



Laboratory Quality Assurance and Quality Control

By Brett Ward
MTAS Utility Operations Specialist

Wastewater-Treatment



Municipal Technical Advisory Service
A statewide agency of
The University of Tennessee's
Institute for Public Service
in cooperation with the
Tennessee Municipal League

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Laboratory
Quality Assurance
and
Quality Control

for the Small
Wastewater Laboratory

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October 2000



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DISCLAIMER

Throughout this manual there are many references to specific companies and products in order to show the lab analyst precisely what should materials should be used and where they may be purchased. Those products mentioned by name were selected based on the personal experience of the author or of those regulators who reviewed the manuscript. Whenever possible, the named companies were those with which most lab analysts are familiar or are already 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 by The University of Tennessee.

ACKNOWLEDGMENTS

There are many people that I must thank for their assistance in making an effective and quality manual. Without their knowledge, advice, and encouragement this project would not have been possible.

First, I want to thank three people in the Region 4 EPA Office of Quality Assurance in Athens, GA,—Gary Bennett, Wayne Turnbull, and Mike Birch. They provided the original motivation for the development of this manual through a Quality Control / Quality Assurance seminar in 1990. Their greatest contribution has been their extensive review of the manual. They provided numerous suggestions and corrections that helped make the manual more usable and more accurate.

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 Jim Pilkin from the Chattanooga office, Lanny Bonds from the Knoxville office, Jere Dougan from the Jackson office, and Felica Hix from the Fleming Training Center.

A special thank you goes to Morris Chandler of the Wastewater Treatment Plant in Milan, TN. Morris' review of the original material was invaluable in helping me keep the material tailored to what is usable by the lab analyst.

Though this is a technical manual, there was 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.

Many people and organizations have provided material that has been incorporated into this work. The original collection of materials came from a 1990 EPA Quality Assurance/Quality Control seminar in Athens, GA. Other materials were provided by the Fleming Training Center, by Barbara Loudermilk with TDEC, and by Dewayne Culpepper with Tennessee Association of Utility Districts.

Appendix 2, Significant Figures and Rounding, was graciously provided by Mr. James Fromm, from his *Third Millennium Online* homepage. Mr. Fromm is a chemistry teacher and city official. His homepage located at www.nidlink.com/~jfromm/ is an outstanding resource in the areas of chemistry, math, and the history of many scientists.

Finally, I owe thanks to friends and coworkers at MTAS—Leah Cox, Carole Graves, Carol Hewlet, Al Major, Sharon Rollins, Beth Sanderbeck, and Steve Wyatt.

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HOW TO USE THIS MANUAL

This manual is intended as a guide for wastewater laboratory analysts in setting up their own Quality Assurance / Quality Control (QA/QC) programs. A laboratory QA/QC program is usually required by regulatory agencies, but there are good reasons to institute such a program voluntarily. A QA/QC program consists of procedures that ensure the precision and accuracy of tests performed on a daily basis. Precision refers to repeatability, or being able to achieve the same test results in subsequent tests. Accuracy refers to the closeness of test results to the correct values.

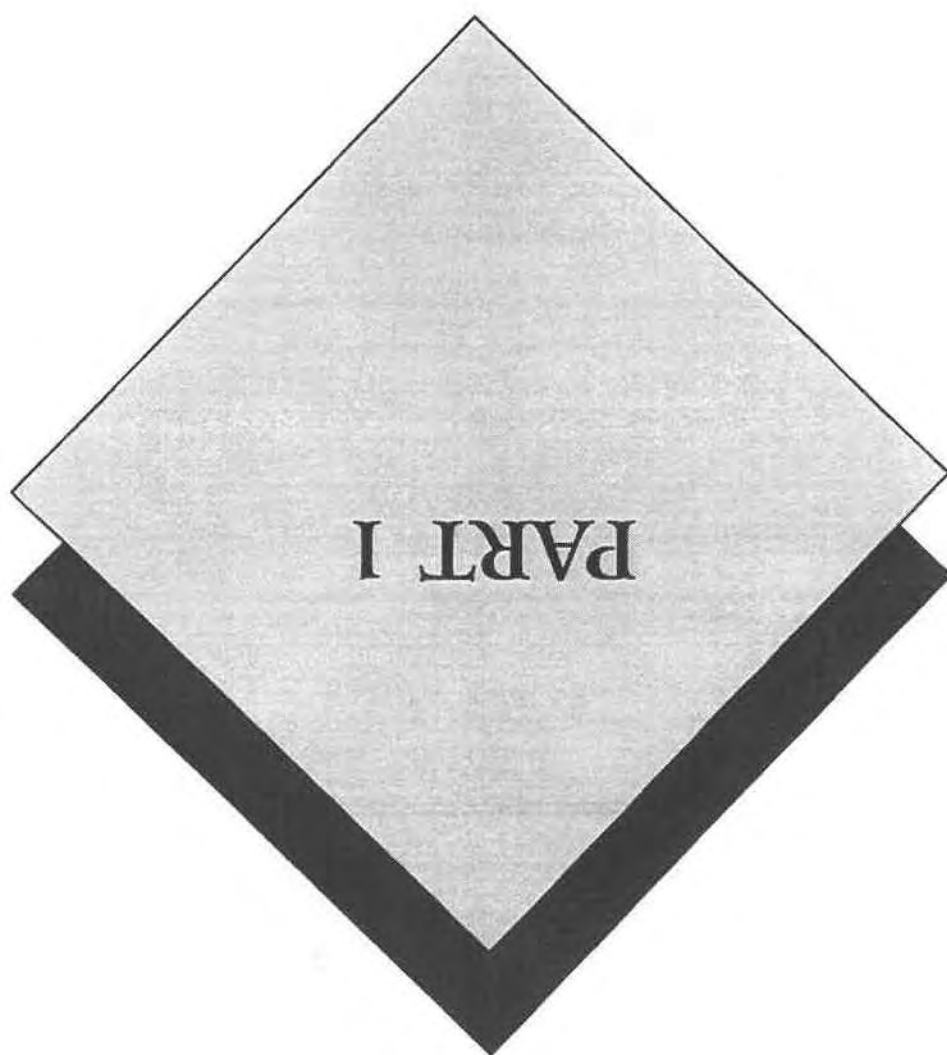
The QA/QC program includes three phases:

- keeping careful and accurate records;
- documenting that equipment is regularly calibrated and temperatures are correct; and
- performing quality control (QC) tests to demonstrate precision and accuracy.

This last phase is particularly important since QC testing tests the laboratory analyst's abilities and techniques. 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 laboratory tests are required by the state. However, it can also be very useful to plant operators or managers. It is the voice of the process, telling you what is happening within the process. Analyzing the data is a fascinating process that can reveal useful insights about how a plant is performing and predict problems before they occur.

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 main Quality Assurance / Quality Control document. Part II of this manual consists of 12 chapters that describe in greater detail the steps in the general outline. Finally, Part III consists of two appendices that contain various forms and reference materials you will need. You should begin by reading Part One to gain a thorough understanding of the QA/QC process and how to set up your documentation system.



PART 1

OUTLINE

Steps to Improvement

DATA & 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 of this manual.)

Step 2

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

Step 3

Maintain a complete and accurate list of all test procedures used. Refer to Table 1, A-B of 40 CFR 136 (Appendix I of this manual) 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 of this manual.)

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; preservatives, if used; and the chain-of-custody report, if needed. When on site testing is done, the information can easily be included on the bench sheet. If 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 of this manual.)

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 instantaneous check falls outside ± 10 percent of the flow meter reading, corrective action must be taken. (See Chapter 5 of this manual.)

LABORATORY CONDITIONS

Step 6

The conditions in the laboratory should be maintained in such a way as 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. It should be 68 degrees Fahrenheit. Ovens and incubators must be checked daily or when used. (See Chapter 6 of this manual.)

TESTING

Step 7

Duplicate testing is the simplest form of Quality Control test. It consists of simply 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 one, then the second. Duplicate tests can be performed on any parameter, even pH, D.O, or chlorine. The general recommendation is to perform a duplicate after every tenth sample. Add a duplicate bottle to the BOD test after 10 sets of samples or, perhaps, one per week. For TSS, perform a duplicate test after 10 filter pads have been used. 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 may be a problem with the procedure. The goal is to have no, or almost no, difference between the results of the duplicate tests. Record the results in table form. The data can be graphed on a control chart (See Step 12).

Step 8

Blanks are another form of Quality Control test. Blanks show interference in the test. Ideally, the results should be zero, indicating there is no interference. 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 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 filter apparatus or the glassware used in the test. If the weight decreases, the filter was not rinsed well enough. Most labs are probably already including a blank in the fecal coliform test. In the ammonia procedure, test using distilled water instead of a sample. The target for blanks is zero. A control chart, described later, will aid the analyst when making decisions about values that are greater.

Step 9

The use of Laboratory Standards determines test accuracy. If the tested value agrees with the true value, the test has been performed accurately. Standards can be mixed on site or purchased from chemical suppliers. Perform standard tests along with the duplicate tests, or about every tenth sample. To avoid the possibility of mixing error, consider the use of purchased standards. For the BOD test, use glucose glutamic acid. To perform a TSS standard, 3M has a product called Filter Aid, or Whatman has Ashless Powder. Each can be used to make a solids standard. Orion, the manufacturer of pH meters, makes an ammonia standard to use with their ammonia probe. A chlorine standard can be purchased or potassium permanganate can be used to mix a standard.

Step 10

Another type of quality assurance test would be to test unknown laboratory standards. Many plants already perform the EPA quality control unknowns each year. These same type of standards are commercially available. 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.

SPIKED SAMPLES

Step 11

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 for spikes is to have 100 percent recovery of spike and the sample. Chapter 11 describes the use of spiked samples.

**CONTROL CHARTS
FOR QUALITY****CONTROL DATA**

Step 12

Quality Control tests produce lots of test data. Chapter 11 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 same 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 to use a set of loose leaf notebooks. Begin with a single notebook that will serve as the main QA/QC document. It should contain 12 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 which may also show the test method. You might also include Appendix 2 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:

Description of lab policy on each major area. Include log sheets and quality test results on reagent water or indicate where these results can be found.

CHAPTERS 7-12:

QUALITY CONTROL SECTION

These chapters document the Quality Control section of your program. Devote one chapter to each type of duplicate 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.

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.

NOTE ON CALCULATING CONTROL LIMITS

Many plants use computer software packages that calculate control limits automatically. Before purchasing a software package, compare its limits with some that have been calculated by hand using Shewhart constants. Shewhart's constants were used in the examples in this manual. Often a software package's limits are simply ± 3 standard deviations. This is fine if the data is all in control. But if it is out of control, the limits will be wrong. Properly used, Shewhart constants will give good limits even when data is out of control.

LABORATORY STANDARD OPERATING PROCEDURE MANUAL

Finally, your QA/QC program should 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.

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

The NPDES Permit

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. Plant operators should know the permit requirements and follow them. Operators should also keep complete records of the plant activities and performance.

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



No. TN00####

Authorization to discharge under the
National Pollutant Discharge Elimination System (NPDES)

Issued By

Tennessee Department of Environment and Conservation
Division of Water Pollution Control
401 Church Street
6th Floor, L & C Annex
Nashville, Tennessee 37243-1534

Under authority of the Tennessee Water Quality Control Act of 1977 (T.C.A. 69-3-101 et seq.) and the delegation of authority from the United States Environmental Protection Agency under the Federal Water Pollution Control Act, as amended by the Clean Water Act of 1977 (33 U.S.C. 1251, et seq.)

Discharger: (Facility name) _____
is authorized to discharge: (Treated municipal wastewater) _____
from a facility located: (Anytown, Tennessee) _____
to receiving waters named: (XYZ River at mile 123) _____

in accordance with effluent limitations, monitoring requirements and other conditions set forth herein.

This permit shall become effective on: _____

This permit shall expire on: _____

Issuance date: _____

Paul E. Davis, Director
Division of Water Pollution Control

CN-0759
RDAs 2352 and 2366

CHAPTER 2

Sample Location

Part 1, section B of the NPDES permit tells 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 must be physically marked with labels or numbers. Make a list of the exact location of the sample points in the plant and identify individuals who will conduct 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 address, phone number, and the name of a contact person. Figure 1 is an example of such a list.

**Fig. 1. Example
Sample Location List**

XYZ Sewer Plant
Sample Locations, Sample Collector, Contract Laboratories

Sample Location

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 bridge on John Doe's farm.

Bio-monitoring 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: Bio-Monitoring, 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 _____

Bio-monitoring _____

Undigested sludge _____

Digested bio-solids _____

SAMPLE COLLECTOR

Composite _____

Grab _____

Stream _____

Bio-monitoring _____

Sludge/Bio-solids _____

CONTRACT LABORATORIES

Tests performed _____

Name _____

Address _____

Phone/Fax _____

Contact person _____

CHAPTER 3

Test Methods

Table 1 A-E, form 40 CFR 136(a), is a listing of the approved test methods that can be used in the wastewater lab. First, check the list for the methods you are using and list them as shown below or on the bench sheet. (See the sample daily report.)

The list begins with tests for bacteria, then inorganic tests are shown alphabetically. Ammonia is listed fourth, BOD is No. 9, CBOD is No. 14, pH is No. 28 under hydrogen ion, solids are No. 53-57 under residue.

Keep a copy of the reference book from which the method was selected on site. If the method from Standard Methods was used, then keep a copy of Standard Methods on hand.

Review the method to make sure this is actually the procedure that is being used in the lab. This material can also be used as a guide when writing a laboratory Standard Operating Procedure (SOP).

Sample Test Methods for Wastewater Laboratory

Test Method Used

TEST METHOD

Dissolved Oxygen	4500-O C
Temperature	5540 C
pH	4500-H+B
Chlorine, Total	4500-Cl G
Residue, TSS	2540 D
Residue, settleable	2540 F
Residue, total	2540 B
Ammonia	4500-NH E
CBOD	5210 B
Fecal Coliform	9222 D

NOTE:

**METHODS HERE ARE
EXAMPLES ONLY.
EACH LAB WILL VARY.**

Table II, 40 CFR 136, lists the approved containers, preservatives, and holding times. This table is included in Appendix I. The list is updated each year and published in July. The copy in Appendix I of this manual is from the 7-1-96 edition. You may find the most up-to-date form of this table at the Government Printing Office web site:

<http://www.access.gpo.gov/cgi-bin/cfrassemble.cgi?title=199840>

Simply scroll down to find the relevant section.

Sampler: _____
 Analyst: _____

TEST and Method		RAW		FINAL		ABOVE		BELOW	
Sample Time									
Daily Test	time		time		time		time		time
D.O. 4500-O C									
Temp. 5540 C									
pH 4500-H+B									
Chlorine 4500-Cl G									
Composite Test time: begin / end									
T.S.S. 2540 D									
Ammonia 4500-NH 3 E									
Settable Solids 2540 F									

Sampler: _____ Sample Time: _____

FECAL COLIFORM

Method 9222D	ml of sample	Time in	Time out	Count	Count*100/mls of sample =	Colonies /100 ml
Control						
Final						
Final						
Final						
Above						
Below						
Control						

TSS WORKSHEET

	RAW	FINAL	ABOVE	BELOW	MIXED LIQUOR	
Final Weight						
Initial Weight						
Difference						
mL used						
TSS						

CHAPTER 4

Sample Data

There are many versions of laboratory bench sheets—some are simple, others 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 indicates 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 who 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. When a contract lab is used, this information is probably already included on the chain-of-custody.

Also, maintain logs of lab equipment temperatures, calibration checks, and other operational logs.

Sample bench sheets, equipment logs, and calibration logs are included below.

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

NOTE: When calculating and recording test data, always use the correct significant figures. Do not just 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 may also consult *Standard Methods*, 19th edition, pages 1-17. Finally, Appendix 2 of this manual includes a thorough discussion of rounding and significant figures.

REAGENT LOG
ACIDS

.02NH2SO4

Boric Acid

[illegible]

0.1N NaOH

[illegible]

FLOW METER CALIBRATION
Annually

[illegible]

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 laboratory is the first step toward assuring quality analyses.

Lab Temperature

The lab temperature should be from 68-78° F. The BOD incubator should register 20° C $\pm$ 1° C. The fecal coliform incubator should be at 44.5 $\pm$ 0.2° C. The TSS drying oven at 103-105° C, and Muffle furnace should be at 550 $\pm$ 50 degrees C. Sample logs for recording these temperatures are included in this chapter.

Clean Glassware

Lab testing always involves the use of some kind of glassware. If this glassware is dirty, the test results are probably wrong. Clean glassware thoroughly by rinsing after use, washing with laboratory detergent, rinsing with tap water and then distilled water. Then rinse again with fresh distilled water. BOD bottles require different cleaning methods. Fecal coliform test equipment must be sterilized.

Dissolved Oxygen (DO) Meter

Calibrate the dissolved oxygen (DO) meter each day. Air calibration and Winkler calibration are acceptable methods. Record settings before and after calibration and document the daily changes. Check air calibrated meters against Winkler Method to verify accuracy. Sodium thiosulfate is an unstable compound that should be standardized daily. There are suppliers that sell stabilized sodium thiosulfate. Also, log the date whenever the probe membrane is changed or cleaned.

pH Meter

Calibrate the pH meter before use with one buffer higher and one lower than the expected value of the sample. If your sample pH is expected to be between four and seven, use these buffers. If it is expected to be between seven and ten, calibrate with the seven and 10 buffers. Also, record probe data such as cleaning times.

Chlorine Test Equipment

A calibration chart is also included for use when checking the calibration of chlorine test equipment. Included at the end of this chapter are charts to log chlorine levels in the contact chamber, and for the weights of chlorine and sulfur dioxide used.

Analytic Balances

It is recommended that analytical balances be checked annually for accuracy by the manufacture 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 2.0 gram, 1.0 gram, and 50.0 mg weight to be able to make checks over the generally used range of 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 is also important to use only fresh ACS 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 this 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 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 commercial laboratory.

The total dissolved solids (TDS) of the water should be less than one milligram per liter ($\text{TDS} < 1.0 \text{ mg/L}$). 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 in performing organic tests like BOD and ammonia. If performing metals tests, use plastic containers to store Type II water. If your plant tests for metals, always check your water for their presence also.

[illegible][illegible]

[illegible][illegible]

Buffer #4 Buffer# 7 Buffer#10

Buffer #4

Buffer# 7

Buffer#10

[illegible]

'Chlorine Weights	'Dechlorination Weights
-------------------	-------------------------

'Chlorine Weights

'Dechlorination Weights

[illegible]

CHAPTER 7

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. The data for the tests are recorded in the sample and duplicate column. The difference between the test values is called the range and should be 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 or solids tests. Unequal sample volumes can obviously 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
- Reagents

Perform duplicate tests on one of every ten 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, 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 will be discussed in Chapter 12.

DUPLICATE TESTS

TEST: _____

ANALYST _____

[illegible]

CHAPTER 8

Blanks

Blanks are another form of Quality Control tests that show interference in the test. The results of a blank test should be zero. Most wastewater labs are probably already using blanks on several tests. Blanks show the absence or presence of a type of error called bias. Often, this error that occurs in all results, can be easily corrected. Eliminate the source of the error where possible. Otherwise, make a note of process bias when reporting results.

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 is often 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

For the fecal coliform test, a blank is included before 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.

A positive control can be run on fecal coliform tests to ensure that the MF-C broth 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 small drop of raw water. The rinse water allows the small sample to spread uniformly across the filter. This is a qualitative test that will 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. 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.

CHAPTER 9

Standards Tests

To show the accuracy of tests performed in the wastewater lab, an analyst should check his/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 is in the center of the bull's eye. The further the shot falls from the center, the less accurate it is. The shooter wants all the shots to be in the bull's eye just as the lab analyst wants all test results to hit the true value dead center. Standard testing should be done at least once every ten 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.

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 may also be purchased from various laboratory suppliers. HACH, for example, has glucose glutamic acid available in 10 ml glass vials. Their product uses 300 mg of glucose and 300 mg of glutamic acid so the true value is 395 mg/L. The acceptable range of values is $395 \text{ mg/L} \pm 60 \text{ mg/L}$. If the standard has 150 mg/L each of glucose and glutamic acid, the true value is 198 mg/L and the range would be $\pm 30.5 \text{ mg/L}$. North Central Labs sells a pre-mixed BOD standard that is 198 ppm; it comes in a 50 ml vial.

BOD acid checks must be done using seeded dilution water. It often takes the experience of several tests to find the right strength of seed to use. As a guide, the seeded dilution water blank should deplete between .6-1.0 mg of dissolved oxygen. The corrected seed depletion (seed control depletion times "*f*") should also be in this range of 0.6-1.0.

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. A mixing chart is included at the end of this chapter.

Chlorine

Chlorine standards can also 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 included at the end of this chapter. Use dilutions in the range of your regular daily tests.

Included in this chapter is a procedure for calibrating a HACH colorimeter using potassium permanganate. 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 two and 10 ml ampules.

Ammonia

Ammonia standards can also be either made in the lab or purchased. As before, mix standards the approximate of the 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 or her own procedure, make whatever improvements need to be made, and 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 a table form. These can be graphed and control charts constructed as the QA/QC program becomes more sophisticated.

Calibrating the HACH DR-100

(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 is typically good for six months.
2. Prepare a working standard KMnO_4 solution by diluting 10.0 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.

<u>ml of working standard dilution with distilled or deionized water</u>	<u>Cl₂ equivalent</u>
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 percent, check the batteries and the stock solution. If the colorimeter is still off by ≥ 10 percent, contact HACH for instructions for data correction or possible repair.
6. A calibration slope may be constructed by graphing the theoretical chlorine values on the vertical axis and the actual reading of the standards on the horizontal axis of standard graph paper. To determine chlorine values of a sample, locate 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.

BOD Standard Solution for Dilution Method
Cat No. 14865-10



HACH Company P. O. Box 907
Ames, Iowa U.S.A. 50010
Telephone 515-232-2533
TWX 910-520-1158
800-227-4224

Proving Dilution Method BOD Test Accuracy

Many factors can affect the performance of the BOD test. To determine reliability of the routine test results, BOD are run on a pure organic standard having a known or determinable BOD. The widely accepted BOD standard is a mixture of glucose and glutamic acid increasing increments (1, 2, 3, and 4 ml) of a BOD standard Voluted Ampule Standard for BOD, Dilution Method, Cat No. 14865-10 are added to the BOD bottles which are then filled with seeded dilution water and incubated at 20 C for five days. The amount of dissolved oxygen remaining after five days is plotted against the volume of standard used and the best straight line through the accepted points is drawn. The slope of the line is determined and this value multiplied by the volume of the BOD bottle gives the BOD of the standard. The sample DO and the Y intercept will be nearly equal (unless there is a substantial blank) and will cancel out this case.

On the basis of a mixed primary standard containing 150 mgL each of glucose and glutamic acid. The five-day BOD varies in magnitude according to the type of seed and in precision according to the quality of seed. Enough seed is needed to assure satisfactory numbers of microorganisms but not so much that the oxygen demand of the seed itself is a major part of the oxygen used during incubation. Determine the BOD of the seeding material as for any other sample. The DO uptake of the seeded dilution water should be between 0.6 and 10 mgL.

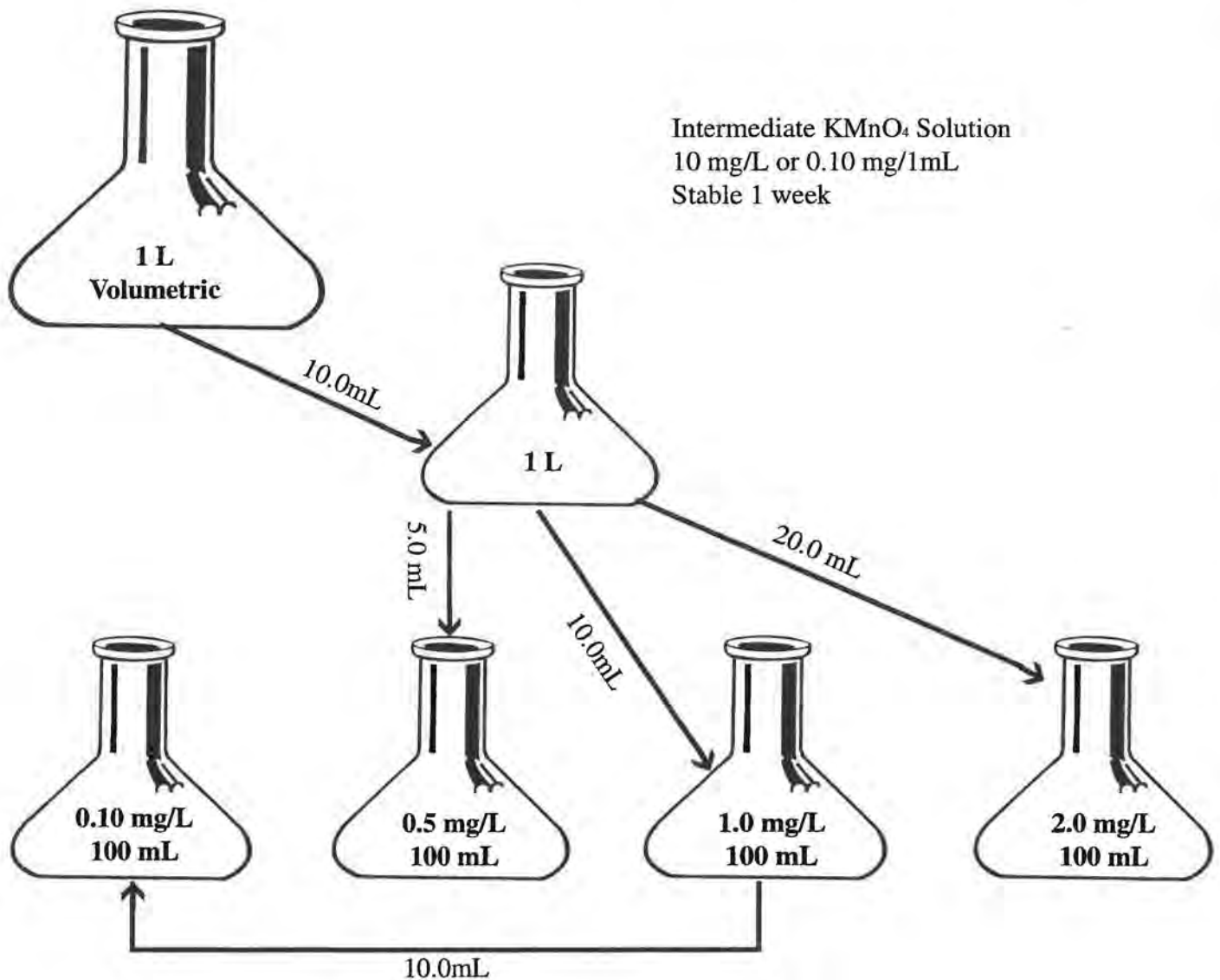
The five-day BOD value of the standard should be in the range of 200-37 mgL. Because the BOD standard prepared by HACH contains 300 mgL each of glucose and glutamic acid, the BOD value determined for the graph must be divided by 2.

Stock Potassium Permanganate Solution

.891 grams or 891 mg in a liter = 1000 mg/l

(stable for several months)

store in amber glass out of sunlight



TSS Check Samples

To prepare TSS check samples from a dry reference material:

1. Dry the reference material in the desiccator (not oven).
2. On an analytical balance, weigh 0.1000 gm of the dry powder, put it in a 1000 mL volumetric flask, bring to the mark with distilled or deionized water and shake well until well suspended.
3. Measure 100 mL and process as usual for environmental samples.
4. A difference of 10 mg should be obtained.
5. Calculation:

$$\frac{(A-B) \times 1000}{\text{VOL used}} = \frac{10 \text{ mg} \times 1000}{100 \text{ mL}} = 100 \text{ mg/L}$$

6.	<u>In 1000 mL</u>	<u>Difference</u>	<u>mg/L</u>
	0.1 gm	10 mg	100
	1.0 gm	100 mg	1000

Material available from Fisher:

Filter Aide (Celite)	Fisher #C211
Whatman Ashless Powder	Whatman #1703-025 Cat. #09-906-6

CHAPTER 10

Laboratory Unknowns and Split Samples

Another self test for accuracy is to test laboratory unknowns. There are several sources for these unknowns. North Central Labs will custom mix standards for fifteen different parameters. Another supplier, Environmental Resource Associates, has 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 on a quarterly basis. The frequency is up to the individual laboratories.

Some wastewater labs split 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 subjectively evaluated 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 12.

CHAPTER 11

Spiked Samples

Spiked samples are a way of performing an accuracy test 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 was 100 and you added 50 in spike material, the value of the spiked sample should equal 150. This would be called 100 percent recovery.

Biochemical Oxygen Demand (BOD) Spike

For the BOD test, a spike bottle can be easily added when doing the glucose glutamic acid (GGA) test. Begin by setting up another bottle. Before adding the dilution water, add the same amount of GGA that was put into the standard test bottles. As with all BOD tests, the final dissolved oxygen level must be above 1.0 mg/L. As a result, the sample and GGA volume might need to be adjusted. For example, if you regularly use BOD dilutions of 10 percent, 15 percent, and 20 percent, and use 4 ml of GGA for the standard test, choose the 10 percent bottle. Add 30 ml of the sample, 4 ml of GGA, then fill with dilution water. To calculate the percent recovery, divide the depletion in the spiked bottle by the sum of the depletion in the sample bottle and the glucose glutamic acid bottle times one hundred:

$$[\text{spiked bottle depletion} / (\text{sample bottle depletion} + \text{GGA bottle depletion})] * 100 = \% \text{ recovery}$$

Example	SAMPLE	DEPLETION	
	Plant effluent	2.0 mg	
	Glucose Glutamic Acid	3.0 mg	
	Spike	4.5 mg	
	Percent Recovery	=	$\frac{4.5}{2.0 + 3.0} * 100 = 90\%$

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 by itself, and the last is for the spike which is the sample and standard. If a 100 ml sample and 100 ml standard sample is regularly tested, 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 net weight of the spike by the sum of the net weight of the sample plus the standard times one hundred:

$$[\text{net weight of spike} / (\text{net weight of sample} + \text{standard})] * 100 = \% \text{ recovery}$$

Example	SAMPLE	NET WEIGHT	
	Plant effluent	0.1 mg	
	TSS standard	0.2 mg	
	Spike	0.35 mg	
	Percent Recovery	=	$\frac{0.35}{0.1 + 0.2} * 100 = 117\%$

Ammonia Spike

When performing the ammonia test with a direct pH meter reading, a spike of ammonia standard can be easily added. When using a 100 ml sample, obtain the sample ammonia value, then add a predetermined 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 logarithmic 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. If you are doing the distillation method, the same ammonia standard can be used to spike the sample. One ml of the 1000 mg/L standard, added to the 500 ml sample, should raise the ammonia level by 2.0 mg/L. If the sample tested to be 0.5 mg/L, adding 1 ml of the 1000 mg/L standard, would raise the level to 2.5 mg/L. With both of these methods, the percent recovery would be calculated the same way as in the other spike tests. Divide the spiked value by the sum of the sample value plus the standard value times one hundred:

$$[\text{spiked value} / (\text{sample value} + \text{standard value})] * 100 = \% \text{ recovery}$$

CHAPTER 12

Control Charts

Control Charts are simply a graph of the quality control test data with some extra lines that allow the analyst to evaluate how well the process is going. An average line or center line is drawn through the middle of the graph. Upper, and perhaps lower, control limits are added to indicate when there is too much variation above or below the average. Control charts can be drawn on plain graph paper or on preprinted forms like the example from SPC Inc.

Charting Blanks

Graph No. 1 shows an average and moving range chart 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.
- 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 will always be one less range value than test value.
- 4) Graph the range data first.
- 5) Compute the average of these 13 numbers (.00012) and draw a center line across the range graph. There is some difference between the computer generated and hand graphs rounding differences.
- 6) To compute the Upper Control Limit (UCL_R), multiply the average range by the constant 3.368. This gives an UCL for the range of .00038, which is drawn on the graph as a broken line.
- 7) Graph the test data on the top half of the page and draw the average line through the graph. The UCL_x and Lower Control Limit (LCL_x) are computed by multiplying the average range (.00012) times the constant of 2.66, then adding the product (.00029) to the average of the test data (-.00017) for the UCL_x , and subtracting .00029 from the average for the LCL_x .

In this example, the TSS blank test process shows control. The data varies up and down between the upper and lower limit. There is, however, a problem with the location of the process average (-0.17 mg) which is below the target value (zero). This procedure indicates bias. From looking at this chart, the analyst would expect that 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 taken 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, thus actually tightening the control limits. Minimizing variation over time shows an improvement in the quality of the testing process.

Charting Standards Tests

Graph No. 2 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 performed weekly on this standard. The control charts were constructed in the same manner as they were for the Blank tests, using the same type of graphs and constants. This example, like the last 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 .23 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 both in control, all the data falls within the control limits and on target.

Duplicate Tests / Relative Percent Difference

Graph No. 3 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 attached log.) 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 could be used if the duplicates were performed on material that always had 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 were done on water with a solids level of 5 mg/L today, and on water with a solids level of 20 mg/L tomorrow, 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 this chapter. 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 No. 3 shows a TSS duplicate test control chart. The relative percent difference is shown on the average graph at the top of the page and the moving range at the bottom.

Purchased Standards

Average Range and Chart

Graph No. 4 is an example of a BOD glucose glutamic acid test control chart. In this example, duplicate 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.

- 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 (UCL_R) for the range by multiplying the average range (14.15) by the constant 3.268. The UCL_R for the range is 46, which is plotted as a line on the graph. (Notice that all the data falls below the UCL_R , which means the data is in control with respect to range. This is a short way of saying that the variation in the BOD values between the two bottles is insignificant. Or, that the test is precise.)
- 5) Graph the average of the two test values and draw a centerline through them. With this data, the centerline is 382.
- 6) Calculate control limits by multiplying the average range (14.15) by a constant of 1.88, then adding this number (27) to 382, to give the $UCL_{\bar{x}}$ (upper control limit of the averages) of 409. Next, subtract 27 from 382 to get 356 — the lower control limit ($LCL_{\bar{x}}$).

The top graph of the average data is out of control, there are points outside the control limits. These points above or below the control limits show excessive variation in the BOD 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 382 mg/L. So again, the analyst needs to work on improving the process location. During the month of January, the analyst had difficulty with 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. 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 Average and Moving Range chart should be used.

Control charts are a way of showing 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. In every process there is variation. 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 charts in this chapter were created using Improvit process control software written by PC Engineering. There are also handmade graphs using blank charts printed by SPC Inc. A plain piece of graph paper can be used for control charts. For actual laboratory work, handmade charts are the preferred method, but for publishing clarity, the electronic version was selected. Whenever choosing a charting 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 is out of control. To have correct statistical process control limits according to Shewhart's rules, the average range and appropriate constant must be used.

References

Donald Wheeler, David Chambers. *Understanding Statistical Process Control*. 1992. SPC Press. Knoxville Tennessee.
P.C. Engineering inc. 6634C Central Avenue, Knoxville Tennessee.

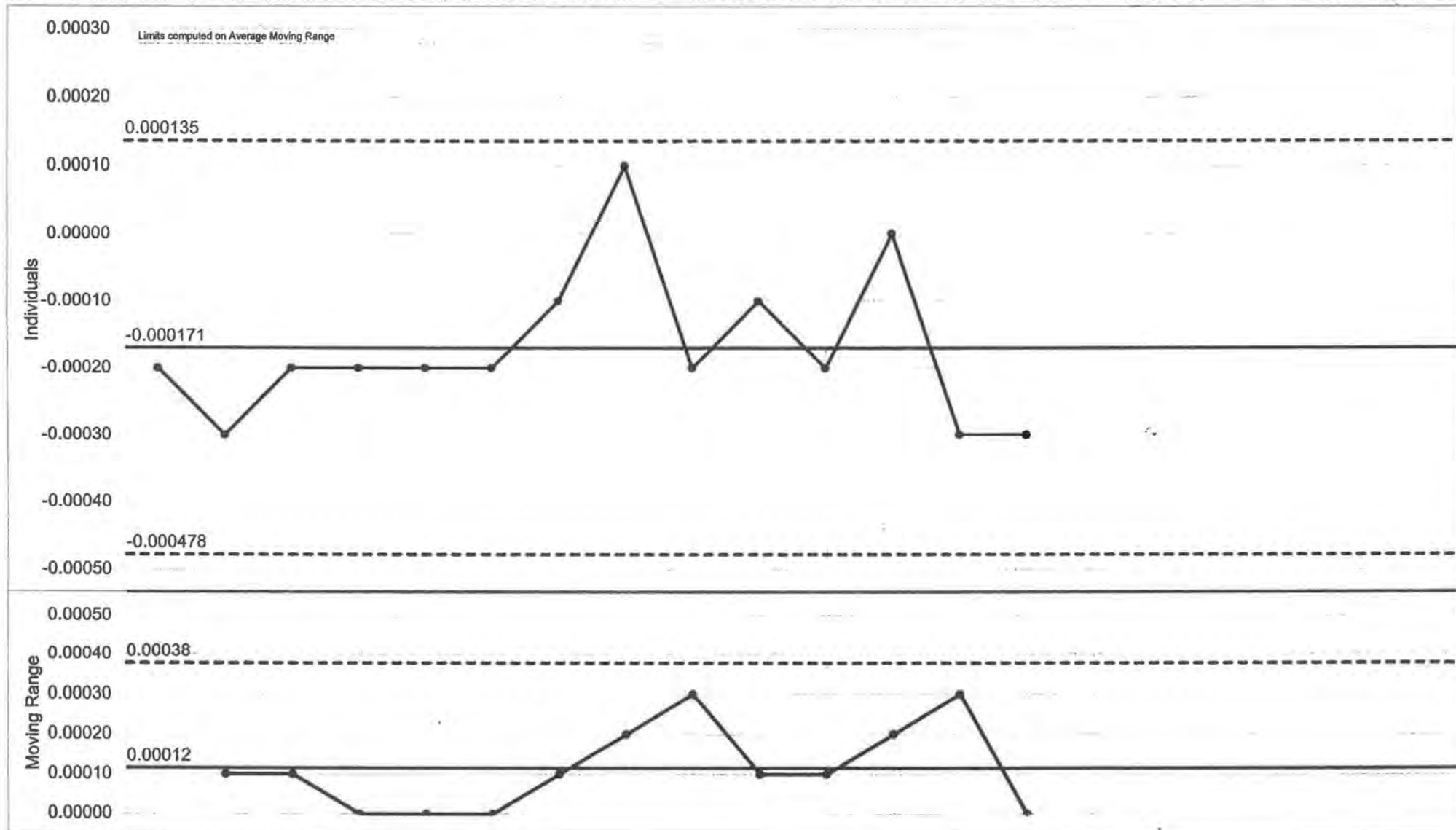
Individuals and Moving Range Chart

Process: TSS Blank
Measure: Target 0.0 mg/L Analyst BNW
Graph #1

Nominal: 0.0
Lower Spec:

Units:
Upper Spec.: Two-Sided Spec.

Date	01/08/95	01/15/95	01/22/95	01/29/95	02/03/95	02/10/95	02/17/95	02/24/95	03/04/95	03/11/95	03/18/95	03/25/95	04/06/95	04/13/95					
Time																			
Notes	1995																		
Measure	-0.0002	-0.0003	-0.0002	-0.0002	-0.0002	-0.0002	-0.0001	0.0001	-0.0002	-0.0001	-0.0002	0.0000	-0.0003	-0.0003					
Range		0.0001	0.0001	0.0000	0.0000	0.0000	0.0001	0.0002	0.0003	0.0001	0.0001	0.0002	0.0003	0.0000					



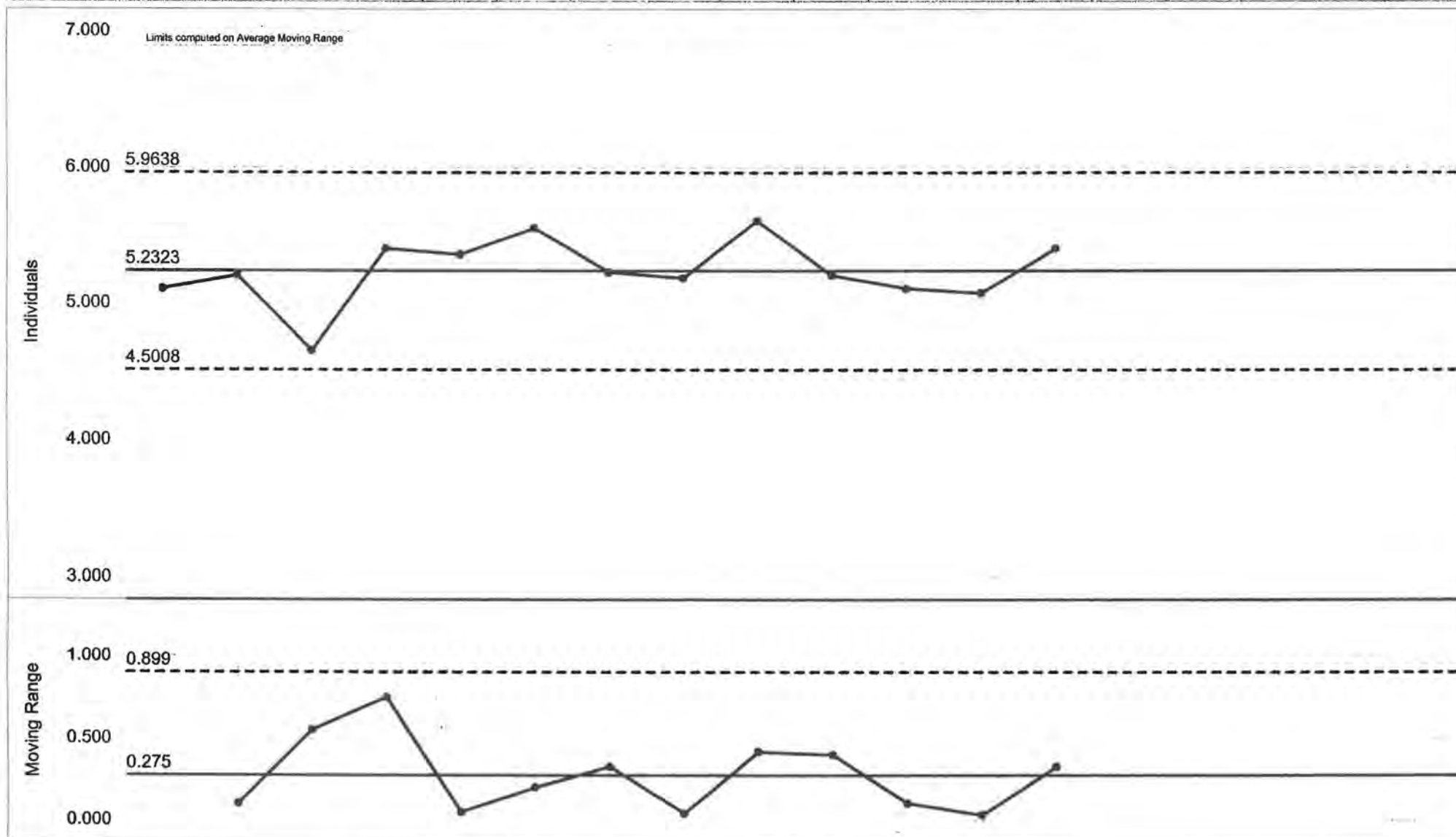
Process: Ammonia Standard
 Measure: Target 5.0 mg/L
 Garph #2

Individuals and Moving Range Chart

Nominal: 0.0
 Lower Spec:

Units:
 Upper Spec.: Two-Sided Spec.

Date	01/26/96	02/02/96	02/09/96	02/16/96	02/23/96	03/05/96	03/12/96	03/19/96	03/26/96	04/01/96	04/08/96	04/15/96	04/22/96					
Time																		
Notes																		
Measure	5.10	5.20	4.65	5.40	5.35	5.55	5.22	5.18	5.60	5.20	5.10	5.07	5.40					
Range		0.10	0.55	0.75	0.05	0.20	0.33	0.04	0.42	0.40	0.10	0.03	0.33					



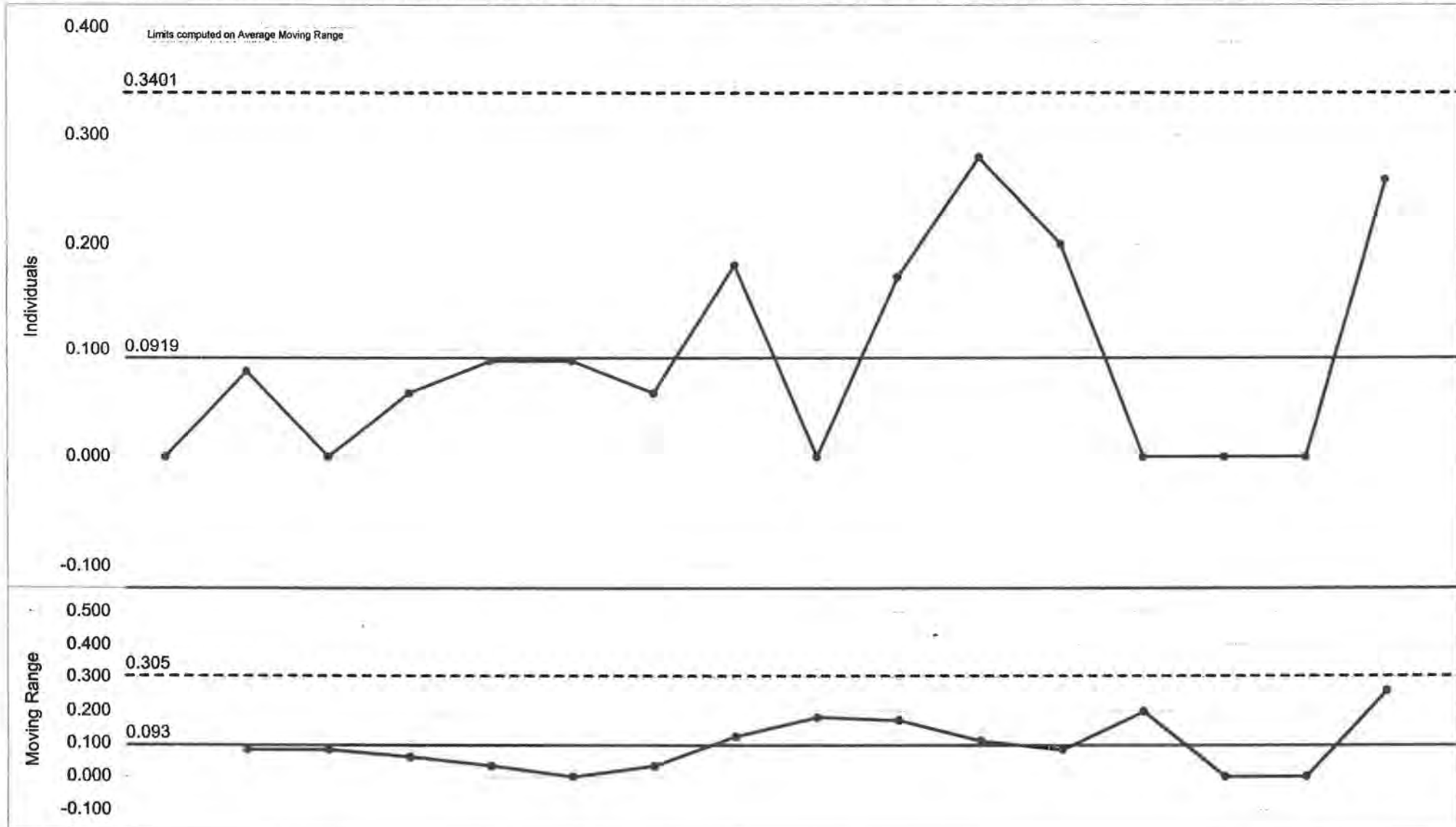
Process: TSS Effluent Duplicate
 Measure: Relative Percent Difference
 Graph #3

Individuals and Moving Range Chart

Nominal: 0.0
 Lower Spec:

Units:
 Upper Spec.: Two-Sided Spec.

Date	01/05/95	01/08/95	01/12/95	03/02/95	03/12/95	05/26/95	05/31/95	05/12/95	05/18/95	07/02/95	07/07/95	07/14/95	07/19/95	09/08/95	09/15/95	09/14/95
Time																
Notes																
Measure	0.00	0.08	0.00	0.06	0.09	0.09	0.06	0.18	0.00	0.17	0.28	0.20	0.00	0.00	0.00	0.26
Range		0.08	0.08	0.06	0.03	0.00	0.03	0.12	0.18	0.17	0.11	0.08	0.20	0.00	0.00	0.26



Process: Glucose Glutamic Acid
Measure: Target 395mg/L +/- 60mg/L

Average and Range Chart

Nominal: 395.0

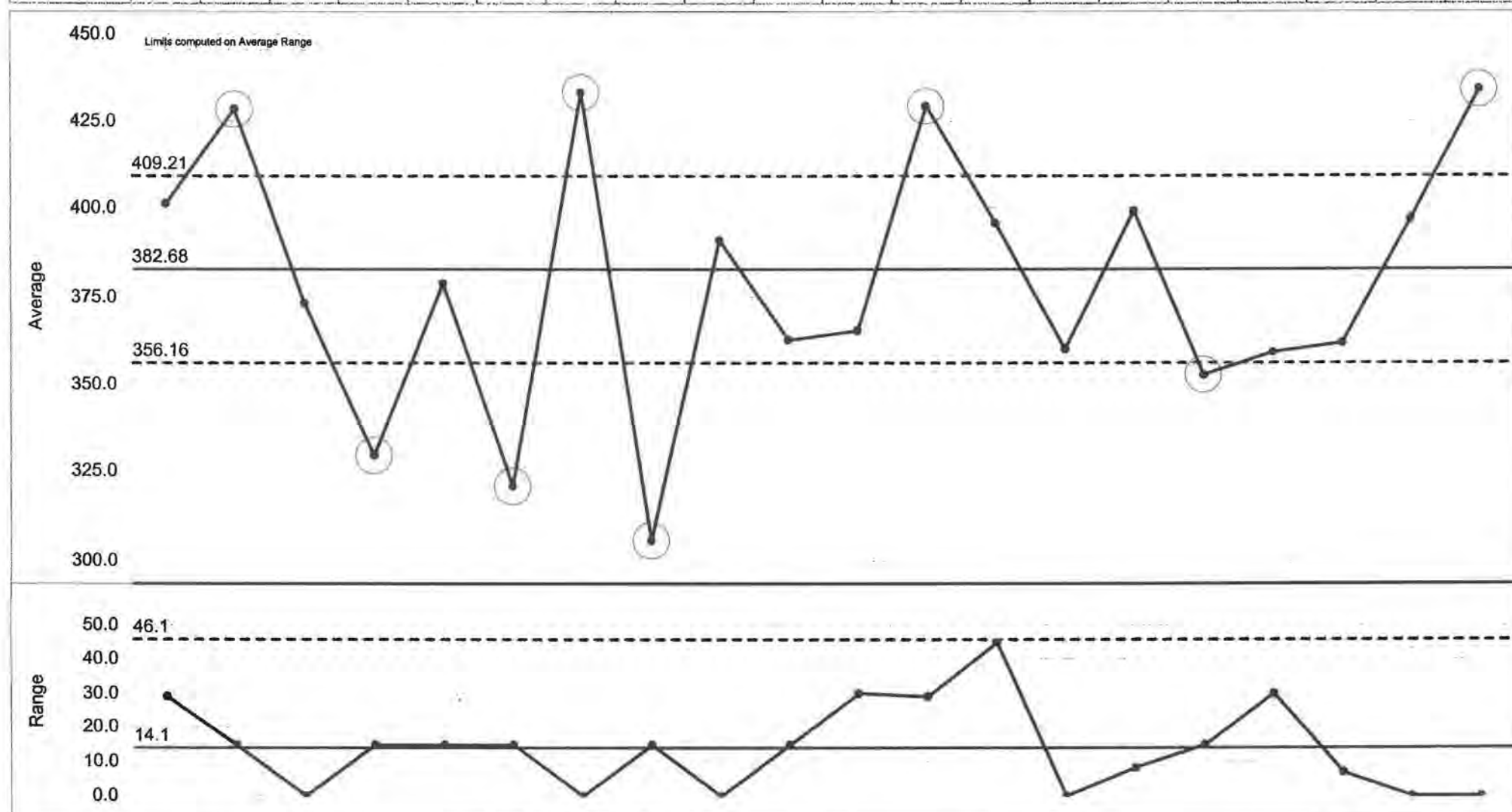
Lower Spec: 335.0

Units:

Upper Spec.: 455.0 Two-Sided Spec.

Graph #4

Date	11/18/94	11/23/94	11/25/94	11/29/94	12/01/94	12/09/94	12/17/94	12/22/94	12/30/94	1/06/95	1/13/95	1/17/95	1/24/95	1/30/95	2/05/95	2/04/95	2/11/95	2/15/95	2/22/95	2/27/95	3/06/95	3/15/95
Time																						
Notes																						
1	416	421	373	322	386	328	433	313	391	370	380	415	373	360	395	360	374	358	397	434		
2	387	436	373	337	371	313	433	298	391	355	350	444	418	360	403	345	344	365	397	434		
Average	401.5	428.5	373.0	329.5	378.5	320.5	433.0	305.5	391.0	362.5	365.0	429.5	395.5	360.0	399.0	352.5	359.0	361.5	397.0	434.0		
Range	29	15	0	15	15	15	0	15	0	15	30	29	45	0	8	15	30	7	0	0		





STATISTICAL
PROCESS
CONTROLS, INC.

CHART for INDIVIDUAL VALUES and MOVING RANGE

1 60 25

PRODUCT TSS Blank BNW

MEASUREMENT 100ml Distilled Water

DATE

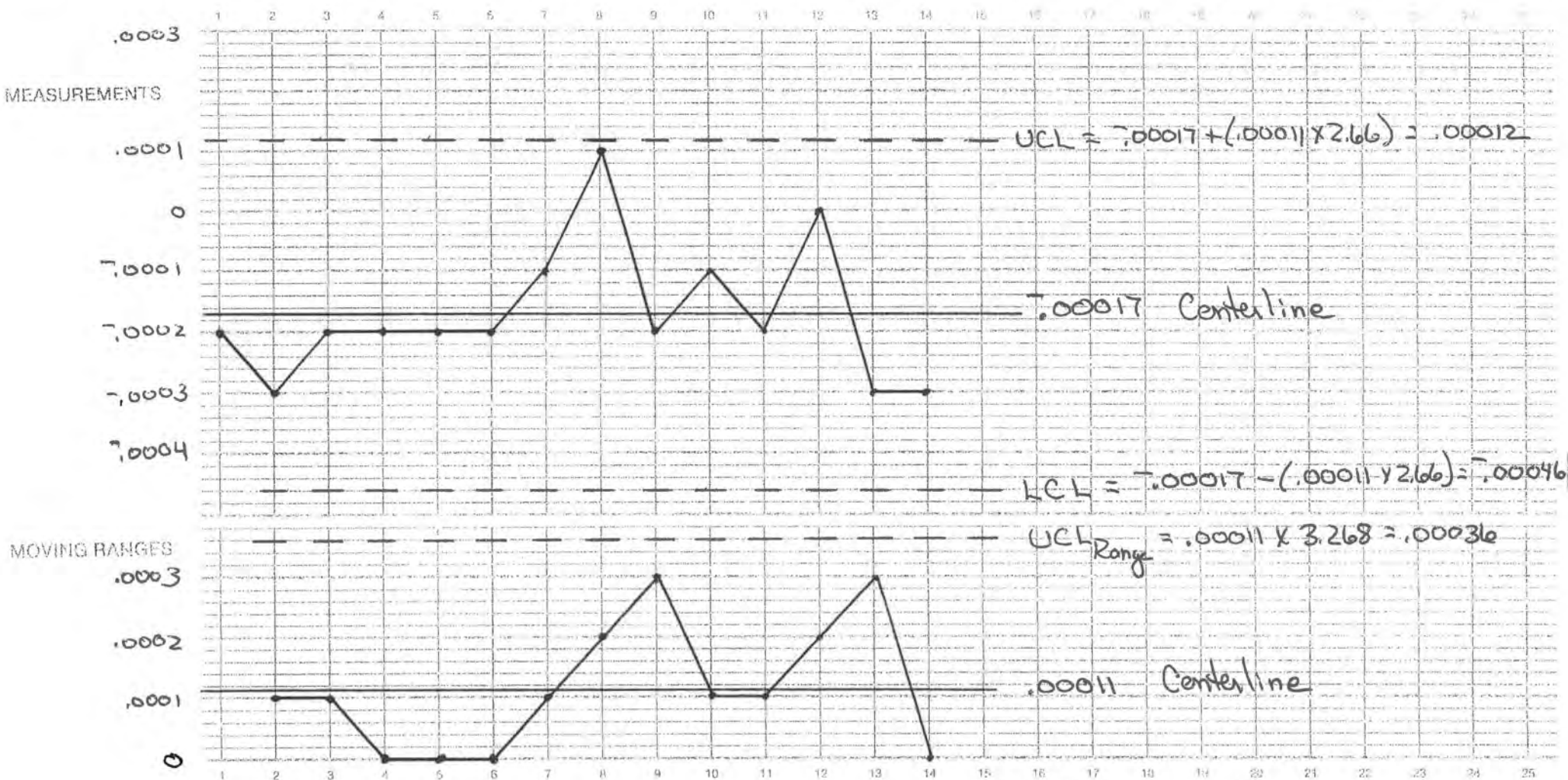
TIME 1-8-95 1-15 1-22 1-29 3-3 3-10 3-17 3-24 5-4 5-11 5-18 5-25 7-6 7-13

NOTES

measurements in grams

MEASUREMENTS -.0002 .0003 .0002 .0002 .0002 .0002 .0001 .0001 .0002 .0001 .0002 .0001 .0003 .0003

MOVING RANGES .0001 .0001 0 0 0 .0001 .0002 .0003 .0001 .0001 .0002 .0003 0



PART III

Appendix 1

40 CFR 136, Table 1A

Table IA.--List of Approved Biological Methods

Parameter and units	Method \1\	EPA	Standard methods, 18th Ed.	USGS
1. Coliform (fecal), number per 100 mL.	Most Probable Number (MPN), 5 tube, 3 dilution, or Membrane filter (MF) \2\, single step.	p. 132 \3\ p. 124 \3\	9221C E \4\ 9222D \4\	B-0050-85 \5\
2. Coliform (fecal) in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or MF, single step \6\.....	p. 132 \3\ p. 124 \3\	9221C E \4\ 9222D \4\	
3. Coliform (total), number per 100 mL. or.	MPN, 5 tube, 3 dilution, MF \2\ single step or two step.	p. 114 \3\ p. 108 \3\	9221B \4\ 9222B \4\	B-0025-85 \5\
4. Coliform (total), in presence of chlorine, number or per 100 mL.	MPN, 5 tube, 3 dilution, MF \2\ with enrichment	p. 114 \3\ p. 111 \3\	9221B \4\ 9222(B+B.5c) \4\	
5. Fecal streptococci, number per 100 mL.	MPN, 5 tube, 3 dilution MF \2\, or Plate count	p. 139 \3\ p. 136 \3\ p. 143 \3\	9230B \4\ 9230C \4\	B-0055-85 \5\
Aquatic Toxicity:				
6. Toxicity, acute, fresh water organisms, LC50, percent effluent.	Daphnia, Ceriodaphnia, Fathead Minnow, Rainbow Trout, Brook Trout, or Bannerfish Shiner mortality.	Sec. 9 \7\		
7. Toxicity, acute, estuarine and marine organisms, LC50, or Menidia spp. mortality, percent effluent.	Mysid, Sheepshead Minnow, Sec. 9 \7\			
8. Toxicity, chronic, fresh water organisms, NOEC or IC25, percent effluent.	Fathead minnow larval survival and growth.	1000.0 \8\ 1001.0 \8\		
	Fathead minnow embryo-larval survival and teratogenicity.	1002.0 \8\ 1003.0 \8\		
	Ceriodaphnia survival and reproduction.			
	Selenastrum growth			
9. Toxicity, chronic, estuarine and marine organisms, NOEC or IC25, percent effluent.	Sheepshead minnow larval survival and growth. Sheep-head minnow embryolarval survival and teratogenicity.	1004.0 \9\ 1005.0 \9\		
	Menidia beryllina larval and growth. Mysidopsis bahia survival, growth, and fecundity.	1006.0 \9\ 1007.0 \9\ 1008.0 \9\		
	Arbacia punctulata fertilization.	1009.0 \9\		
	Champia parvula reproduction.			

Notes to Table IA:

\1\ The method must be specified when results are reported.

\2\ A 0.45 um membrane filter (MF) or other pore size certified by the manufacturer to fully retain organisms to be cultivated and to be free of extractables which could interfere with their growth.

\3\ USEPA. 1978. Microbiological Methods for Monitoring the Environment, Water, and Wastes. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA/600/8-78/017.

\4\ APHA. 1992. Standard Methods for the Examination of Water and Wastewater. American Public Health Association. 18th Edition. Amer. Publ. Hlth Assoc., Washington, DC.

\5\ USGS. 1989. U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Laboratory Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples, U.S. Geological Survey, U.S. Department of Interior, Reston, Virginia.

\6\ Because the MF technique usually yields low and variable recovery from chlorinated wastewaters, the Most Probable Number method will be required to resolve any controversies.

\7\ USEPA. 1993. Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms. Fourth Edition. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio. August 1993, EPA/600/4-90/027F.

\8\ USEPA. 1994. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. Third Edition. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency USEPA. 1994, Cincinnati, Ohio (July 1994, EPA/600/4-91/002).

\9\ Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms. Second Edition. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio (July 1994, EPA/600/4-91/003). These methods do not apply to marine waters of the Pacific Ocean.

Table IB.--List of Approved Inorganic Test Procedures

Parameter, units and method	EPA	STD methods 18th ed.	ASTM	USGS \2\	Other
1. Acidity, as CaCO ₃ <INF>3, mg/L: Electrometric endpoint or phenolphthalein endpoint.	305.1	2310 B(4a)	D1067-92		
2. Alkalinity, as CaCO ₃ <INF>3, mg/L: Electrometric or Colorimetric titration to pH 4.5, manual or automated.	310.1 310.2	2320 B	D1067-92	I-1030-85 I-2030-85.	973.43.\3\
3. Aluminum--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration \36\.	202.1	3111 D		I-3051-85	
AA furnace	202.2	3113 B			
Inductively Coupled Plasma/ \5\	200.7	3120 B			
Atomic Emission Spectrometry (ICP/AES) \36\.					
Direct Current Plasma(DCP) \36\.			D4190-82(88)		Note 34.
Colorimetric (Eriochrome cyanine R)		3500-Al D			
4. Ammonia (as N), mg/L: Manual, distillation (at pH 9.5),\6\ followed by. Nesslerization	350.2	4500-NH<INF>3B			973.49.\3\
Titration	350.2	4500-NH<INF>3C	D1426-93(A)	I-3520-85	973.49.\3\
Electrode	350.3	4500-NH<INF>3E	D1426-93(B)		
Automated phenate, or. Automated electrode	350.1	4500-NH<INF>3F or G 4500-NH<INF>3H		I-4523-85	Note 7.
5. Antimony- Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration \36\.	204.1	3111 B			
AA furnace	204.2	3113 B			
ICP/AES \36\ \5\	200.7	3120 B			
6. Arsenic-Total,\4\ mg/L; Digestion \4\ followed by. AA gaseous hydride	206.5				
AA furnace	206.3	3114 B 4.d.	D2972-93(B)	I-3062-85	
ICP/AES,\36\ or \5\	206.2	3113 B	D2972-93(C)		
Colorimetric (SDDC)	200.7	3120 B			
206.4		3500-As C	D2972-93(A)	I-3060-85	
7. Barium--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration \36\.	208.1	3111 D		I-3084-85	
AA furnace	208.2	3113 B	D4382-91		
ICP/AES \36\ \5\	200.7	3120 B			Note 34.
DCP \36\.					
8. Beryllium--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration	210.1	3111 D	D3645-93(88)(A)	I-3095-85	
AA furnace	210.2	3113 B	D3645-93(88)(B)		
ICP/AES \5\	200.7	3120 B			
DCP, or. Colorimetric (aluminum)3500-Be D			D4190-82(88)		Note 34..
9. Biochemical oxygen demand (BOD<INF>5), mg/L: Dissolved Oxygen Depletion	405.1	5210 B		I-1578-78 \8\	973.44.\3\ p.
17.\9\					
10. Boron \37\--Total, mg/L: Colorimetric (curcumin)	212.3	4500-B B		I-3112-85	
ICP/AES, or. \5\	200.7	3120 B			
DCP.			D4190-82(88)		Note 34
11. Bromide, mg/L: Titrimetric.	320.1		D1246-82(88)(C)	I-1125-85	p. S44.\10\
12. Cadmium--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration \36\.	213.1	3111 B or C.	D3557-90(A or B)	I-3135-85/ I-3136-85	974.27.\3\
p.37.\9\					
AA furnace	213.2	3113 B	D3557-90(D)		
ICP/AES \36\ \5\	200.7	3120 B.		I-1472-85	
DCP \36\			D4190-82(88)		Note 34.
Voltametry,\11\ or Colorimetric (Dithizone)		3500-Cd D	D3557-90(C)		

13. Calcium--Total, \4\ mg/L; Digestion \4\ followed by: AA direct aspiration ICP/AES \5\ DCP, or Titrimetric (EDTA)	215.1 200.7 215.2	3111 B. 3120 B 3500-Ca D	D511-93(B) D511-93(A)	I-3152-85	Note 34.
14. Carbonaceous biochemical oxygen demand (CBOD<INF>5), mg/L\12\; Dissolved Oxygen Depletion with nitrification inhibitor.		5210 B			
15. Chemical oxygen demand (COD), mg/L; Titrimetric, or.	410.1 410.2 410.3	5220 C	D1252-88(A)	I-3560-85 I-3562-85	973.46,\3\ p. 17,\9\
Spectrophotometric, manual or automated.	410.4	5220 D	D1252-88(B)	I-3561-85.	Notes 13 or 14.
16. Chloride, mg/L: Titrimetric (silver nitrate) or. (Mercuric nitrate) Colorimetric, manual or. Automated (Ferricyanide)	 325.3 325.1 or 325.2	4500-Cl-B 4500-Cl-C 4500-Cl-E.	D512-89(B) D512-89(A)	I-1183-85 I-1184-85 I-1187-85 I-2187-85	973.51,\3\
17. Chlorine--Total residual, mg/L; Titrimetric: Amperometric direct. Iodometric direct Back titration ether end- point \15\ or. DPD-FAS Spectrophotometric, DPD Or Electrode	330.1 330.3 330.2 330.4 330.5	4500-Cl D. 4500-Cl B 4500-Cl C 4500-Cl F 4500-Cl G	D1253-86(92)		Note 16.
18. Chromium VI dissolved, mg/ L; 0.45 micron filtration followed by: AA chelation-extraction or Colorimetric (Diphenylcarbazide).	218.4	3111 C 3500-Cr D	D1687-92(A)	I-1232-85 I-1230-85	
19. Chromium--Total, \4\ mg/L, Digestion \4\ followed by: AA direct aspiration \36\ AA chelation-extraction. AA furnace ICP/AES \36\ \5\ DCP,\36\ or. Colorimetric (Diphenylcarbazide)	218.1 218.3 218.2 200.7	3111 B. 3111 C 3113 B 3120 B	D1687-92(B) D1687-92(C) D4190-82(88)	I-3236-85	974.27,\3\ Note 34.
20. Cobalt--Total, \4\ mg/L; Digestion \4\ followed by: AA direct aspiration AA furnace ICP/AES \5\ DCP.	219.1 219.2 200.7	3111 B or C. 3113 B. 3120 B	D3558-90(A or B) D3558-90(C) D4190-82(88)	I-3239-85	p. 37,\9\ Note 34.
21. Color platinum cobalt units or dominant wavelength, hue, luminance purity: Colorimetric (ADMI), or (Platinum cobalt), or Spectrophotometric.	110.1 110.2 110.3	2120 E 2120 B 2120 C		I-1250-85	Note 18.
22. Copper--Total, <SUP>4 mg/L; Digestion <SUP>4 followed by: AA direct aspiration\36	220.1	3111 B or C	D1688-90(A or B)	I-3270-85 or I3271-85	974.27 3 p.
37.<SUP>9 AA furnace ICP/AES 36- 5 DCP 36 or. Colorimetric (Neocuproine) or. (Bicinchoninate). Or E	220.2 200.7	3113 B. 3120 B	D1688-90(C) D4190-82(88)		Note 34.
23. Cyanide--Total, mg/L: Manual distillation with MgCl<INF>2 followed by. Titrimetric, or Spectrophotometric, manual or. Automated	335.2 2031	4500-CN C 4500-CN D. 4500-CN E 335.3	D2036-91(A) D2036-91(A)	I-3300-85	p. 22.
24. Cyanide amenable to chlorination,mg/L:					

Manual distillation with MgCl ₂ followed by titrimetric or Spectrophotometric.	335.1	4500-CN G	D2036-91(B)		
25. Fluoride--Total, mg/L: Manual distillation <SUP>6 followed by.		4500-F B			
Electrode, manual or Automated.	340.2	4500-F C	D1179-93(B)	I-4327-85	
Colorimetric (SPADNS)	340.1	4500-F D.	D1179-93(A)		
Or Automated complexone	340.3	4500-F E			
26. Gold--Total, <SUP>4 mg/L; Digestion <SUP>4 followed by:					
AA direct aspiration	231.1	3111 B			
AA furnace, or	231.2			Note 34.	
DCP.					
27. Hardness--Total, as CaCO ₃ , mg/L					
Automated colorimetric	130.1				
Titrimetric (EDTA), or Ca plus Mg as their carbonates, by inductively coupled plasma or AA direct aspiration. (See Parameters 13 and 33).	130.2	2340 B or C	D1126-86(92)	I-1338-85	973.52B.<SUP>3
28. Hydrogen ion (pH), pH units Electrometric measurement, or. Automated electrode	150.1	4500-H<SUP>+ B	D1293-84(90)(A or B)	I-1586-85	973.41.<SUP>3 Note 21.
29. Iridium--Total, <SUP>4 mg/L; Digestion <SUP>4 followed by:					
AA direct aspiration or	235.1	3111 B			
AA furnace	235.2				
30. Iron--Total, <SUP>4 mg/L; Digestion <SUP>4 followed by:					
AA direct aspiration <SUP>36	236.1	3111 B or C	D1068-90(A or B)	I-3381-85	974.27.<SUP>3
AA furnace	236.2	3113 B.	D1068-90(C)		
ICP/AES <SUP>36<SUP>5	200.7	3120 B			
DCP <SUP>36 or.<SUP><SUP>			D4190-82(88)		Note 34.
Colorimetric (Phenanthroline).		3500-Fe D.	D1068-90(D)		Note 22.
31. Kjeldahl Nitrogen--Total, (as N), mg/L:					
Digestion and distillation followed by	351.3	4500-NH<INF>3B or C	D3590-89(A)		
Titration	351.3	4500-NH<INF>3E.	D3590-89(A)		973.48<INF>3.
Nesslerization	351.3	4500-NH<INF>3C	D3590-89(A)		
Electrode.	351.3	4500-NH<INF>3F or G.			
Automated phenate colorimetric.	351.1			I-4551-78	<INF>8<INF>
Semi-automated block	351.2		D3590-89(B)		
Manual or block digester	351.4		D3590-89(A)		
Block Digester, followed by:					
Auto distillation and Titration, or.					Note 39.
Nesslerization.					Note 40.
Flow injection gas diffusion.					Note 41.
32. Lead--Total, <SUP>4 mg/L; Digestion <SUP>4 followed by:					
AA direct aspiration <SUP>36	239.1	3111 B or C	D3559-90(A or B)	I-3399-85	974.27.<SUP>3
AA furnace	239.2	3113 B	D3559-90(D)		
ICP/AES <SUP>36<SUP>5	200.7	3120 B			
DCP <SUP>36<SUP><SUP>			D4190-82(88)		Note 34.
Voltametry <SUP>11 or<SUP>.			D3559-90(C)		
Colorimetric (Dithizone)		3500-Pb D			
33. Magnesium--Total, <SUP>4 mg/L; Digestion <SUP>4 followed by:					

AA direct aspiration. ICP/AES \5\ DCP, or Gravimetric.	242.1 200.7	3111 B 3120 B 3500MgD		D511-93(B)	I-3447-85	974.27.\3\ Note 34.
34. Manganese--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration \36\ AA furnace ICP/AES \36\5\ DCP \36\ or. Colorimetric (Persulfate), or.(Periodate)	243.1 243.2 200.7	3111 B 3113 B 3120 B 3500MnD.		D858-90(A or B) D858-90(C) D4190-82(88)	I-3454-85 Note 23	974.27.\3\ Note 34. 920.203.\3\
35. Mercury--Total,\4\ mg/L: Cold vapor, manual or. Automated.	245.1 245.2	3112 B.		D3223-91	I-3462-85.	977.22.\3\
36. Molybdenum--Total,\4\ mg/ L; Digestion \4\ followed by: AA direct aspiration AA furnace ICP/AES \5\ 200.7 DCP	246.1 246.2	3111 D. 3113 B 3120 B			I-3490-85	 Note 34.
37. Nickel--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration \36\ AA furnace ICP/AES \36\5\ DCP \36\, or. Colorimetric (heptoxime)	249.1 249.2 200.7	3111 B 3113 B 3120 B 3500-NiD		D1886-90(A or B) D1886-90(C) D4190-82(88)	I-3499-85	 Note 34.
38. Nitrate (as N), mg/L: Colorimetric (Brucinesulfate)or Nitratenitrite N minus Nitrite N (See parameters 39 and 40).		352.1				973.50,\3\ 419 D,\17\ p. 28.\9\
39. Nitrate-nitrite (as N), mg/ L: Cadmium reduction, Manual or. Automated, or Automated hydrazine		353.3 353.2 353.1	4500-NO<INF>3- E. 4500-NO<INF>3- F 4500-NO<INF>3- H	D3867-90(B) D3867-90(A)	I-4545-85	
40. Nitrite (as N), mg/L; Spectrophotometric: Manual or. Automated (Diazotization).		354.1	4500-NO<INF>2- B.		I-4540-85	Note 25.
41. Oil and grease--Total recoverable, mg/L: Gravimetric (extraction)		413.1	5520 B <SUP>38			
42. Organic carbon--Total (TOC), mg/L Combustion or oxidation		415.1	5310 B, C, or D	D2579-93 (A or B).		973.47,3 p. 14.24
43. Organic nitrogen (as N), mg/L: Total Kjeldahl N (Parameter 31) minus ammonia N (Parameter 4)						
44. Orthophosphate (as P), mg/ L; Ascorbic acid method: Automated, or Manual single reagent		365.1 365.2	4500-P.F. 4500-P.E	D515-88(A)	I-4601-85.	973.56.3
973.55 3. Manual two reagent.		365.3				
45. Osmium--Total <SUP>4, mg/L; Digestion <SUP>4 followed by: AA direct aspiration, or.. AA furnace.		252.1 252.2	3111 D			
46. Oxygen, dissolved, mg/L: Winkler (Azide 973.45B.3 modification), or. Electrode		360.2 360.1	4500-O C 4500-O G	D888-92(A) D888-92(B)		I-1575-78 <SUP>8 I-1576-78 <SUP>8
47. Palladium--Total,<SUP>4 mg/L; Digestion <SUP>4 followed by: AA direct aspiration, or AA furnace. DCP.	253.1 253.2	3111 B				p. S27.<SUP>1 p. S28.<SUP>10 Note 34.

48. Phenols, mg/L: Manual distillation \26\..	420.1				Note 27.
Followed by:					
Colorimetric (4AAP)	420.1				Note 27.
manual, or					
Automated \19\	420.2				
49. Phosphorus (elemental), mg/ L: Gas-liquid chromatography.					Note 28.
50. Phosphorus--Total, mg/L:					
Persulfate digestion	365.2	4500-P B.5.			973.55.\3\
followed by:					
Manual or	365.2	4500-P E	D515-88(A)		
	365.3				
Automated ascorbic acid	365.1	4500-P F.		I-4600-85	973.56.\3\
reduction.					
Semi-automated block	365.4		D515-88(B)		
digestor.					
51. Platinum--Total,\4\ mg/L; Digestion \4\ followed by:					
AA direct aspiration.	255.1	3111 B			
AA furnace	255.2				
DCP					Note 34.
52. Potassium-- Total,\4\ mg/L; Digestion \4\ followed by:					
AA direct aspiration	258.1	3111 B.		I-3630-85.	973.53.\3\
ICP/AES.\5\ 200.7 3120 B					
Flame photometric, or.		3500-K D			
Colorimetric.					
53. Residue--Total, mg/L: Gravimetric, 103-105 deg.	160.3	2540 B		I-3750-85	
54. Residue--filterable, mg/L: Gravimetric, 180 deg	160.1	2540 C		I-1750-85	
55. Residue--nonfilterable (TSS), mg/L:					
Gravimetric, 103-105 deg.	160.2	2540 D		I-3765-85	
post washing of residue.					
56. Residue--settleable, mg/L: Volumetric, (Imhoff cone),	160.5	2540 F			
or gravimetric.					
57. Residue--Volatile, mg/L: Gravimetric, 550 deg	160.4			I-3753-85	
58. Rhodium--Total,\4\ mg/L; Digestion \4\ followed by:					
AA direct aspiration, or..	265.1	3111 B			
AA furnace.	265.2				
59. Ruthenium--Total,\4\ mg/L; Digestion \4\ followed by:					
AA direct aspiration, or..	267.1	3111 B			
AA furnace.	267.2				
60. Selenium--Total,\4\ mg/L; Digestion \4\ followed by:					
AA furnace	270.2	3113 B	D3859-93(B)		
ICP/AES.\36\ or\5\	200.7	3120 B			
AA gaseous hydride	3114 B		D3859-93(A)	I-3667-85	
61. Silica \37\--Dissolved, mg/ L; 0.45 micron filtration					
followed by:					
Colorimetric, Manual or...	370.1	4500-Si D	D859-88	I-1700-85	
Automated				I-2700-85	
(Molybdosilicate), or.					
ICP. \5\	200.7	3120 B			
62. Silver--Total,\4\ mg/L; Digestion <SUP>4, <SUP>29					
followed by:AA direct aspiration	272.1	3111 B or C		I-3720-85	974.27,\3 p. 37.\9\
AA furnace	272.2	3113 B			
ICP/AES\5\	200.7	3120 B			
DCP					Note 34.
63. Sodium--Total,\4\ mg/L; Digestion \4\ followed by:					
AA direct aspiration	273.1	3111 B		I-3735-85	973.54.\3\
ICP/AES.\5\	200.7	3120 B			
DCP, orNote 34.					
Flame photometric3500 Na D					

64. Specific conductance, micromhos/cm at 25 deg.C: Wheatstone bridge 120.1	2510 B.		D1125-91(A)	I-1780-85	973.40.\3\
65. Sulfate (as SO<INF>4), mg/L: Automated colorimetric (barium chloranilate). Gravimetric. Turbidimetric, or.	375.1 375.3 375.4	4500-SO<INF>4-2 C or D.	D516-90		925.54.\3\ 426C.\30\
66. Sulfide (as S), mg/L: Titrimetric (iodine), or. Colorimetric (methylene blue).	376.1 376.2	4500-S<SUP>-2E 4500-S<SUP>-2D		I-3840-85	
67. Sulfite (as SO<INF>3), mg/L: Titrimetric (iodine-iodate).	377.1	4500-SO<INF>3-2 B			
68. Surfactants, mg/L: Colorimetric (methylene blue).	425.1	5540 C.	D2330-88		
69. Temperature, deg.C: Thermometric	170.1	2550 B.			Note 32.
70. Thallium--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration AA furnace. ICP/AES, or,\5\	279.1 279.2 200.7	3111 B 3120 B			
71. Tin--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration AA furnace, or ICP/AES \5\	282.1 282.2 200.7	3111 B. I-3850-78 \8\ 3113 B			
72. Titanium--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration AA furnace DCP	283.1 283.2	3111 D			Note 34.
73. Turbidity, NTU: Nephelometric	180.1	2130 B.D1889-88(A)		I-3860-85	
74. Vanadium--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration AA furnace ICP/AES \5\ DCP, or. Colorimetric (Gallic acid)	286.1 286.2 200.7 3500-V D	3111 D 3120 B	D3373-93 D4190-82(88)		Note 34.
75. Zinc--Total,\4\ mg/L; Digestion \4\ followed by: AA direct aspiration \36\ AA furnace ICP/AES \36\5\ DCP,\36\ or. Colorimetric (Dithizone) or.(Zincon)	289.1 289.2 200.7	3111 B or C 3120 B 3500-Zn E 3500-Zn F	D1691-90 (A or B) D4190-82(88)	I-3900-85.	974.27,\3\ p. 37.\9\ Note 34. Note 33.

Table IB Notes:

\1\ "Methods for Chemical Analysis of Water and Wastes", Environmental Protection Agency, Environmental Monitoring Systems Laboratory-Cincinnati (EMSL-CI), EPA-600/4-79-020, Revised March 1983 and 1979 where applicable.

\2\ Fishman, M.J., et al, "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments," U.S. Department of the Interior, Techniques of Water--Resource Investigations of the U.S. Geological Survey, Denver, CO, Revised 1989, unless otherwise stated.

\3\ "Official Methods of Analysis of the Association of Official Analytical Chemists," methods manual, 15th ed. (1990).

\4\ For the determination of total metals the sample is not filtered before processing. A digestion procedure is required to solubilize suspended material and to destroy possible organic-metal complexes. Two digestion procedures are given in "Methods for Chemical Analysis of Water and Wastes, 1979 and 1983". One (section 4.1.3), is a vigorous digestion using nitric acid. A less vigorous digestion using nitric and hydrochloric acids (section 4.1.4) is preferred; however, the analyst should be cautioned that this mild digestion may not suffice for all samples types. Particularly, if a colorimetric procedure is to be employed, it is necessary to ensure that all organo-metallic bonds be broken so that the metal is in a reactive state. In those situations, the vigorous digestion is to be preferred making certain that at no time does the sample go to dryness. Samples containing large amounts of organic materials may also benefit by this vigorous digestion, however, vigorous digestion with concentrated nitric acid will convert antimony and tin to insoluble oxides and render them unavailable for analysis. Use of ICP/AES as well as determinations for certain elements such as antimony, arsenic, the noble metals, mercury, selenium, silver, tin, and titanium require a modified sample digestion procedure and in all cases the method write-up should be consulted for specific instructions and/or cautions.

Note to Table IB Note 4: If the digestion procedure for direct aspiration AA included in one of the other approved references is different than the above, the EPA procedure must be used.

Dissolved metals are defined as those constituents which will pass through a 0.45 micron membrane filter. Following filtration of the sample, the referenced procedure for total metals must be followed. Sample digestion of the filtrate for dissolved metals (or digestion of the original sample

solution for total metals) may be omitted for AA (direct aspiration or graphite furnace) and ICP analyses, provided the sample solution to be analyzed meets the following criteria:

- a. has a low COD (20)
- b. is visibly transparent with a turbidity measurement of 1 NTU or less
- c. is colorless with no perceptible odor, and
- d. is of one liquid phase and free of particulate or suspended matter following acidification.

\5\ The full text of Method 200.7, "Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes," is given at Appendix C of this Part 136.

\6\ Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.

\7\ Ammonia, Automated Electrode Method, Industrial Method Number 379-75 WE, dated February 19, 1976, (Bran & Luebbe (Technicon) Auto Analyzer II, Bran & Luebbe Analyzing Technologies, Inc., Elmsford, NY 10523.

\8\ The approved method is that cited in "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments", USGS TWRI, Book 5, Chapter A1 (1979).

\9\ American National Standard on Photographic Processing Effluents, Apr. 2, 1975. Available from ANSI, 1430 Broadway, New York, NY 10018.

\10\ "Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency", Supplement to the Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater (1981).

\11\ The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.

\12\ Carbonaceous biochemical oxygen demand (CBOD<INF>5) must not be confused with the traditional BOD<INF>5 test which measures "total BOD". The addition of the nitrification inhibitor is not a procedural option, but must be included to report the CBOD<INF>5 parameter. A discharger whose permit requires reporting the traditional BOD<INF>5 may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states CBOD<INF>5 is required can the permittee report data using the nitrification inhibitor.

\13\ OIC Chemical Oxygen Demand Method, Oceanography International Corporation, 1978, 512 West Loop, P.O. Box 2980, College Station, TX 77840.

\14\ Chemical Oxygen Demand, Method 8000, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

\15\ The back titration method will be used to resolve controversy.

\16\ Orion Research Instruction Manual, Residual Chlorine Electrode Model 97-70, 1977, Orion Research Incorporated, 840 Memorial Drive, Cambridge, MA 02138. The calibration graph for the Orion residual chlorine method must be derived using a reagent blank and three standard solutions, containing 0.2, 1.0, and 5.0 ml 0.00281 N potassium iodate/100 ml solution, respectively.

\17\ The approved method is that cited in Standard Methods for the Examination of Water and Wastewater, 14th Edition, 1976.

\18\ National Council of the Paper Industry for Air and Stream Improvement, (Inc.) Technical Bulletin 253, December 1971.

\19\ Copper, Biocinchonate Method, Method 8506, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

\20\ After the manual distillation is completed, the autoanalyzer manifolds in EPA Methods 335.3 (cyanide) or 420.2 (phenols) are simplified by connecting the re-sample line directly to the sampler. When using the manifold setup shown in Method 335.3, the buffer 6.2 should be replaced with the buffer 7.6 found in Method 335.2.

\21\ Hydrogen ion (pH) Automated Electrode Method, Industrial Method Number 378-75WA, October 1976, Bran & Luebbe (Technicon) Autoanalyzer II. Bran & Luebbe Analyzing Technologies, Inc., Elmsford, NY 10523.

\22\ Iron, 1,10-Phenanthroline Method, Method 8008, 1980, Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

\23\ Manganese, Periodate Oxidation Method, Method 8034, Hach Handbook Wastewater Analysis, 1979, pages 2-113 & 2-117, Hach Chemical Co., Loveland, CO 80537.

\24\ Wershaw, R.L., et al, "Methods for Analysis of Organic Substances in Water," Techniques of Water-Resources Investigation of the U.S. Geological Survey, Book 5, Chapter A3, (1972 Revised 1987) p. 14.

\25\ Nitrogen, Nitrite, Method 8507, Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

\26\ Just prior to distillation, adjust the sulfuric-acid-preserved sample to pH 4 with 1 + 9 NaOH.

\27\ The approved method is cited in Standard Methods for the Examination of Water and Wastewater, 14th Edition. The colorimetric reaction is conducted at a pH of 10.00.2. The approved methods are given on pp 576-81 of the 14th Edition: Method 510A for distillation, Method 510B for the manual colorimetric procedure, or Method 510C for the manual spectrophotometric procedure.

\28\ R. F. Addison & R.G. Ackman, "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography," Journal of Chromatography, vol. 47, No. 3, pp. 421-426, 1970.

\29\ Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M Na<INF>2S<INF>2O<INF>3 and NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the approved method is satisfactory.

\30\ The approved method is that cited in Standard Methods for the Examination of Water and Wastewater, 15th Edition.

\31\ EPA Methods 335.2 & 335.3 require the NaOH absorber solution final concentration to be adjusted to 0.25 N before colorimetric determination of total cyanide.

\32\ Stevens, H.H., Ficke, J.F., and Smoot, G.F., "Water Temperature--Influential Factors, Field Measurement and Data Presentation", Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1, 1975.

\33\ Zinc, Zincon Method, Method 8009, Hach Handbook of Water Analysis, 1979, pages 2-231 and 2-333, Hach Chemical Company, Loveland, CO 80537.

\34\ "Direct Current Plasma (DCP) Optical Emission Spectrometric Method for Trace Elemental Analysis of Water and Wastes, Method AES0029," 1986-- Revised 1991, Fison Instruments, Inc., 32 Commerce Center, Cherry Hill Drive, Danvers, MA 01923.

\35\ Precision and recovery statements for the atomic absorption direct aspiration and graphite furnace methods, and for the spectrophotometric SDDC method for arsenic are provided in Appendix D of this part titled, "Precision and Recovery Statements for Methods for Measuring Metals".

\36\ "Closed Vessel Microwave Digestion of Wastewater Samples for Determination of Metals", CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200, April 16, 1992. Available from the CEM Corporation.

\37\ When determining boron and silica, only plastic, PTFE, or quartz laboratory ware may be used from start until completion of analysis.

\38\ Only the trichlorofluoromethane extraction solvent is approved.

\39\ Nitrogen, Total Kjeldahl, Method PAI-DK01 (Block Digestion, Steam Distillation, Titrimetric Detection), revised 12/22/94, Perstop Analytical Corporation.

\40\ Nitrogen, Total Kjeldahl, Method PAI-DK02 (Block Digestion, Steam Distillation, Colorimetric Detection), revised 12/22/94, Perstop Analytical Corporation.

\41\ Nitrogen, Total Kjeldahl, Method PAI-DK03 (Block Digestion, Automated FIA Gas Diffusion), revised 12/22/94, Perstop Analytical Corporation.

Table II--Required Containers, Preservation Techniques, and Holding Times

Parameter No./name	Container \1\	Preservation \2\<SUP>,\3\	Maximum holding time \4\
Table IA--Bacteria Tests:			
1-4 Coliform, fecal and total.	P,G.	Cool, 4C, 0.008% Na<INF>2S<INF>2O<INF>3 <SUP>5	6 hours
5 Fecal streptococci	P,G	Cool, 4C, 0.008% Na<INF>2S<INF>2O<INF>3 <SUP>5	6 hours
Table IA--Aquatic Toxicity Tests:			
6-10 Toxicity, acute and chronic.	P,G	Cool, 4C <SUP>16.	6 hours
Table IB--Inorganic Tests:			
1. Acidity	P, G	Cool, 4C	14 days
2. Alkalinity	P, G.	do	
4. Ammonia	P, G	Cool, 4C, H<INF>2SO<INF>4 to pH<2	28 days.
9. Biochemical oxygen demand	P, G	Cool, 4C	48 hours
10. Boron Quartz.	P, PFTE, or	HNO<INF>3 TO pH2.	6 months
11. Bromide	P, G	None required	28 days
14. Biochemical oxygen demandcar bonaceous.	P, G	Cool, 4C	48 hours
15. Chemical oxygen demand	P, G	Cool, 4C, H<INF>2SO<INF>4 to pH<2.	28 days
16. Chloride	P, G	None required.Do.	
17. Chlorine, total residual	P, G	do	Analyze immediately.
21. Color	P, G	Cool, 4C	48 hours
23-24. Cyanide, total and <SUP>6	P, G	Cool, 4C, NaOH to pH>12, 0.6g	14 days
amenable to chlorination. ascorbic acid <SUP>5.			
25. Fluoride.	P.	None required	28 days
27. Hardness	P, G	HNO<INF>3 to pH<2, H<INF>2SO<INF>4 to pH<2	6 months
28. Hydrogen ion (pH)	P, G	None required	Analyze immediately.
31, 43. Kjeldahl and organic nitrogen.	P, G	Cool, 4C, H<INF>2SO<INF>4 to pH<2	28 days
Metals:<SUP>7			
18. Chromium VI	P, G	Cool, 4C	24 hours
35. Mercury.	P, GHNO <INF>3 to pH		
3, 5-8, 12, 13, 19, 20, 22, 26, 29, 30, 32-34, 36, 37, 45, 47, 51, 52, 58-60, 62, 63, 70-72, 74, 75. Metals, except boron, chromium VI and mercury.	P, G.	do	228 days 6 months
38. Nitrate	P, G	Cool, 4C	48 hours
39. Nitrate-nitrite	P, G	Cool, 4C, H<INF>2SO<INF>4 to pH<2	28 days
40. Nitrite.	P, G	Cool, 4C	48 hours
41. Oil and grease	G	Cool to 4C, HCl or H<INF>2SO<INF>4 to pH<2 28 days.	
42. Organic Carbon	P, G	Cool to 4 deg.C HCl or H<INF>2SO4 or 28 days.	
	H<INF>3 PO4 to pH2		
44. Orthophosphate	P, G.	Filter immediately Cool, 4C	48 hours.
46. Oxygen, Dissolved Probe	G	Bottle and top. None required	Analyze immediately.
47. Winkler		do	Fix on site and store in dark 8 hours
48. Phenols	G only	Cool, 4C, H<INF>2SO<INF>4 to pH<2	28 days
49. Phosphorus (elemental)	G	Cool, 4C	48 hours
50. Phosphorus, total	P, G	Cool, 4C, H<INF>2SO<INF>4 to pH<2	28 days
53. Residue, total	P, G	Cool, 4C.	7 days
54. Residue, Filterable	P, G	do	7 days
55. Residue, Nonfilterable (TSS).	P, G	do	7 days
56. Residue, Settleable	P, G	do	48 hours
57. Residue, volatile	P, G	do	7 days
61. Silica Quartz.	P, PFTE, or	Cool, 4 deg.C	28 days
64. Specific conductance	P, G	do Do.	
65. Sulfate	P, G	do Do.	
66. Sulfide	P, G	Cool, 4C add zinc acetate plus sodium hydroxide to pH>9.	7 days.
67. Sulfite	P, G	None required	Analyze immediately
68. Surfactants	P, G.	Cool, 4C	48 hours
69. Temperature	P, G	None required	Analyze
73. Turbidity	P, G.	Cool, 4C	48 hours

Table II Notes

\1 Polyethylene (P) or glass (G). For microbiology, plastic sample containers must be made of sterilizable materials (polypropylene or other autoclavable plastic).

<SUP>2 Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4C until compositing and sample splitting is completed.

<SUP>3 When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

\4 Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional Administrator under Sec. 136.3(e). Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See Sec. 136.3(e) for details. The term "analyze immediately" usually means within 15 minutes or less of sample collection.

<SUP>5 Should only be used in the presence of residual chlorine.

<SUP>6 Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

<SUP>7 Samples should be filtered immediately on-site before adding preservative for dissolved metals.

<SUP>8 Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

<SUP>9 Sample receiving no pH adjustment must be analyzed within seven days of sampling.

<SUP>10 The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

<SUP>11 When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re the requirement for thiosulfate reduction of residual chlorine), and footnotes 12, 13 (re the analysis of benzidine).

<SUP>12 If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0/0.2 to prevent rearrangement to benzidine.

<SUP>13 Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

<SUP>14 For the analysis of diphenylnitrosamine, add 0.008% Na₂S₂O₃ and adjust pH to 7-10 with NaOH within 24 hours of sampling.

<SUP>15 The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% Na₂S₂O₃.

\16 Sufficient ice should be placed with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, it is necessary to immediately measure the temperature of the samples and confirm that the 4C temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature can not be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of the increased holding temperature.

[38 FR 28758, Oct. 16, 1973, as amended at 41 FR 52781, Dec. 1, 1976; 49 FR 43251, 43258, 43259, Oct. 26, 1984; 50 FR 691, 692, 695, Jan. 4, 1985; 51 FR 23693, June 30, 1986; 52 FR 33543, Sept. 3, 1987; 55 FR 24534, June 15, 1990; 55 FR 33440, Aug. 15, 1990; 56 FR 50759, Oct. 8, 1991; 57 FR 41833, Sept. 11, 1992; 58 FR 4505, Jan. 31, 1994; 60 FR 17160, Apr. 4, 1995; 60 FR 39588, 39590, Aug. 2, 1995; 60 FR 44672, Aug. 28, 1995; 60 FR 53542, 53543, Oct. 16, 1995; 62 FR 48403, 48404, Sept. 15, 1997]

Appendix 2

Significant Figures and Rounding

Measuring Underlies Significant Figures

Human-built Instruments Always have Error

At the most basic level, chemistry (indeed all of science) depends upon experimentation; experimentation in turn requires numerical measurements. And measurements are always taken from instruments made by other human beings.

Some information about measurements:

- 1) Examples we will study include the metric ruler, the thermometer, the graduated cylinder, and the triple-beam balance.
- 2) Because of the involvement of human beings, NO measurement is exact; some error is always involved. This means that every answer in science has some uncertainty associated with it. We might be fairly confident we have the correct answer, but we can never be 100% certain we have the EXACT correct answer.
- 3) Measurements always have two parts - a numerical part (sometimes called a factor) and a dimension (sometimes called a label or a unit). The reason for this is that we are measuring quantities - length, elapsed time, temperature, mass, etc. Not only do we have to tell how much there is, but we have to tell how much of what.

In a mathematics class, units are inconsistently used. This is because much of mathematics discusses the relationships between pure numbers, not the use of a number which describes an amount of something. Many students have the unfortunate tendency to see units are unnecessary. THEY ARE NOT.

Measuring gives significance (or meaning) to each digit in the number produced. This concept of significance, of what is and what is not significant is VERY IMPORTANT. Especially the "what is not" portion. Pay close attention to the examples presented. The concept of significant figures (or significant digits) is important and will play a role in almost every unit studied.

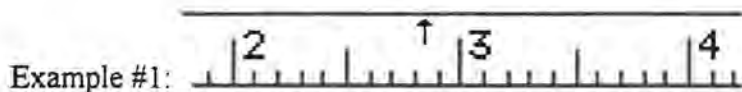
A measurement can be defined as the comparison of the dimensions of an object to some standard.

The dimensions of an object refer to some property the object possesses. Examples include mass, length, area, density, and electrical charge. Dimensions are often called units.

For example, the meter is the standard unit of length in science. It was first defined as one ten-millionth of the distance from the equator to the pole. Then, a standard meter was made out of a platinum-iridium alloy and kept in a carefully controlled environment in Paris. The third definition was the distance of a certain number of wave crests of a certain wavelength in the emission spectrum of krypton. The most recent definition of the meter is the length of the path travelled by light in a vacuum during a time interval of $1/299,792,458$ of a second.

We will just use a ruler, thank you very much!

The metric ruler will be the first example of a measuring device. The whole numbers in the images represent centimeters. The divisions are tenths of a centimeter, otherwise called millimeters. An arrow will represent the end of an object being measured. Zero is always to the left.



- 1) We know for sure the object is more than 2 cm, but less than 3 cm.
- 2) We know for sure the object is more than 0.8 cm, but less than 0.9 cm.

How do we know these two things?

Look where the arrow is, it is to the right of 2, but short of 3. It is to the right of 0.8, but short of 0.9. So, I can say the object is more than 2.8 cm, but less than 2.9 cm. We can say this with complete confidence because of the markings on the ruler.

Can I say anything more about the length?

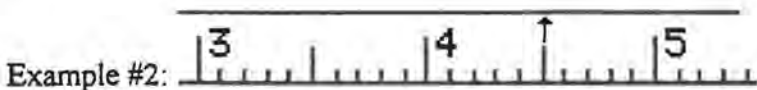
- 1) Look at the gap between the 0.8 and 0.9 cm, where the arrow is and, mentally, divide that gap into 10 equal divisions.
- 2) Estimate how many tenths to the right the arrow is from the 0.8 cm.

Let us say your answer is two-tenths. We then say the object's length as 2.82 cm. The first two digits are 100% certain, but the last, since it was estimated, has some error in it. But all three digits are significant.

This issue of estimation is important. Experience tells us that the human mind is capable of dividing a short distance into tenths with acceptable reliability. However, there is error built in and it cannot be escaped. Since the reliability is acceptable, we say the digit is significant, even with the built-in error.

However, the process stops there. ONLY ONE estimated digit is allowed to be significant.

Make sure to always include the unit with the number. In the classroom, the coach says "2.82 what? Apples?" when the units are dropped in an oral answer.



What length is indicated by the arrow?

- 1) More than 4 cm, but less than 5 cm.
- 2) More than 0.5 cm, but less than 0.6 cm.

Correct answer = 4.50 cm. The arrow is pointing directly at the mark and is neither to the left nor to the

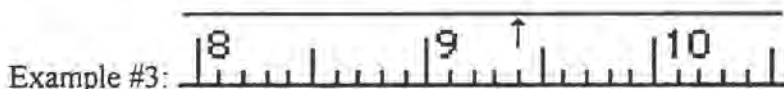
right of it. At least, according to the ChemTeam.

Notice that whatever the smallest division in your scale is, you can always estimate to the next decimal place after. In this case, the smallest division is in the tenth place, so we can estimate to the 0.01 place.

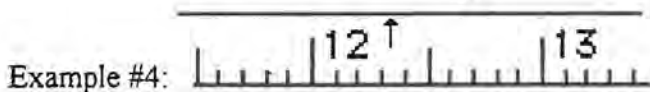
Be aware that there is some error, some uncertainty in the last digit of 4.50. While one should make an effort to estimate as carefully as possible, there is still some room for error.

The rule about uncertain digits is that there can be one and only one estimated or uncertain digit in a measurement. It is always the last digit in the measurement.

Here are two more examples of centimeter rulers. Decide what length is being shown, then click the link for the answer.



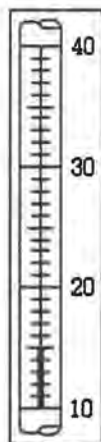
[Check Answer to Example #3](#)



[Check Answer to Example #4](#)

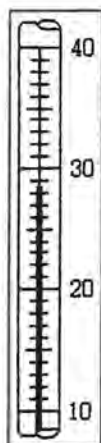
Celsius thermometers used in high school typically have a scale with only whole numbers marked on the scale. The gap between each whole number does not have any register marks for tenths.

Example #1:



Answer = 15.0 °C. Since the line stops exactly on the 15 line and DOES NOT go any farther, we estimate that it has gone zero-tenths of the way from 15 to 16. We are allowed to include the tenth degree value and have it be considered significant. Remember that when you use thermometers in chemistry experiments. Many students have left off the 'point zero' and get deducted for it.

Example #2:

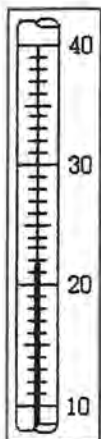


The indicated temperature is 28.5 °C.

Remember to mentally divide up the gap between 28 and 29, then make your best estimate of how many tenths are covered by the mark.

The best estimate was 0.5, but yours might have been a bit different. 0.4 and 0.6 are both acceptable.

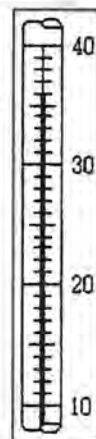
You might be interested to learn that sometimes magnifying glasses are used to make the scale bigger. This aids in the estimation process.



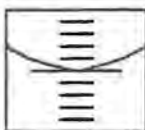
Here are two more examples of Celsius thermometers. Example #3 is to the left and example #4 is to the right. Decide what length is being shown, then click the link for the answer.

[Check Answer to Example #3](#)

[Check Answer to Example #4](#)



The graduated cylinder is another common component found in the chemistry laboratory. When reading cylinders made of glass, the water forms a meniscus. This is the downward-curved surface of the water. (Mercury forms an upward-curved meniscus.) Readings should always be made to the bottom point of the meniscus.

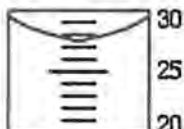


³⁵ What are the volumes indicated by these two graduated cylinders, first the left one (example #1) and then the right one (example #2)? Keep in mind that you are allowed to estimate ONE decimal place PAST the smallest scale division.



The left graduate indicates a volume of 30.0 mL, since you can estimate one digit BEYOND the smallest division. The smallest division is in the one's place, so that means you can estimate the tenth's place.

The bottom graduate indicates a volume of 4.28 mL. The smallest division is the tenth place, so we are allowed to estimate to the hundredth place.



Here are two other graduated cylinder examples:
[Answer to example #4](#)

[Answer to example #3](#)

A short bridge between this measurement lesson and the next major lesson (significant figure rules) is called "From Measurement to Significance." You may wish to examine it before continuing on.

[Return to Significant Figures Menu](#)

Significant Figure Rules

There are three rules on determining how many significant figures are in a number:

1. Non-zero digits are always significant.
2. Any zeros between two significant digits are significant.
3. A final zero or trailing zeros in the decimal portion ONLY are significant.

Focus on these rules and learn them well. They will be used extensively throughout the remainder of this course. You would be well advised to do as many problems as needed to nail the concept of significant figures down tight and then do some more, just to be sure.

Please remember that, in science, all numbers are based upon measurements (except for a very few that are defined). Since all measurements are uncertain, we must only use those numbers that are meaningful. A common ruler cannot measure something to be 22.4072643 cm long. Not all of the digits have meaning (significance) and, therefore, should not be written down. In science, only the numbers that have significance (derived from measurement) are written.

If you're not convinced significant figures are important, you may want to read this [Significant Figure Fable](#).

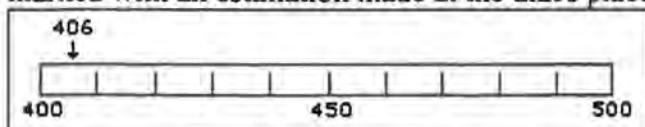
Rule 1: Non-zero digits are always significant.

Hopefully, this rule seems rather obvious. If you measure something and the device you use (ruler, thermometer, triple-beam balance, etc.) returns a number to you, then you have made a measurement decision and that ACT of measuring gives significance to that particular numeral (or digit) in the overall value you obtain.

Hence a number like 26.38 would have four significant figures and 7.94 would have three. The problem comes with numbers like 0.00980 or 28.09.

Rule 2: Any zeros between two significant digits are significant.

Suppose you had a number like 406. By the first rule, the 4 and the 6 are significant. However, to make a measurement decision on the 4 (in the hundred's place) and the 6 (in the unit's place), you HAD to have made a decision on the ten's place. The measurement scale for this number would have hundreds and tens marked with an estimation made in the unit's place. Like this:



Rule 3: A final zero or trailing zeros in the decimal portion ONLY are significant.

This rule causes the most difficulty for students. Here are two examples of this rule with the zeros this rule affects in boldface:

0.005**00**

0.030**40**

Here are two more examples where the significant zeros are in boldface:

2.30 $\times 10^{-5}$

4.500 $\times 10^{12}$

What Zeros are Not Discussed Above

Zero Type #1: Space holding zeros on numbers less than one.

Here are the first two numbers from just above with the digits that are NOT significant in boldface:

0.**00**500

0.**03**040

These zeros serve only as space holders. They are there to put the decimal point in its correct location. They DO NOT involve measurement decisions. Upon writing the numbers in scientific notation (5.00×10^{-3} and 3.040×10^{-2}), the non-significant zeros disappear.

Zero Type #2: the zero to the left of the decimal point on numbers less than one.

When a number like 0.00500 is written, the very first zero (to the left of the decimal point) is put there by convention. Its sole function is to communicate unambiguously that the decimal point is a decimal point. If the number were written like this, .00500, there is a possibility that the decimal point might be mistaken for a period. Many students omit that zero. They should not.

Zero Type #3: trailing zeros in a whole number.

200 is considered to have only ONE significant figure while 25,000 has two.

This is based on the way each number is written. When whole numbers are written as above, the zeros, BY DEFINITION, did not require a measurement decision, thus they are not significant.

However, it is entirely possible that 200 really does have two or three significant figures. If it does, it will be written in a different manner than 200.

Typically, scientific notation is used for this purpose. If 200 has two significant figures, then 2.0×10^2 is used. If it has three, then 2.00×10^2 is used. If it had four, then 200.0 is sufficient. See rule #2 above.

How will you know how many significant figures are in a number like 200? In a problem like below, divorced of all scientific context, you will be told. If you were doing an experiment, the context of the experiment and its measuring devices would tell you how many significant figures to report to people who read the report of your work.

Zero Type #4: leading zeros in a whole number.

00250 has two significant figures. 005.00×10^{-4} has three.

Exact Numbers

Exact numbers, such as the number of people in a room, have an infinite number of significant figures. Exact numbers are counting up how many of something are present, they are not measurements made with instruments. Another example of this are defined numbers, such as 1 foot = 12 inches. There are exactly 12 inches in one foot. Therefore, if a number is exact, it DOES NOT affect the accuracy of a calculation nor the precision of the expression. Some more examples:

There are 100 years in a century.

2 molecules of hydrogen react with 1 molecule of oxygen to form 2 molecules of water.

There are 500 sheets of paper in one ream.

Interestingly, the speed of light is now a defined quantity. By definition, the value is 299,792,458 meters per second.

Practice Problems

Identify the number of significant figures:

1) 3.0800

2) 0.00418

3) 7.09×10^{-5}

4) 91,600

5) 0.003005

6) 3.200×10^9

7) 250

8) 780,000,000

9) 0.0101

10) 0.00800

Answers to Problems

If you're STILL not convinced significant figures are important, you may want to read this Significant Figure Fable.

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1) 3.0800 - five significant figures. All the rules are illustrated by this problem. Rule one - the 3 and the 8. Rule Two - the zero between the 3 and 8. Rule three - the two trailing zeros after the 8.

2) 0.00418 - three significant figures: the 4, the 1, and the 8. This is a typical type of problem where the student errs by giving five significant figures as the answer.

3) 7.09×10^{-5} - three significant figures. When a number is written in scientific notation, only significant figures are placed into the numerical portion. If this number were taken out of scientific notation, it would be 0.0000709.

4) 91,600 - three significant figures. The last two zeros are not considered to be significant (at least normally). Suppose you had information that showed the zero in the tens place to be significant. How would you show it to be different from the zero in the ones place, which is not significant? The answer is scientific notation. Here is how it would be written: 9.160×10^4 . This CLEARLY indicates the presence of four significant figures.

5) 0.003005 - four significant figures. No matter how many zeros there are between two significant figures, all the zeros are to be considered significant. A number like 70.000001 would have 8 significant figures.

6) 3.200×10^9 - four significant figures. Notice the use of scientific notation to indicate that there are two zeros which should be significant. If this number were to be written without scientific notation (3,200,000,000) the significance of those two zeros would be lost and you would - wrongly - say that there were only two significant figures.

7) 2

8) 2

9) 3

10) 3

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Rules for Rounding Off

Now that "everyone" has a calculator that will give a result to six or eight (or more) figures, it is important that we know how to round the answer off correctly. The typical rule taught is that you round up with five or more and round down with four or less.

THIS RULE IS WRONG!

However, please do not rush off to your elementary school teacher and read 'em the riot act!

The problem lies in rounding "up" (increasing) the number that is followed by a 5. For example, numbers like 3.65 or 3.75, where you are to round off to the nearest tenth.

OK, let's see if I can explain this. When you round off, you change the value of the number, except if you round off a zero. Following the old rules, you can round a number down in value four times (rounding with one, two, three, four) compared to rounding it upwards five times (five, six, seven, eight, nine).

Suppose you had a very large sample of numbers to round off. On average you would be changing values in the sample downwards 4/9ths of the time, compared to changing values in the sample upward 5/9ths of the time.

This means the average of the values AFTER rounding off would be greater than the average of the values BEFORE rounding.

This is not acceptable.

We can correct for this problem by rounding "off" (keeping the number the same) in fifty percent of the roundings-even numbers followed by a 5. Then, the roundings "off" will cancel out the roundings "up."

The following rules dictate the manner in which numbers are to be rounded to the number of figures indicated. The first two rules are more-or-less the old ones. Rule three is the change in the old way.

When rounding, examine the figure following (i.e., to the right of) the figure that is to be last. This figure you are examining is the first figure to be dropped.

1. If it is less than 5, drop it and all the figures to the right of it.
 2. If it is more than 5, increase by 1 the number to be rounded, that is, the preceeding figure.
 3. If it is 5, round the number so that it will be even.
-

Example #1 - Suppose you wish to round 62.5347 to four significant figures. Look at the fifth figure. It is a 4, a number less than 5. Therefore, you will simply drop every figure after the fourth, and the original number rounds off to 62.53.

Example #2 - Round 3.78721 to three significant figures. Look at the fourth figure. It is 7, a number greater than 5, so you round the original number up to 3.79.

Example #3 - Round 726.835 to five significant figures. Look at the sixth figure. It is a 5, so now you must look at the fifth figure also. That is a 3, which is an odd number, so you round the original number up to 726.84.

Example #4 - Round 24.8514 to three significant figures. Look at the fourth figure. It is a 5, so now you must also look at the third figure. It is 8, an even number, so you simply drop the 5 and the figures that follow it. The original number becomes 24.8.

When the value you intend to round off is a five, you **MUST** look at the previous value **ALSO**. If it is even, you round down. If it is odd, you round up.

Here are some more examples of the "five rule." Round off at the five.

3.075

3.85

22.73541

0.00565

2.0495

This last one is tricky (at least for high schoolers being exposed to this stuff for the first time!). The nine rounds off to a ten (not a zero), so the correct answer is 2.050, NOT 2.05.

Would your teacher be so mean as to include problems like this one on a test? In the classroom, the sufferers (oops, I mean students) have learned to shout "YES" in unison to such easy questions.

Lastly, before we get to the problems. Students, when they learn this rule, like to apply it across the board. For example, in 2.0495, let's say we want to round off to the nearest 0.01. Many times, a student will answer 2.04. When asked to explain, the rule concerning five will be cited. However, the important number in this problem is the nine, so the rule is to round up and the correct answer is 2.05.

Practice Problems

Round the following numbers as indicated

To four figures:	To nearest 0.1	To nearest 0.01	To nearest whole number
1. 2.16347×10^5	13. 3.64	25. 6.675	37. 56.912
2. 4.000574×10^6	14. 4.55	26. 0.04203	38. 3.4125
3. 3.682417	15. 7.250	27. 0.03062	39. 251.7817
4. 7.2518	16. 0.0865	28. 4.500	40. 112.511
5. 375.6523	17. 0.5182	29. 2.473	41. 63.541
6. 21.860051	18. 2.473	30. 7.555	42. 7.777

To two figures:	To one decimal place	To nearest 0.001	Round off farthest right digit
7. 3.512	19. 54.7421	31. 5.687524	43. 2.473
8. 25.631	20. 100.0925	32. 39.861214	44. 5.396
9. 40.523	21. 1.3511	33. 104.97055	45. 8.235
10. 2.751×10^8	22. 79.2588	34. 41.86632	46. 3.05
11. 3.9814	23. 0.9114	35. 0.3775	47. 8.25
12. 22.494	24. 0.2056	36. 0.0045	48. 8.75

Answers

These are the answers.

To four figures:	To nearest 0.1:	To nearest 0.01:	To nearest whole number
1. 2.163×10^5	13. 3.6	25. 6.68	37. 57
2. 4.000×10^6	14. 4.6	26. 0.04	38. 3
3. 3.682	15. 7.2	27. 0.03	39. 252
4. 7.252	16. 0.1	28. 4.50	40. 112
5. 375.6	17. 0.5	29. 2.47	41. 64
6. 21.86	18. 2.5	30. 7.56	42. 8

To two figures:	To one decimal place:	To nearest 0.001	Round off farthest right digit
7. 3.5	19. 54.7	31. 5.688	43. 2.47
8. 26	20. 100.1	32. 39.861	44. 5.40
9. 40	21. 1.4	33. 104.970	45. 8.24
10. 2.8×10^8	22. 79.2	34. 41.866	46. 3.0
11. 4.0	23. 0.9	35. 0.378	47. 8.2
12. 22	24. 0.2	36. 0.004	48. 8.8

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