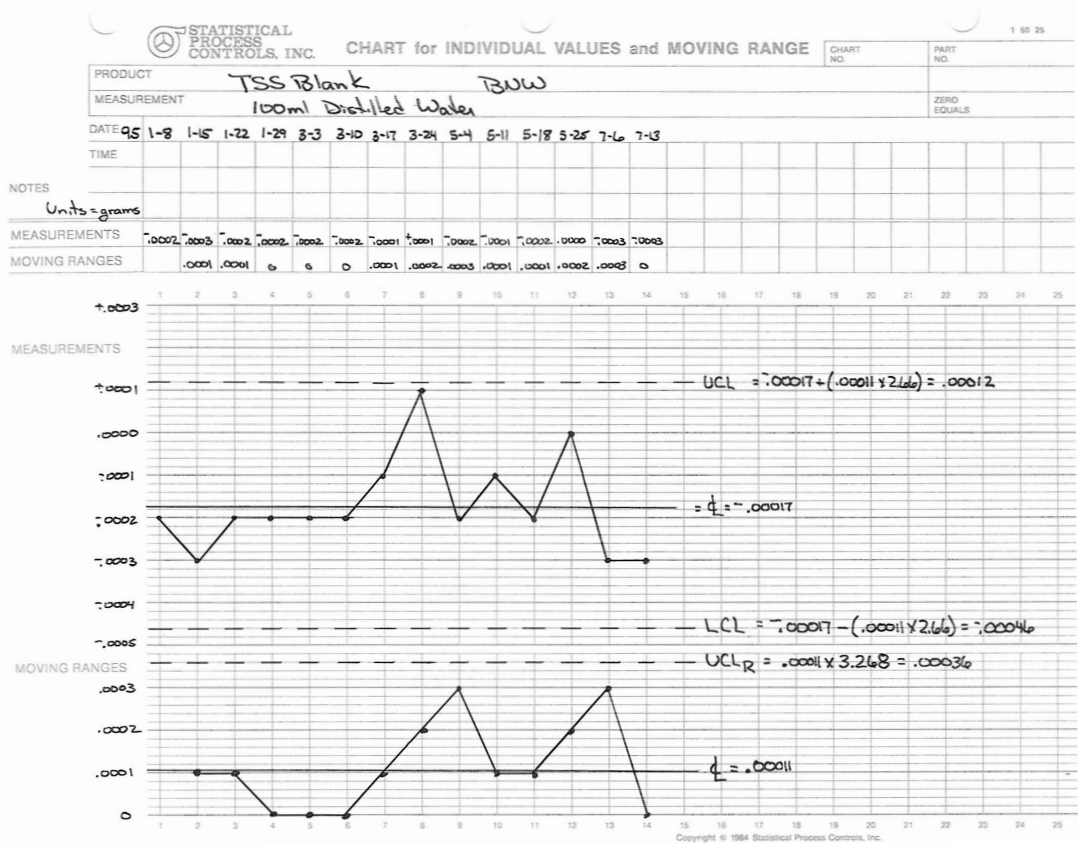
NOTE ON CALCULATING CONTROL LIMITS

Walter Shewhart of Bell Laboratories developed a method of describing variation in a manufacturing

process. This method also works in the wastewater laboratory testing process. Shewhart's control charts and constants are used in this description. Many plants use computer software packages that automatically calculate control limits. Before you purchase a software package, compare its limits with some that have been calculated by hand
using Shewhart constants. Often a software package's limits are simply ± 3 standard deviations. This is fine if the data are all in statistical control. But if it is out of control, the limits will be wrong. Properly used, Shewhart constants will give good limits even when data are out of control. For more details on using statistical process control contact the SPC press listed in the reference section or the business or statistics departments of your local college. The use of control charts and the practical part of statistics are somewhat different from
the theoretical statistics that are taught in introductory classes.

Charting Blanks Graph 1 shows an average and a moving range graph for TSS blanks. In this test, 100 mL of distilled water was filtered through a TSS filter. There should be no effect on the filter weight.

1. Enter the dates and test data along the top of the chart. In this data set many of the weights were negative numbers indicating that the filter pad lost weight during the test process. This most likely indicates that the filters should be rinsed better prior to use.
2. In the range row, enter the difference between consecutive values. The difference between the first value (-.0002) and the second value (-.0003) is .0001.
3. Continue to find the range between the second and third values, between third and fourth values, and so on for all the other values across the row. There always will be one less range value than test value.
4. Graph the range data first.
5. Compute the average of these 13 numbers (.00011) and draw a center line across the range graph. There is some difference between the computer-generated and hand-drawn graphs rounding differences. Graphs 1 and 2.

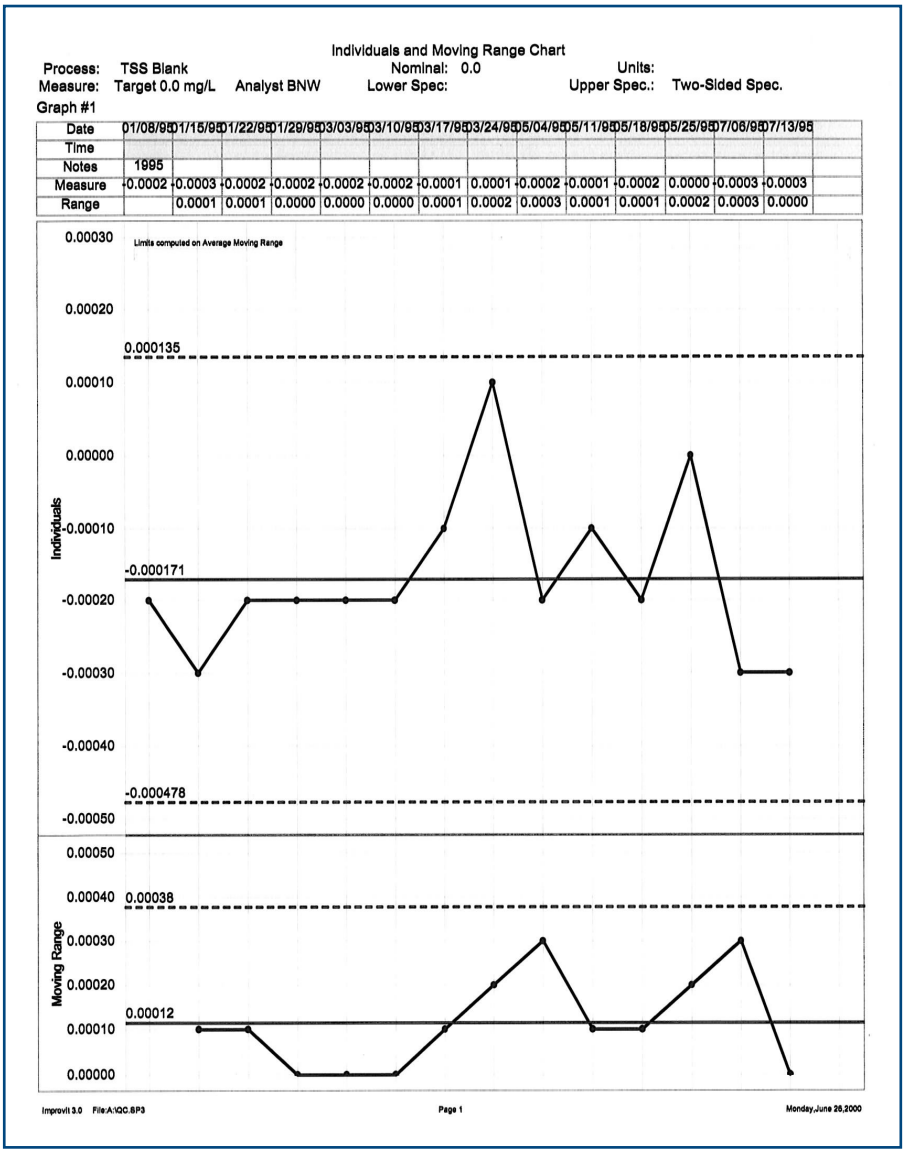


Graph 1

6. To compute the upper control limit (UCL) for the range chart (UCLR), multiply the average range by the constant 3.368. This gives a UCL for the range of .00036, which is drawn on the graph as a broken line.
7. Graph the test measurement data on the top half of the page, and draw the average, or center line through the graph. The test measurements UCL is computed by multiplying the average range (.00011) by the constant of 2.66, then adding the product (.00029) to the average of the test data (-.00017). That makes the UCL 0.00017+(0.00011*2.66)=0.00012. The LCL for the test measurements is -0.00017-(0.00011*2.66) = -0.00046.

In this example, the TSS blank test process shows control. The data vary up and down between the upper and lower limits. There is, however, a problem with the location of the process average (-0.17 mg), which is below the target (zero). This procedure indicates bias. From looking at this chart, the analyst would expect that all TSS tests would average 0.17 mg below the actual weight. It should be the goal of this analyst to determine why there was a loss of weight and correct the bias.

Control charts tell you when to take action, but not what action to take. As you continue charting test results, the chart will tell you if the action you took actually corrected the problem. In this case, when the average chart centerline is on 0.0000 instead of -0.00017, the testing process is correctly hitting the target. While working on this location or target problem, it is important to maintain control of the process, not allowing the process ups and downs or variation to become so great that a point falls outside the control limits. Another step in improving the process is to work toward reducing the amount of variation and actually tighten the control limits. Minimizing variation over time shows an improvement in the quality of the testing process. Graph 2 is a computer-generated control chart of the same data. There are many software companies that make spreadsheet-based charting software. When you choose a charting

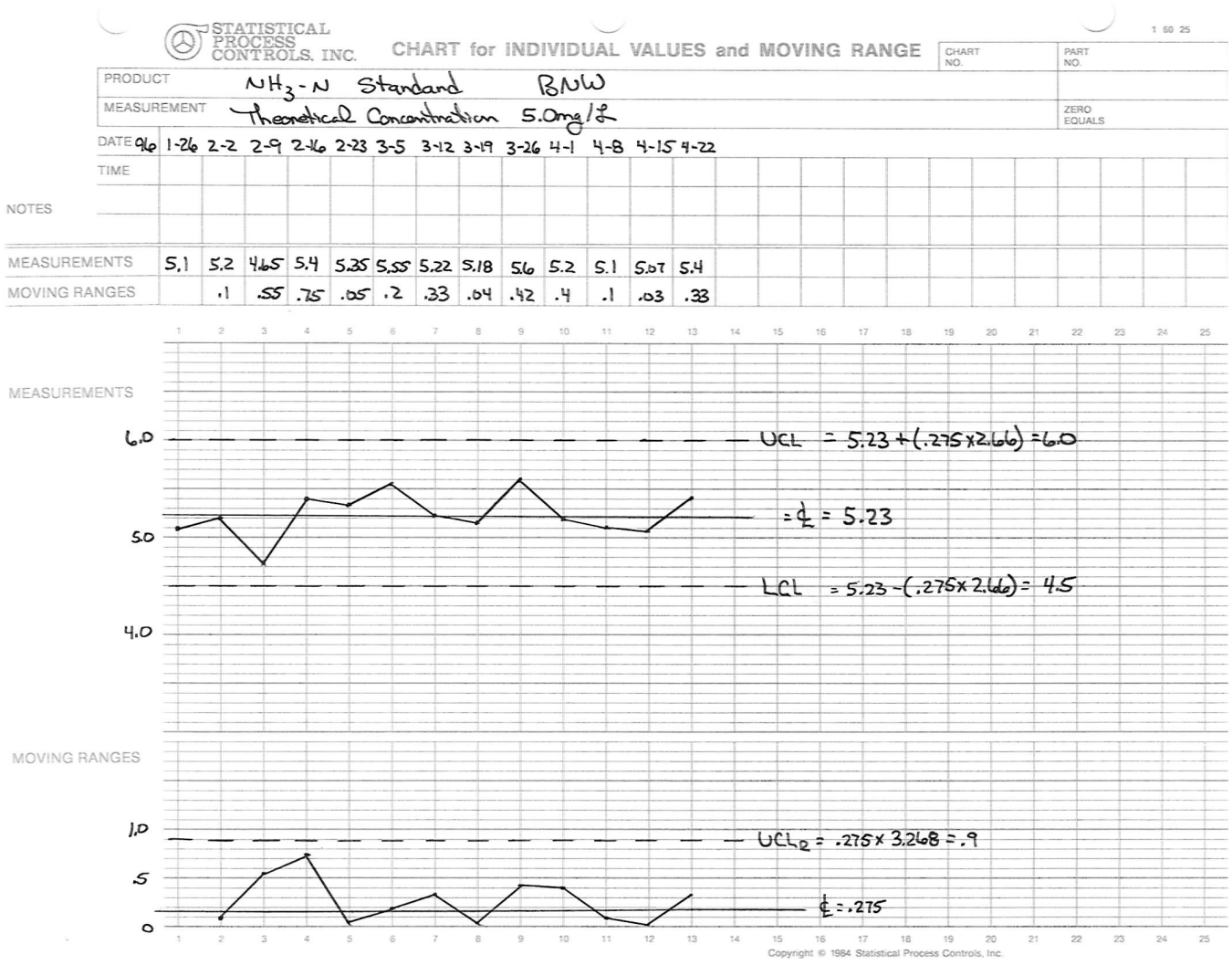


Graph 2

software package, always test the software against hand-produced charts. Many software packages simply calculate upper and lower control limits using standard deviation; this can lead to poor quality limits when the data are out of control. To have correct statistical process control limits according to Shewhart's rules, the average range and appropriate constant must be used.

Charting Standards Tests

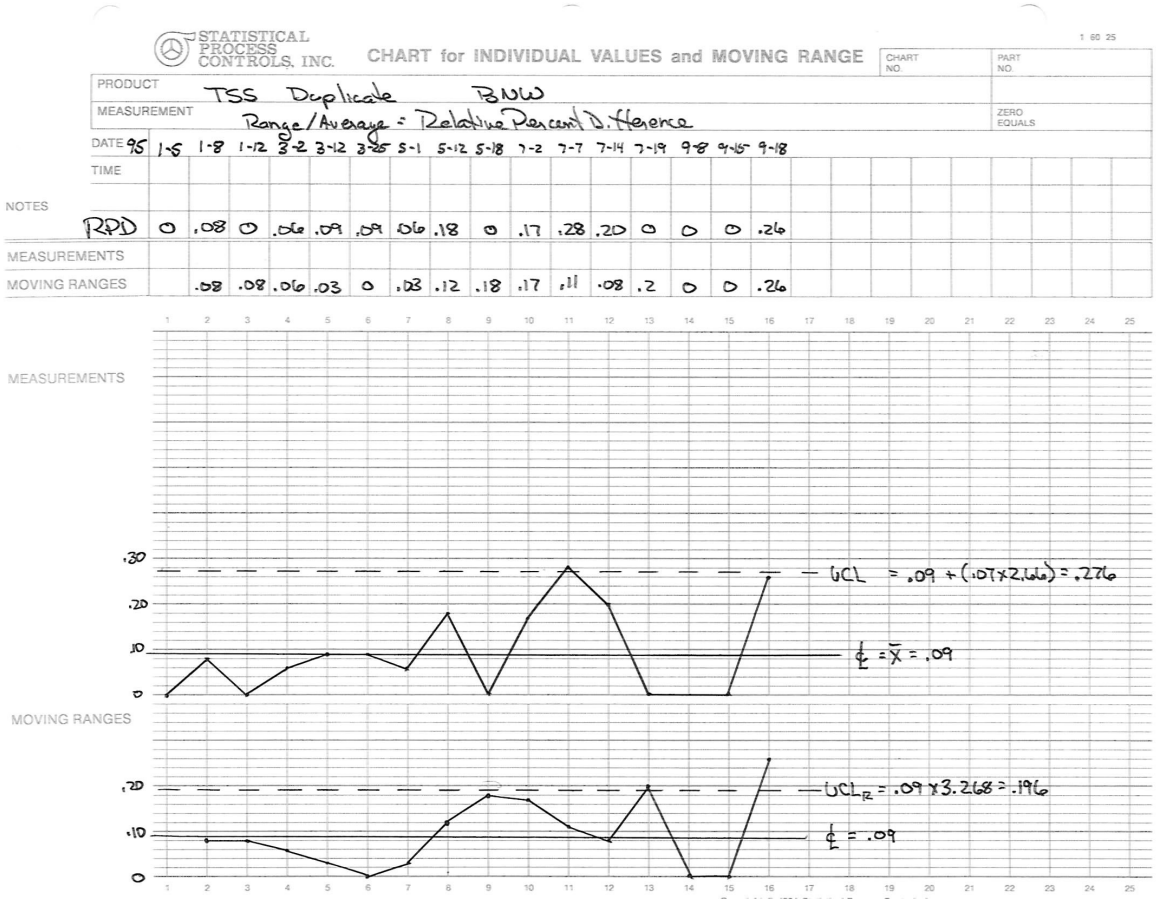
Graph 3 shows an average and moving range chart for the ammonia standard test. A theoretical 5.0 mg/L standard was mixed in the plant lab. One replication of the regular ammonia nitrogen test was preformed weekly on this standard. The control charts were constructed in the same manner as they were for the blank tests using the same types of graphs and constants. This example, like the previous one, shows a process that is in control with respect to range and average. Once again, however, there is a problem in this process; it is biased 0.25 mg high. The process is located above the target or theoretical value. To improve the process the analyst needs to work on this bias. The control chart will show the progress of improvement efforts and when the bias has been eliminated. It should be the goal of the analyst to have the test process in control so that all data fall within the control limits and on target.



Graph 3

Duplicate Tests/Relative Percent Difference

Graph 4 shows control charts for effluent TSS duplicate tests. In this case, the relative percent difference is used to compare values that vary from 3-18 mg/L. See the duplicate test log sheet in Figure 6. As discussed in Chapter Seven, duplicate tests show the precision of the analyst and the method. The smaller the difference, or range, between two replications, the more precise the test. A simple range chart can be used if the duplicates are performed on material that always has the same theoretical value, such as glucose glutamic acid. But where there are daily variations in the test level, a different approach is needed. If a TSS duplicate test was done today on water with a solids level of 5 mg/L and tomorrow on water with a solids level of 20 mg/L, a range of 1.0 mg/L would have a very different meaning from one day to the next. To compare the two tests on an equal level, simply convert the range to a relative percent of the difference. Refer to the duplicate log in Figure 3. Column six shows the relative percent difference (range ÷ average). This value shows that the range is a certain percent of the average of the two duplicate tests. Chart the relative percent difference on an average and moving range chart. Use the same procedure and constants that were used with the blank and standard tests. Graph 4 shows a TSS duplicate test control chart. The relative percent difference is shown on the measurements graph at the top of the page and the moving range at the bottom. These graphs both show out-of-control points. The large relative percent difference on July 7 and September 18 were each identified as out of control. The analyst should investigate the cause of these high numbers.

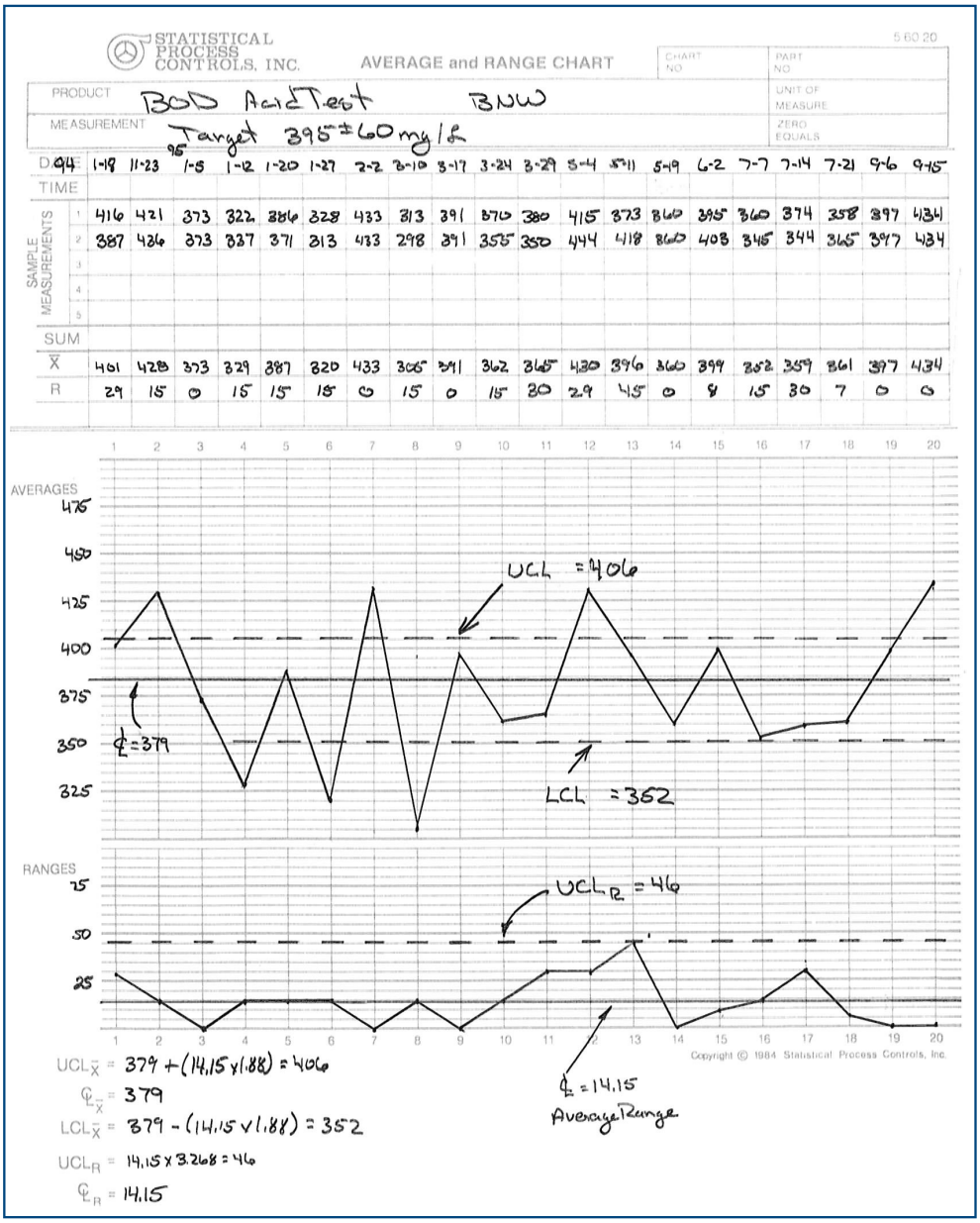


Graph 4

Purchased Standards, Average and Range Chart

Graph 5 is an example of a BOD glucose glutamic acid test control chart. In this example, duplicate glucose glutamic acid (GGA) bottles were tested, so this test shows both precision and accuracy. This is called an average and range chart. The average graph charts the average of the two test values; the range graph charts the range between the two values. These tests were conducted using HACH's double-strength GGA where the true value is 395 mg/L.

1. At the top of the chart, record the date and test results.
2. Begin by graphing the range values in the lower portion of the page.
3. Average these ranges, and draw the average line through the range graph.
4. Calculate the upper control limit (UCLR) for the range by multiplying the average range (14.15) by the constant 3.268. The UCLR for the range is 46, which is plotted as a line on the graph. (Notice that all the data fall below the UCLR, which means the data are in control with respect to range. This is a short way of saying that the variation in BOD values between the two bottles is insignificant, or that the test is precise.)
5. Graph the average of the two test values on the top half of the page in the graph area called average, and draw a centerline through them. With this data, the centerline is 379.
6. Calculate control limits by multiplying the average range (14.15) by a constant of 1.88, then add this number (27) to 379 to give the UCLX (upper control limit of the averages) of 406. Next, subtract 27 from 379 to get 352, the lower control limit (LCLX).



Graph 5

The top graph of the average data is out of control; there are points outside the control limits. The points above and below the control limits show excessive variation in the BOD-GGA levels. There could be several reasons for this error: seed strength, sample measurement, calculations, etc. For this process, the target is 395 mg/L. But the process is averaging 379 mg/L. So again, the analyst needs to work on improving the process location. During the month of January, the analyst had difficulty not only with low strength results, but with lots of up and down movement in the process. The glucose glutamic acid strength would be weak, then strong. The seed also could vary. Correcting this inconsistency will improve the process. In the next months, there was an improvement in average strength and the amount of variation, representing a process improvement. To continue to improve this process of BOD glucose glutamic acid testing, the analyst should work toward consistently hitting the test target of 395 mg/L and reducing the amount of variation in the test average.

This is the pattern for control charts when the true value or target remains the same and a duplicate test is performed at the same time. For example, if the analyst mixed 1000 mL of a 20 mg/L TSS standard and always did two replications, an average and range chart would be used until that 1000 mL of standard was used. A second chart should be started when a second batch of standard is mixed. If only one replication is to be done, the individual value and moving range chart should be used.

Control charts are a way to show the location of a process and qualifying variation within a process. The process average shows the location of a process. If it is located on the target, no adjustment is needed. But if the location is off the target, as in the examples, then there is an opportunity for improvement. There is variation in every process. Some variation is normal, that is, built into the process, such as the daily ups and downs in flow through a wastewater plant. On a control chart, normal variation occurs between the control limits. Special cause variation is what happens when a point falls outside the limits. Control charts give operators a way to determine when a process is under the influence of a special cause so they can remove that influence on the process.

The graphs used in this publication were printed by SPC Inc. A plain piece of graph paper can be used for control charts. For actual laboratory work, hand-drawn charts are the preferred method, but the electronic version was selected for clarity in this publication. When you review charting software packages, always test the software against hand-produced charts. Many software packages simply calculate upper and lower control limits using standard deviation, which can lead to poor quality limits when the data are out of control. To have correct statistical process control limits according to Shewhart's rules, the average range and appropriate constant must be used.

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Donald Wheeler, David Chambers. *Understanding Statistical Process Contro*l. 1992. SPC Press. Knoxville Tenn., 865-584-5005.

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